Portable VA Analyzer Software

Manual

8.0105.8002EN / 2017-07-15

Metrohm

Metrohm AG
CH-9100 Herisau
Switzerland
Phone +41 71 353 85 85
Fax +41 71 353 89 01
info@metrohm.com
www.metrohm.com

Portable VA Analyzer Software

Manual

8.0105.8002EN / 2017-07-15 zst

Technical Communication
Metrohm AG
CH-9100 Herisau
techcom@metrohm.com

This documentation has been prepared with great care. However, errors can never be entirely ruled out. Please send comments regarding possible errors to the address above.

Table of contents

Table of figures

1 Introduction

The **Portable VA Analyzer** software is an easy-to-use computer software to control a modern hand-held voltammetry stand for trace analysis of metals and other electronchemically active substances, the 946 Portable Analyzer.

The software controls the measurements, records the measured data and evaluates it, thus ensuring a straightforward measuring process. Built on Windows operating principles, intuitive handling is guaranteed. Fixed method structures in the Portable VA Analyzer software make your determinations easy and quick. This comes in handy especially when dealing with routine applications.

2 Overview of the software

Portable VA Analyzer software provides the control of all instrument functions. An intuitive interface helps the user to control the following measuring modes:

- Square wave *(see Chapter 11.3, page 62)*
- Linear sweep *(see Chapter 11.1, page 57)*
- Differntial pulse *(see Chapter 11.2, page 59)*

NOTE

More details about the hardware can be found in the 946 Portable VA Analyzer manual (8.946.8001EN).

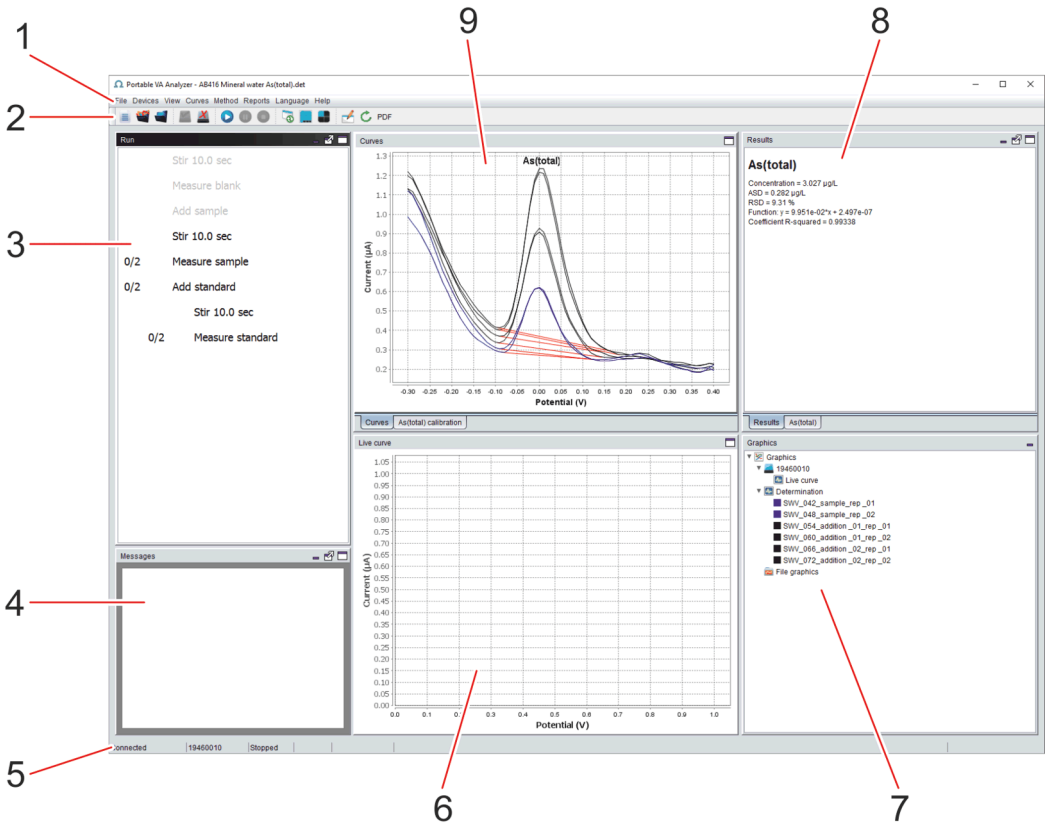


Figure 1 Portable VA Analyzer software - overview (default workplace layout)

1	**Menu bar**	**2**	**Toolbar**
3	**Run subwindow**	**4**	**Messages subwindow**

5	**Status bar**	**6**	**Live curve**
7	**Graphics subwindow**	**8**	**Results subwindow**
9	**Curves subwindow**		

Menu bar *(1-**1**)*

File	Load and save a method. Load and save a determination. Reprocess the curve evaluation.
Devices	Connect / disconnect the potentiostat. Start / Hold / Stop the determination.
View	Selections regarding the general appearance of the curves subwindows, such as scaling, labels, and background color. Selection of the workplace layout.
Curves	Selections regarding appearance of curves, such as name, visibility, and color. Export functions for determination curves.
Method	Open the dialog window to edit method or determination parameters.
Reports	Create PDF report
Language	Select the software language English or Chinese
Help	Information regarding the device. Information regarding the software version. Link to the PDF file of the manual.

Toolbar *(1-**2**)*

New method	Load and open a method with default square-wave parameters.
Load determination	Opens the dialog window to load an existing determination file. By default, determinations are saved in the folder ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Determination***. Example determinations can be found in the folder ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Examples\Determinations***.
Load method	Opens the dialog window to load an existing method file.

	By default, methods are saved in the folder ***%USERPROFILE%\Documents \Metrohm\Portable VA Analyzer\Method***. Example methods can be found in the folder ***%USERPROFILE%\Documents \Metrohm\Portable VA Analyzer\Examples\Methods***.
Connect	Establish a connection between the software and the instrument by means of a USB cable *(see Chapter 3, page 7)*. Inactive when an instrument is connected.
Disconnect	Disconnect the software from the instrument. Inactive when no instrument is connected.
Start	Start the determination. Inactive when no instrument is connected.
Hold	Hold the determination. Click the button again to continue. Inactive when no instrument is connected.
Stop	Stop the determination. Inactive when no instrument is connected.
Default workplace	Change the view of the workplace to default. This layout shows **Live curve** and **Curves** in separate subwindows. ▪ The **Live curve** subwindow is only displayed when an instrument is connected. ▪ The **Curves** subwindow can have up to 5 tabs. – The tab **Curves** shows an overlay of voltammograms belonging to the determination. – The tab(s) **'Substance name' calibration** show the calibration curve for a substance. Each calibration curve is displayed on an individual tab.
Tabs workplace	Change the view of the workplace to tabs. This layout has only one subwindow **Curves** with a maximum of 6 tabs. ▪ The tab **Live curve** is only displayed when an instrument is connected. ▪ The tab **Curves** shows an overlay of voltammograms belonging to the determination. ▪ The tab(s) **'Substance name' calibration** show the calibration curve for a substance. Each calibration curve is displayed on an individual tab.
Mosaic workplace	Change the view of the workplace to a mosaic.

	This layout shows all curves in individual subwindows. The actual layout depends on the number of calibration curves displayed. ▪ The **Live curve** subwindow is only displayed when an instrument is connected. ▪ The **Curves** subwindow shows an overlay of voltammograms belonging to the determination. ▪ The calibration curve of each substance defined in the method is shown in an individual subwindow with the name **'Substance name' calibration**.
Edit method parameters	Open the dialog window to edit method or determination parameters. The parameters can be found on four tabs: ▪ **General** General settings for the determination, such as information on sample identifier, user name and sensor as well as selection of documentation. ▪ **Determination** Settings related to the execution of the determination, such as sample and total volume, stirring rate and time, blank value correction and number of replications and additions. ▪ **Voltammetric** Settings related to the voltammetric measurement. Exact parameters depend on the chosen measuring mode. Available measuring modes: **Square wave**, **Linear sweep** and **Differential pulse**. ▪ **Evaluation** Settings related to data processing, peak recognition and calibration.
Reprocess	Reprocess the curve evaluation after deactivating individual curves or editing base points in the **Results** subwindow. Details on the reevaluation of peaks can be found in *Chapter 4.4 Reevaluating a determination (page 31)*.
Create PDF	Open the dialog window to select the report elements which should be printed in a PDF report.

Run subwindow *(1-**3**)*

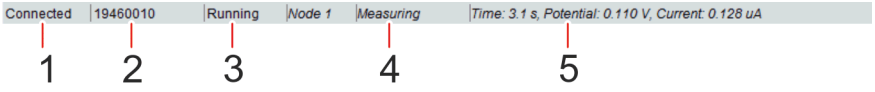
Display of the general method sequence and the progress of the determination

Messages subwindow *(1-**4**)*

Display of messages which stop the process of the determination and require actions by the operator, e.g. addition of standard solution.

Status bar *(1-**5**)*

Display of the potentiostat status.



1. Connection status: Connected / Disconnected
2. Instrument type (only displayed when connected): 19460010
3. Potentiostat status (only displayed when connected): Stopped / Running
4. Status of the voltammetric measurement: Potential / Equilibration / Measuring
5. Display of time, potential and current related to the voltammetric measurement.

Live curve *(1-**6**)*

Live display of the currently measured voltammogram.

Subwindow in the **Default workplace** and **Mosaic workplace** layout. In the **Tabs workplace** layout, it is found in the **Curves** subwindow as separate tab.

Graphics subwindow *(1-**7**)*

Display of color and name of the curves belonging to the currently running or loaded determination. In this subwindow, the curves have to be selected for which name, color or visibility should be changed. Also for individual export the curves have to be selected in this subwindow.

Results subwindow *(1-**8**)*

This subwindow includes 2 to 5 tabs. The tab **Results** shows the overview of the results calculated for all substances specified in the method. Evaluation details, like peak potentials and peak heights can be found on up to 4 additional tabs. One tab for each substance, tagged with **'Substance name'**.

Curves subwindow *(1-**9**)*

This subwindow includes maximum 6 tabs. The tab **Curves** shows all voltammograms belonging to the determination. Calibration curves for each substance can be found on up to 4 additional tabs. One tab for each substance, tagged with **'Substance name' calibration**. In the **Tabs workplace** layout, one additional tab **Live curve** is displayed in this subwindow.

3 Connecting the software with the instrument

Prerequisites

- The potentiostat is connected to the measuring stand.

1
- Connect the USB type B mini connector of the cable (6.02108.000) to the connection socket **USB** on the rear of the potentiostat.
- Connect the USB type A connector of the USB cable to the PC or laptop.

2 Start the Portable VA Analyzer software by double-clicking the desktop icon  or selecting the link **Portable VA Analyzer** under **Windows start menu ▸ All programs ▸ Metrohm ▸ Portable VA Analyzer**

3 Switch on the instrument. Press the **ON/OFF** button on the rear of the potentiostat.

The green status LED on the front of the potentiostat indicates when the power is on.

4 In the Portable VA Analyzer software click on  or **Menu bar ▸ Devices ▸ Connect**.

When the instrument is correctly connected and ready to use:

- the status bar shows **Connected** and the instrument type 19460010.
- An additional subwindow **Live curve** appears.
- The  button is available for disconnecting the instrument.

Connecting the instrument manually

Prerequisites

- The potentiostat is connected to the measuring stand.
- The potentiostat is connected to the computer.
- The potentiostat is switched on.

1 In the menu bar click on **Devices ▸ Manual connect…**

2
- Choose the COM port where the instrument is connected.
- Click on **[Connect]**

NOTE

The correct COM port can be found in the Windows Device Manager. More information on how to open the Device Manager can be found in *Chapter 3* of the *Installation manual* of the Portable VA Analyzer Software (8.946.8002EN).

Connecting the instrument after a connection error

Prerequisites

- The potentiostat is connected to the measuring stand.
- The potentiostat is connected to the computer.
- The potentiostat is switched on.

1
- Click on to properly disconnect the instrument.
- Restart the software.

2
- Switch off the instrument.
- Wait 3 seconds.
- Switch the instrument back on.

3 Click on or **Menu bar ▸ Devices ▸ Connect**.

4 Software operation

4.1 Creating a new method

Dialog window: **Menu bar ▸ File ▸ New Method**

1
- In the toolbar, click on  , or
- in the menu bar click on **File ▸ New Method**

The **Method parameters** dialog window opens.

2
- Enter or change the method parameters.
- Click on **[OK]**

If all method parameters are correct, the parameters are saved and the dialog window is closed.

If the method parameters contain errors, the dialog window cannot be closed. An **[Errors]** button is activated.

3 Click on **[Errors]**.

An **Errors** dialog window is opened.

4 Correct the errors listed in the **Errors** dialog window, and click on **[OK]**.

If all method parameters are correct, the parameters are saved and the dialog window is closed.

Method parameters dialog window

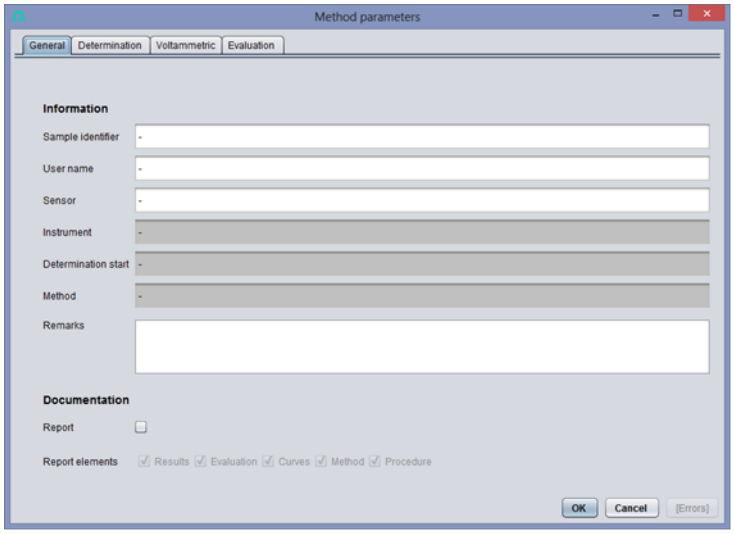


Figure 2 «General» tab of «Method parameters» dialog window

In the **Method parametes** window, the parameters for the method are defined.

General

Contains information fields and selections to define the automatic PDF printout at the end of the determination. *For details see Chapter 4.1.1, page 11*.

Determination

Contains specifications regarding the general sequence of the determination. The parameters displayed depend on the selected calibration technique and measurement technique. *For details see Chapter 4.1.2, page 13*.

Voltammetric

Contains parameters for preparation procedures and measuring mode. The parameters displayed for the sweep depend on the measuring mode selected. *For details see Chapter 4.1.3, page 15*.

Evaluation

Contains parameters for data processing, peak evaluation, and concentration calculation. *For details see Chapter 4.1.4, page 21*

OK

Closes the dialog window.

The method parameters are validated for wrong values or values out of the specified limits. If the method parameters contains errors, the dialog window cannot be closed.

Cancel

Closes the dialog window. All changes to the parameters are lost.

Errors

Opens an Errors dialog window which lists all the errors in the method parameters.

4.1.1 Method parameters – General

Tab: **Menu bar ▸ File ▸ New Method ▸ General**

Information

Identification for samples.

This name is inserted in the Sample field of all reports and results windows. The Sample identifier is also used as part of the file name.

Sample identifier

Entry	**34 characters**

User name

Name of the User. This name is inserted in the User field of all reports and results windows.

Sensor

Name for the sensor used. This name is inserted in the **Sensor** field of all reports and results windows.

Instrument

Name of the instrument.

Non-editable. Data automatically filled in from determination data.

Determination start

Date and time of determination start.

Non-editable. Data automatically filled in from determination data.

Method

Name of the method used.

Non-editable. Data automatically filled in from determination data.

Remarks

Remark regarding the method. This remark is inserted in the Report field of all reports and results windows.

Documentation

Report

on | off (Default value: **off**)

Activate this check box to enable automatic printout and storage of a PDF report at the end of the determination.

Report elements

Sections of report contents can be selected.

Results

on | off (Default value: **on**)

Activate this check box to print the follwing information:

- General and determination information.
- Table with concentration result for all substances in the determination.

Evaluation

on | off (Default value: **on**)

Activate this check box to print the follwing information:

- Table with evaluation details, like peak potential and peak height, for each substance and curve.
- Table with regression data for each substance.

Curves

on | off (Default value: **on**)

Activate this check box to print the follwing information:

- Overlay of all voltammograms which are visible.
- Individual calibration curve for each substance.

Method

on | off (Default value: **on**)

Activate this check box to print the method parameters.

Procedure

on | off (Default value: **on**)

Activate this check box to print the method sequence.

4.1.2 Method parameters – Determination

Tab: **Menu bar ▸ File ▸ New Method ▸ Determination**

The **Determination** tab of the **Method parameters** dialog window contains specifications regarding the general sequence of the determination. The parameters displayed depend on the selected calibration technique and measurement technique.

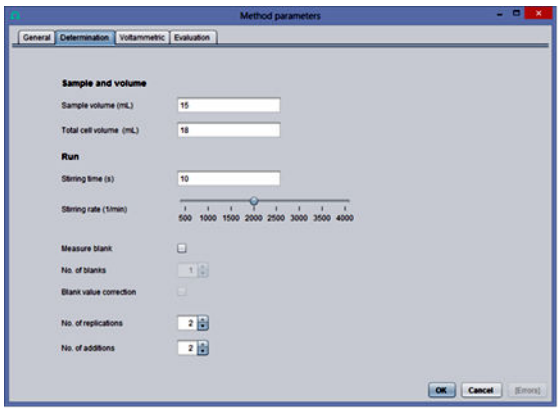


Figure 3 «Determination» tab of «Method parameters» dialog window

Sample and volume

Sample volume (mL)

Volume of sample to be added in the measuring vessel. The volume is used for the calculation of the final result.

Input range	**0.000001 - 9999999 mL**
Default value	**15 mL**

Total cell volume (mL)

Total volume of solutions (sample + auxiliary solution, e.g. buffer, additional water) in the measuring vessel prior to the first standard addition.

Input range	**0.000001 - 9999999 mL**
Default value	**18 mL**

The **Total cell volume** must be ≥ **Sample volume**.

Run

Stirring time (s)

Time for stirring the measuring solution. Stirring is carried out:

- At the beginning of the determination.
- After the addition of sample (only if **Blank** is active).
- After each addition of standard solution.

Input range	**0 - 9999 s**
Default value	**10 s**

Stirring rate (1/min)

Rotations per minute of the stirrer. The stirrer is active during the stirring time and remains active during all preparation procedure steps (**Cyclovoltammetric pretreatment** and **Potentiostatic pretreatment**) until the start of the measuring sweep.

Input range	**500 - 4000 1/min**
Default value	**2000 1/min**

Measure blank

on | off (Default value: **off**)

Measure a blank solution before sample determination. This background compensation is mainly used to reduce interference due to the supporting electrolyte. Such interference includes both the presence of the analyte (blank value) and that of foreign substances electroactive in the same range.

Activating the check box **Measure blank**, enables the following parameters:

No. of blanks

Number of measurements to determine the blank curve. If the blank solution is measured several times, a mean blank curve is determined from the different measurements.

Input range	**1 - 10**
Default value	**1**

Blank value correction

on | off (Default value: **off**)

If the check box is activated, a blank peak is taken into account in the result calculation.

In determinations with **Blank value correction** a potential blank peak at the defined peak potential is subtracted from sample and standard addition peaks.

No. of replications

Number of replications (= total number of measurements) for each variation (sample, standard addition).

Input range	**1 - 10**
Default value	**2**

No. of additions

Number of standard additions.

Input range	**1 - 10**
Default value	**2**

4.1.3 Method parameters – Voltammetric

Tab: **Menu bar ▸ File ▸ New Method ▸ Voltammetric**

The **Voltammetric** tab of the **Method parameters** dialog window contains parameters for preparation procedures and measuring mode. The parameters displayed for the sweep depend on the measuring mode selected.

Sequence of a measurement:

The following steps are successively executed in the method run.

- The stirrer is switched on.
- Cyclovoltammetric pretreatment (only if **No. of cycles** > 0)
  - **Start potential** is applied.
  - Sweep is carried out towards **Vertex potential** with the defined **Potential step** and **Sweep rate**.
  - At the **Vertex potential** the sweep direction is reversed and the sweep continued towards **Start potential** with the defined **Potential step** and **Sweep rate**.
  - The sweep ends at **Start potential**.
  - The cycle **Start potential** – **Vertex potential** – **Start potential** is repeated in accordance with the **No. of cycles**.
- Potentiostatic pretreatment
  - **Potential 1** is applied during **Waiting time 1** (if **Waiting time 1** > 0 s)
  - **Potential 2** is applied during **Waiting time 2** (if **Waiting time 2** > 0 s)
  - The stirrer is switched off.
  - **Start potential** is applied.
  - The system is idle for the time defined under **Equilibration time**.
- Sweep
  - Measurement is carried out from **Start potential** towards **End potential** with the **Potential step** which defines the resolution of the curve and the **Sweep rate** which defines the rate of potential change and some additional parameters specific to the measuring mode.
  - The curve resulting from the sweep is saved and evaluated.

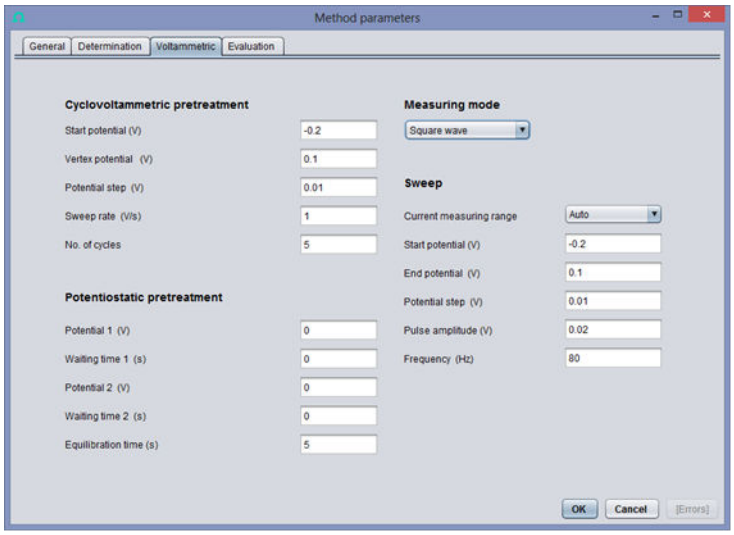


Figure 4 «Voltammetric» tab of «Method parameters» dialog window

Cyclovoltammetric pretreatment

Start potential (V)

Potential where the cyclic sweep starts. The end potential is always the same as start potential.

Input range	**-4.095 - +4.095 V**
Default value	**-0.2 V**

Vertex potential (V)

Potential where the sweep direction is reversed.

Input range	**-4.095 - +4.095 V**
Default value	**-0.1 V**

Potential step (V)

Potential step for potential ramp.

Input range	**0.001 - 0.5 V**
Default value	**0.01 V**

Sweep rate (V/s)

Rate of potential change used for the cyclic sweeps.

Input range	**0.001 - 500 V/s**
Default value	**1 V/s**

No. of cycles

Number of cyclic sweeps to be carried out.

Input range	**0 - 100**
Default value	**5**

NOTE

The following condition applies to the definition of **Potential step** and **Sweep rate**:

0.001 s < Potential step / Sweep rate ≤ 1.3 s.

Potentiostatic pretreatment

Potential 1 (V)

Potential that is applied to the working electrode during the **Waiting time 1**. This potential can be used e.g. as cleaning potential for the electrochemical cleaning of solid-state electrode surfaces that have been contaminated with reaction products of electrode redox processes.

Input range	**-4.095 - +4.095 V**
Default value	**0 V**

Waiting time 1 (s)

Time during which the **Potential 1** is applied to the working electrode. With **Waiting time 1** = 0 s **Potential 1** is not applied.

Input range	**0 - 1300 s**
Default value	**0 s**

Potential 2 (V)

Potential that is applied to the working electrode during the **Waiting time 2**. This potential can be used e.g. as deposition potential for the electrochemical deposition in stripping voltammetry.

Input range	**-4.095 - +4.095 V**
Default value	**0 V**

Waiting time 2 (s)

Time during which the **Potential 2** is applied to the working electrode. With **Waiting time 2** = 0 s **Potential 2** is not applied.

Input range	**0 - 1300 s**
Default value	**0 s**

Equilibration time (s)

Time before the sweep during which the stirrer is already switched off and the start potential is applied to the electrode.

Input range	**0 - 1300 s**
Default value	**5 s**

Measuring mode

Click over the text box and select the measuring mode. After the selection, the parameters displayed for the sweep change according to the mode selected.

Selection	**Sqaure wave** | **Linear sweep** | **Differential pulse**
Default value	**Sqaure wave**

Sweep

The parameters displayed for the sweep change according to the measuring mode selected, but some parameters are common for the three techniques:

Common sweep parameters

Current measuring range

Selection of the current measuring range of the potentiostat used for the measurement. With the setting «Auto» the measuring range is automatically selected at the beginning of each sweep.

Selection	**Auto** | **±10 mA** | **±1 mA** | **±100 µA** | **±10 µA** | **±1 µA** | **±100 nA** | **±10 nA** | **±1 nA**
Default value	**Auto**

Start potential (V)

Potential where the sweep starts.

Input range	**-4.095 - +4.095 V**
Default value	**-0.2 V**

End potential (V)

Potential where the sweep ends.

Input range	**-4.095 - +4.095 V**
Default value	**0.1 V**

Potential step (V)

Potential step for potential ramp.

Input range	**0.001 - 0.5 V**
Default value	**0.01 V**

Sweep parametes for Square wave

(see Chapter 11.3, page 62)

Pulse amplitude (V)

NOTE

Appears only if measuring mode **Square wave** is selected.

Amplitude of the rectangular potential pulse superimposed on the potential step first in sweep direction and then against sweep direction.

Input range	**0.001 - 0.25 V**
Default value	**0.02 V**

Frequency (Hz)

NOTE

Appears only if measuring mode **Square wave** is selected.

Frequency of the superimposed potential pulses.

Input range	**1 - 400 Hz**
Default value	**80 Hz**

Sweep parametes for Linear sweep

(see Chapter 11.1, page 57)

Sweep rate (V/s)

NOTE

Appears only if measuring mode **Linear sweep** is selected.

Applied sweep rate. The sweep rate defines the rate of potential change during the sweep.

Input range	**0.001 - 500 V/s**
Default value	**1 V/s**

Sweep parametes for Differential pulse

(see Chapter 11.2, page 59)

Pulse amplitude (V)

NOTE

Appears only if measuring mode **Differential pulse** is selected.

Pulse amplitude of the rectangular potential pulse superimposed on the potential step. The pulse is always applied in sweep direction.

Input range	**0.001 - 0.25 V**
Default value	**0.05 V**

Pulse time (s)

NOTE

Appears only if measuring mode **Differential pulse** is selected.

Time interval during which the potential pulse is superimposed on the potential step.

Input range	**0.001 - 1.3 s**
Default value	**0.04 s**

Sweep rate (V/s)

NOTE

Appears only if measuring mode **Differential pulse** is selected.

Applied sweep rate. The sweep rate defines the rate of potential change during the sweep.

NOTE

The following conditions apply to the definition of Potential step, Sweep rate and Pulse time:

0.001 s < Potential step / Sweep rate ≤ 1.3 s

Pulse time ≤ Potential step / Sweep rate - 0.0001 s

4.1.4 Method parameters – Evaluation

Tab: **Menu bar ▸ File ▸ New Method ▸ Evaluation**

The **Evaluation** tab of the **Method parameters** dialog window contains parameters for data processing, peak evaluation, and concentration calculation.

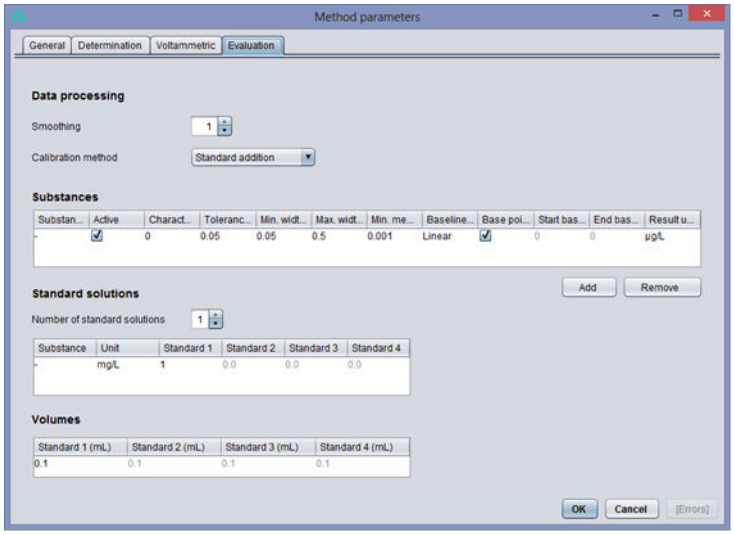


Figure 5 «Evaluation» tab of «Method parameters» dialog window

Data Processing

Smoothing

The measured values are smoothed. This is done by weighted moving average method using the Savitzky/Golay algorithm. The number of points for averaging depends on the smoothing factor selected. The applicable smoothing factor heavily depends on the number of points in the data set. The more points within the curve, the higher the smoothing factor can be without modifying the curve too much.

Input range	**1 - 20**
Default value	**1**

Calibration method

Content determination using single or multiple addition of a standard solution. *For more information on standard addition see Chapter 11.7.1, page 68*.

Selection	**Standard addition**

Substances

The **Substances** table of the **Evaluation** tab contains parameters for the definition and recognition of substances, for peak evaluation and results

calculation. For more information on peak recognition *(see Chapter 11.4, page 65)*.

Substance

Name of the substance. A maximum of 4 substances can be defined.

Entry	**9 characters**
Default value	**-**

Active

on | off (Default value: **on**)

Activate or deactivate the evaluation of the substance.

Characteristic potential

Potential for the assignment of a peak to a substance.

Input range	**-4.095 - +4.095 V**
Default value	**0 V**

Tolerance (V)

Tolerance of the characteristic potential for the assignment of a peak to a substance.

Input range	**0.001 - 1 V**
Default value	**0.05 V**

Min. width (V)

Minimum width to accept a signal as peak.

Input range	**0.001 - Max. width V**
Default value	**0.5 V**

Max. width (V)

Maximum width to accept a signal as peak.

Input range	**Min. width - 1 V**
Default value	**0.5 V**

Min. measured quantity (µA)

Minimum peak height to distinguish noise from a peak.

Input range	**0.000001 - 99999 µA**
Default value	**0.001 µA**

Baseline type

The evaluation of detected peaks is carried out using approximated baselines *(see Chapter 11.6, page 67)*.

Selection	**Linear** | **Exponential** | **Polynomial** | **Horizontal start** | **Horizontal end**
Default value	**Linear**

Base points automatically (V)

on | off (Default value: **on**)

With the check box activated, the software automatically defines start and endpoint of the baseline for each individual curve.

Start base point (V)

NOTE

Only active if the option **Base points automatically** is deactivated, and if the baseline type **Horizontal end** is not selected.

Defines the start potential of the baseline which is used for all curves.

Input range	**-4.095 - +4.095 V**
Default value	**0 V**

End base point (V)

NOTE

Only active if the option **Base points automatically** is deactivated, and if the baseline type **Horizontal start** is not selected.

Defines the end potential of the baseline which is used for all curves.

Input range	**-4 - +4 V**
Default value	**0 V**

Result unit

Final result unit.

NOTE

The result unit depends on the unit of the standard solution. If the concentration of the standard solution is a mass concentration, e.g. mg/L, the result unit has to be a mass concentration as well, e.g. µg/L. If the concentration of the standard solution is a molar concentration, e.g. µmol/L, the result unit has to be a molar concentration as well, e.g. nmol/L.

Selection	**g/L** | **mg/L** | **µg/L** | **ng/L** | **mg/mL** | **µg/mL** | **ng/mL** | **pg/mL** | **mmol/mL** | **µmol/mL** | **nmol/mL** | **pmol/mL** | **mol/L** | **mmol/L** | **µmol/L** | **nmol/L**
Default value	**µg/L**

[Add]

Adds a new substance.

[Remove]

Removes the selected substance.

Standard solutions

The table of standard solutions contains the standard solutions defined for the method with the corresponding concentrations for the substances. The substance names are automatically displayed according to the substances defined in the **Substances** table. The number of editable standard solutions for each substance depends on the **Number of standard solutions** selected in the spin box.

Number of standard solutions

The maximum number of standard solutions is related with the number of substances. It is possible to have less, but not more standard solution than substances. With one substance, only one standard solution can be defined. With two substances, both can be in one standard solution but also separated into two individual standard solutions.

Selection	**1** | **2** | **3** | **4**
Default value	**1**

Substance

Name of the substance. The name cannot be edited and is automatically taken from the table **Substances**.

Unit

Concentration unit of the substance in the selected standard solution.

Selection	**g/L** | **mg/L** | **µg/L** | **ng/L** | **mg/mL** | **µg/mL** | **ng/mL** | **pg/mL** | **mmol/mL** | **µmol/mL** | **nmol/mL** | **pmol/mL** | **mol/L** | **mmol/L** | **µmol/L** | **nmol/L**
Default value	**mg/L**

Standard 1

Concentration value of the selected substance in the standard solution 1. The concentration unit is specified in the column **Unit** of this table.

Input range	**0 - 999** (Increment: **0.001**)
Default value	**0** In a new method, The default value for the first substance in Standard 1, is 1 instead of 0.

Standard 2

NOTE

Only editable if at least 2 substances have been defined in the **Substances** table and the **Number of standard solutions** is 2.

Concentration value of the selected substance in the standard solution 2. The concentration unit is specified in the column **Unit** of this table.

Input range	**0 - 999** (Increment: **0.001**)
Default value	**0**

Standard 3

NOTE

Only editable if at least 3 substances have been defined in the **Substances** table and the **Number of standard solutions** is 3.

Concentration value of the selected substance in the standard solution 3. The concentration unit is specified in the column **Unit** of this table.

Input range	**0 - 999** (Increment: **0.001**)
Default value	**0**

Standard 4

NOTE

Only editable if at least 4 substances have been defined in the **Substances** table and the **Number of standard solutions** is 4.

Concentration value of the selected substance in the standard solution 3. The concentration unit is specified in the column **Unit** of this table.

Input range	**0 - 999** (Increment: **0.001**)
Default value	**0**

NOTE

It is not possible to have one substance in multiple standard solutions. One substance can only be contained in one standard solution. For standard solutions which do not contain the substance the concentration has to be set to 0.

Volumes

In the table **Volumes**, the volume to be added per standard addition is defined for each standard solution. The number of editable volumes depends on the **Number of standard solutions** selected in the spin box of the **Standard solutions** table. *For more information on standard addition see Chapter 11.7.1, page 68*.

Standard 1 (mL)

Addition volume for **Standard 1**.

Input range	**0.01 - 999 mL** (Increment: **0.001**)
Default value	**0.1 mL**

Standard 2 (mL)

Addition volume for **Standard 2**.

Input range	**0.01 - 999 mL** (Increment: **0.001**)
Default value	**0.1 mL**

Standard 3 (mL)

Addition volume for **Standard 3**.

Input range	**0.01 - 999 mL** (Increment: **0.001**)
Default value	**0.1 mL**

Standard 4 (mL)

Addition volume for **Standard 4**.

Input range	**0.01 - 999 mL** (Increment: **0.001**)
Default value	**0.1 mL**

4.2 Loading and saving a file

Loading a method

1 Click on or on **Menu bar ▸ File ▸ Load method…**.

2 Select the desired method file ***.detp** in the **Load file** dialog window. If necessary, browse for the location of the method. Click on **[Open]** to load the method.

The default directory for methods is ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Method*** .

Example methods can be found in the folder ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Examples\Methods***.

3 To check or edit method parameters of the loaded method click on or **Menu bar ▸ Method ▸ Edit method parameters…**.

NOTE

Some method parameters, e.g. voltammetric parameters, cannot be edited anymore once a determination was carried out with the loaded method. If voltammetric parameters have to be adapted, the method file has to be reloaded.

Saving a method

1 If a modified method should be saved under the same name, click on **Menu bar ▸ File ▸ Save method**. The existing method file will be overwritten.

NOTE

Example methods are read-only and cannot be overwritten. In this case, use the function **Save method as…** and save the method under a new name.

2 If a modified method should be saved under a new name, click on **Menu bar ▸ File ▸ Save method as…**.

3 In the **Save method** dialog window, select the folder where the method should be saved, type in a file name and click on **[Save]**.

Loading a determination

1 Click on  or on **Menu bar ▸ File ▸ Load determination…**.

2 Select the desired determination file ***.det** in the **Load file** dialog window. If necessary, browse for the location of the determination. Click on **[Open]** to load the determination.

The default directory for determinations is ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Determination***.

Example determinations can be found in the folder ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Examples\Determinations***.

3 To check or edit determination parameters of the loaded determination click on  or **Menu bar ▸ Method ▸ Edit method parameters…**.

NOTE

Some method parameters, e.g. voltammetric parameters, cannot be edited in a determination file. Nonetheless the reevaluation of peaks and recalculation of standard additions is still possible. *For more information on the reevaluation of a determination see Chapter 4.4, page 31*.

If the voltammetric parameters of the determination method should be adapted for future measurements, the parameters have to be saved first, using the function **Save method as…**. The new method, containing all parameters of the determination method, can then be loaded and edited.

Saving a determination

1 If a modified determination should be saved under the same name, click on **Menu bar** ▸ **File** ▸ **Save determination**. The existing determination file will be overwritten.

NOTE

Automatically saved determinations and example determinations are read-only. In these cases use the function **Save determination as…** and save the determination under a new name.

2 If a modified determination should be saved under a new name, click on **Menu bar** ▸ **File** ▸ **Save determination as…**.

3 In the **Save determination** dialog window, select the folder where the determination should be saved, type in a file name and click on **[Save]**.

4.3 Running a determination

1 Establish the connection between the instrument and the software.

2 Load the method.

3 Prepare the measuring solution and place it in the measuring stand. Assemble the measuring stand so that electrode and stirrer are immersed in the measuring solution.

4 Click on or **Menu bar** ▸ **Devices** ▸ **Start**.

5 Adapt the information in the dialog window **Determination information** if necessary. When all details are correct click on **[OK]**.

6 If the option **Measure blank** is active in the method, a message is displayed in the subwindow **Messages**, as soon as the addition of sample is required.

Add the specified volume of sample through one of the two pipetting openings in the transparent ring and confirm the addition by clicking into the subwindow **Messages**.

7 When the addition of standard solution is required a message is displayed in the subwindow **Messages**. Add the specified volume of standard solution(s) through one of the two pipetting openings in the transparent ring and confirm the addition by clicking into the subwindow **Messages**.

- The subwindow **Run** shows the progress of the determination.
- The subwindow **Live curve** displays the currently measured voltammogram.
- The subwindow **Curves** displays an overlay of already measured voltammograms on the tab **Curves**. On the tab **Substance name**, the calibration of the corresponding calibration curve can be found.
- The subwindow **Results** displays the results of all substances specified in the method on the tab **Results**. Evaluation details, like peak heights and peak positions, can be found on the tab **Substance name**.

When the determination has ended, the determination file and, if thus defined in the method, a PDF file with the report is automatically saved.

NOTE

Directories for automatic saving of determinations and reports are predefined and cannot be modified.

Determination files are saved in the directory ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Determination*** . The file name is automatically generated from date and time of the determination start and the sample identifier. The format is **YYYYMMDD-hhmmss 'Sample identifier'.det**.

The PDF file with the report is saved in the directory ***%USERPROFILE%\Documents\Metrohm\Portable VA Analyzer\Report***. The format is **YYYYMMDD-hhmmss 'Sample identifier'.det_Report.pdf**.

NOTE

Automatically saved determinations are read-only. Changes of a reevaluated determination must be saved under a new name.

4.4 Reevaluating a determination

In this section short instructions can be found how to:

- *Adapting the peak recognition (page 31)*
- *Changing the final result unit (page 32)*
- *Excluding a curve from the evaluation (page 32)*
- *Adapting the baseline parameters for all curves (page 33)*
- *Adapting the base points for an individual curve (page 33)*
- *Adapting the settings for the standard addition (page 34)*
- *Adapting the sample size (page 35)*

NOTE

Changes will not automatically be saved to the determination. To save changes use the function **Save determination** or **Save determination as…** *(page 29)*.

NOTE

Some method parameters, e.g. voltammetric parameters, cannot be edited in a determination file.

If the voltammetric parameters of the determination method should be adapted for future measurements, the parameters have to be saved first, using the function **Save method as…** *(page 27)*. The new method, containing all parameters of the determination method, can then be loaded and edited.

Adapting the peak recognition

1 Click on or **Menu bar ▸ Method ▸ Edit method parameters…**.

2 In the dialog window **Method parameters**, go to the tab **Evaluation**. In the section **Substances**, change the settings for the peak recognition, e.g. **Characteristic potential** or **Tolerance** as required.

3 Close the dialog window **Method parameters** with **[OK]**.

The determination will automatically be recalculated with the new settings.

Changing the final result unit

1 Click on or **Menu bar ▸ Method ▸ Edit method parameters…**.

2 In the dialog window **Method parameters** go to the tab **Evaluation**. In the section **Substances** go to the column **Result unit** and select a unit from the drop-down menu.

NOTE

The **Result unit** depends on the unit of the standard solution. If the concentration of the standard solution is a mass concentration, e.g. mg/L, also the result unit has to be a mass concentration, e.g. µg/L. If the concentration of the standard solution is a molar concentration, e.g. µmol/L, the result unit has to be a molar concentration too, e.g. nmol/L.

3 Close the dialog window **Method parameters** with **[OK]**.

The determination will automatically be recalculated and displayed with the new result unit.

Excluding a curve from the evaluation

1 On the workplace go to the subwindow **Results** and select the tab with the name of the substance for which a curve should be excluded from the evaluation.

2 In the column **Used** deactivate the check box of the curve which should be excluded from the evaluation.

3 Click on or **Menu bar** ▸ **File** ▸ **Reprocess** to reprocess the evaluation and calculation without the excluded curve.

Adapting the baseline parameters for all curves

1 Click on or **Menu bar** ▸ **Method** ▸ **Edit method parameters…**.

2 In the dialog window **Method parameters** go to the tab **Evaluation**, section **Substances**.

To set manual base points, deactivate the check box **Base points automatically** and type in values for **Start base point** and/or **End base point**.

A different baseline type can be selected from the drop-down menu **Baseline type**.

3 Close the dialog window **Method parameters** with **[OK]**.

The determination will automatically be recalculated with the new settings.

Adapting the base points for an individual curve

1 On the workplace, go to the subwindow **Results** and select the tab with the name of the substance for which the base point(s) should be adapted.

2 In the column **Manual base points**, activate the check box for the curve for which the base point(s) should be adapted.

3 Type in the new values for the base points in the column **Start base point** and/or **End base point**.

4 Click on or **Menu bar** ▸ **File** ▸ **Reprocess** to reprocess the evaluation and calculation with the new settings for the base point(s).

Adapting the settings for the standard addition

NOTE

The number of additions cannot be adapted subsequently. However, curves can be excluded from the evaluation as described above *(see "Excluding a curve from the evaluation", page 32)*.

1 Click on or **Menu bar ▸ Method ▸ Edit method parameters…**.

2 In the dialog window **Method parameters**, go to the tab **Evaluation**.

3 To adapt the concentration of the standard solution go to the section **Standard solutions**. Adapt concentration and/or concentration unit of the substance in the standard solution as required.

NOTE

A substance can only be contained in one standard solution. In case of multiple standards, the concentration in the other standard solution(s) has to be 0.

NOTE

The **Unit** of the standard solution is linked to the **Result unit** of the final result of the substance. If the concentration of the standard solution is a mass concentration, e.g. mg/L, also the result unit has to be a mass concentration, e.g. µg/L. If the concentration of the standard solution is a molar concentration, e.g. µmol/L, the result unit has to be a molar concentration too, e.g. nmol/L.

4 To adapt the volume of the standard addition go to the section **Volumes** and adapt the addition volume of the standard solution as required.

NOTE

The addition volume has to be specified in mL (milliliter).

5 Close the dialog window **Method parameters** with **[OK]**.

The determination will automatically be recalculated with the new settings.

Adapting the sample size

1 Click on or **Menu bar ▸ Method ▸ Edit method parameters…**.

2 In the dialog window **Method parameters** go to the tab **Determination**.

3 In the section **Sample and volume** adapt the volume for **Sample volume** and/or **Total cell volume**.

NOTE

All volumes have to be in mL (milliliter).

The **Total cell volume** is the volume of all solutions at the start of the determination. This includes sample volume and auxiliary solutions such as additional water and electrolyte, but not volumes for standard addition. The standard addition volume will automatically be taken into account.

4 Close the dialog window **Method parameters** with **[OK]**.

The determination will automatically be recalculated with the new settings.

4.5 Printing of result and method

Printing a determination result

1 Load the determination file for which the report should be printed, if not already loaded in the software.

2 Click on PDF or **Menu bar ▸ Reports ▸ Create PDF …**.

3 In the dialog window **Create PDF report**, select the **Report elements** which should be documented in the report. The following report elements can be freely combined by selection via check box.

- Results
  - General and determination information.
  - Table with concentration result for all substances in the determination.
- Evaluation
  - Table with evaluation details, like peak potential and peak height, for each substance and curve.
  - Table with regression data for each substance.
- Curves
  - Overlay of all voltammograms which are visible.
  - Individual calibration curve for each substance.
- Method
  - Method parameters
- Procedure
  - Method sequence

Confirm your selection by clicking on **[OK]**.

4 In the dialog window **Save PDF file as**, type in the file name under which the report should be saved. If necessary, browse for a different directory to save the report. Confirm the entries by clicking on **[Save]**.

The PDF file with the selected report elements will be created and saved in the specified directory.

Printing a method

1 Load the method file for which the parameters should be printed, if not already loaded in the software.

2 Click on PDF or **Menu bar ▸ Reports ▸ Create PDF …**.

3 In the dialog window **Create PDF report** the following **Report elements** can be selected via check box.

- Method
  - Method parameters
- Procedure
  - Method sequence

Confirm your selection by clicking on **[OK]**.

4 In the dialog window **Save PDF file as** type in the file name under which the method report should be saved. If necessary, browse for a different directory to save the report. Confirm the entries by clicking on **[Save]**.

The PDF file with the method parameters will be created and saved in the specified directory.

5 Curves

During a measurement, a live curve can be observed in the **Live curve** subwindow.

After the sweep is finished, the curve is displayed in the **Curves** subwindow on the tab **Curves**. All curves belonging to a determination are overlayed.

All curves displayed in the subwindow **Curves** are also listed in the subwindow **Graphics**. In the subwindow **Graphics**, you can edit the color and visibility of the curves.

If a peak can be evaluated, the corresponding calibration point is displayed in the subwindow **Curves** on the tab **'substance name' calibration**.

5.1 Live curve subwindow

The subwindow **Live curve** *(1-**6**)* is only visible, if an instrument is connected to the computer. It shows the currently measured voltammogram.

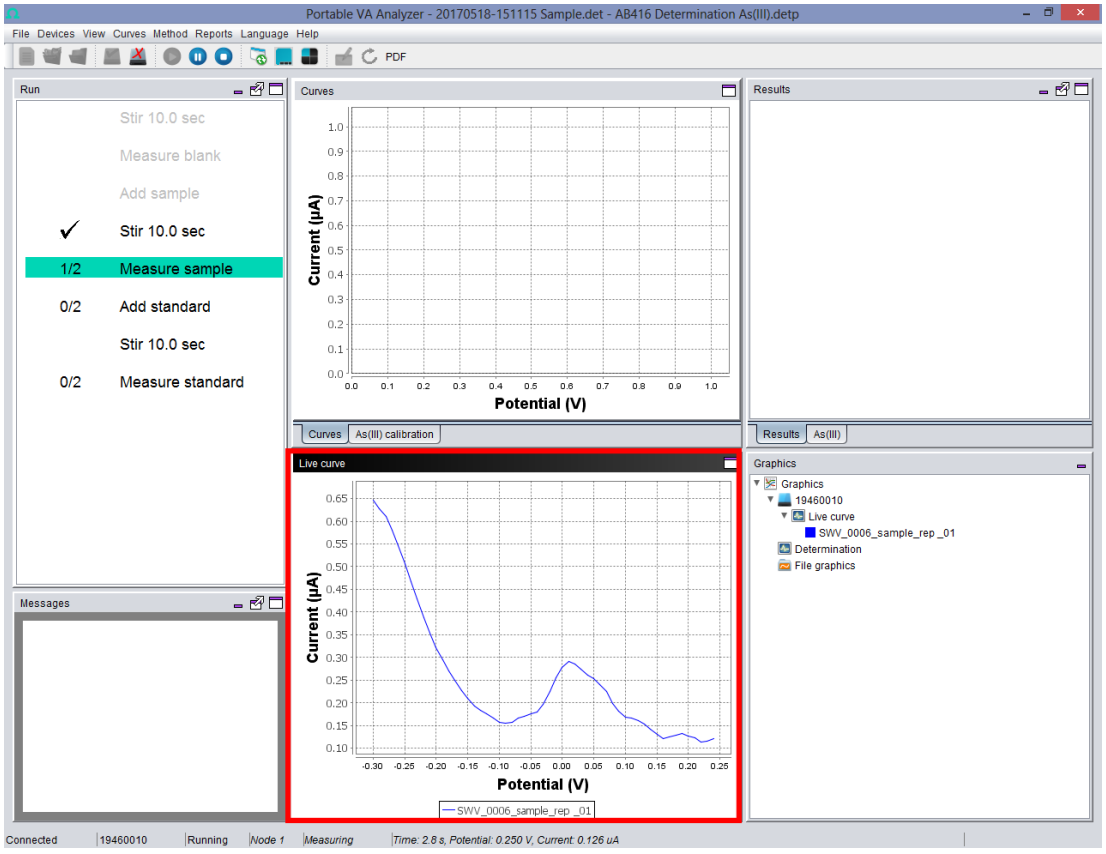


Figure 6 Live curve subwindow

During a measurement, all voltammetric sweeps, including the cyclovoltammetric pretreatment sweeps, are displayed in the subwindow **Live curve**.

After the sweeps are finished, the curves are copied to the tab **Curves** of the subwindow **Curves**, except for the pretreatment curves. Pretreatment curves are not copied, since they are neither evaluated nor saved.

In the **Default workplace** and **Mosaic workplace** layout the **Live curve** is displayed in a separate subwindow. In the **Tabs workplace** layout the **Live curve** appears as a tab in the **Curves** subwindow.

5.2 Curves subwindow

This subwindow includes maximum 6 tabs, depending on the workspace layout selected.

In the **Default workplace** layout, the subwindow **Curves** has up to 5 tabs:

- The tab **Curves** shows all voltammograms belonging to the determination.
- The tab **'Substance 1' calibration** shows calibration curve of substance 1.
- The tab **'Substance 2' calibration** shows calibration curve of substance 2, if substance 2 is used.
- The tab **'Substance 3' calibration** shows calibration curve of substance 3, if substance 3 is used.
- The tab **'Substance 4' calibration** shows calibration curve of substance 4, if substance 4 is used.

In the **Tabs workplace** layout, the subwindow **Curves** has up to 6 tabs:

- The tab **Curves** shows all voltammograms belonging to the determination.
- The tab **'Substance 1' calibration** shows calibration curve of substance 1.
- The tab **'Substance 2' calibration** shows calibration curve of substance 2, if substance 2 is used.
- The tab **'Substance 3' calibration** shows calibration curve of substance 3, if substance 3 is used.
- The tab **'Substance 4' calibration** shows calibration curve of substance 4, if substance 4 is used.
- The tab **Live curve** shows the currently measured voltammogram.

In the **Tabs workplace** layout, the curves are shown in a larger window, because the other tabs are hidden behind the current tab.

In the **Mosaic workplace** layout, each curve, voltammogram or calibration curve, is displayed in a separate subwindow.

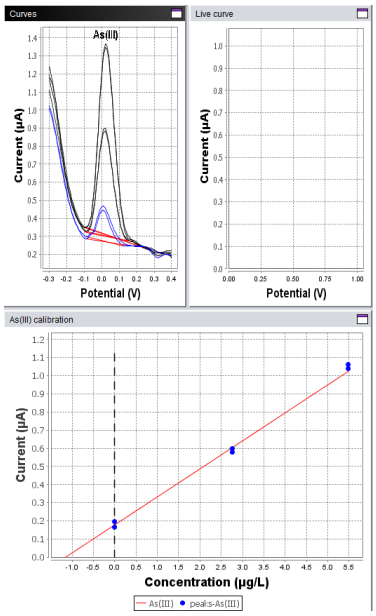


Figure 7 Curve subwindow: mosaic-based view

You can change the size of each window and drag and drop it in the desired position.

Options for manipulating the curve

With the options in the **View** menu, you can change the general appearance of the **Curves** subwindows, such as scaling, labels, and background color. You can also print the curve or save it as a *.PNG file.

With the options in the **Curves** menu or the context menu of the subwindow **Graphics** you can do the following:

- Change the name and the color of the curve.
- Select visibility options.
- Export data of the selected curve to a *.csv file
- Copy data of the selected curve to the clipboard
- Export all the curves to a *.csv file.

5.3 Displaying a 3D plot of a curve

1 Click on **View ▸ 3D plot**.

The **Curves selection** dialog window opens.

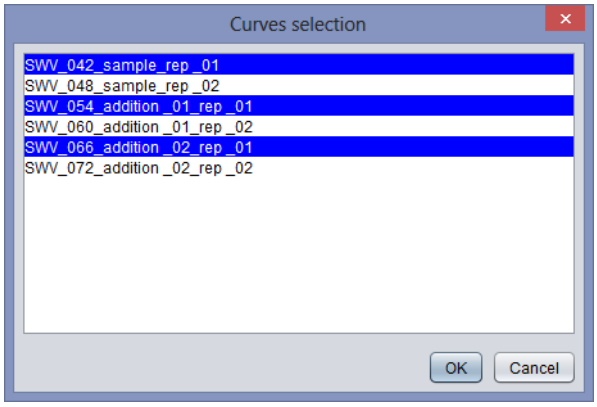


Figure 8 Select curves window for 3D plot

2
- Select the curves to be included in the 3D plot. Use standard **[Ctrl]**+click or **[shift]**+click actions to select multiple curves.
- Click on **[OK]**

The **3D settings and curve values** dialog window opens.

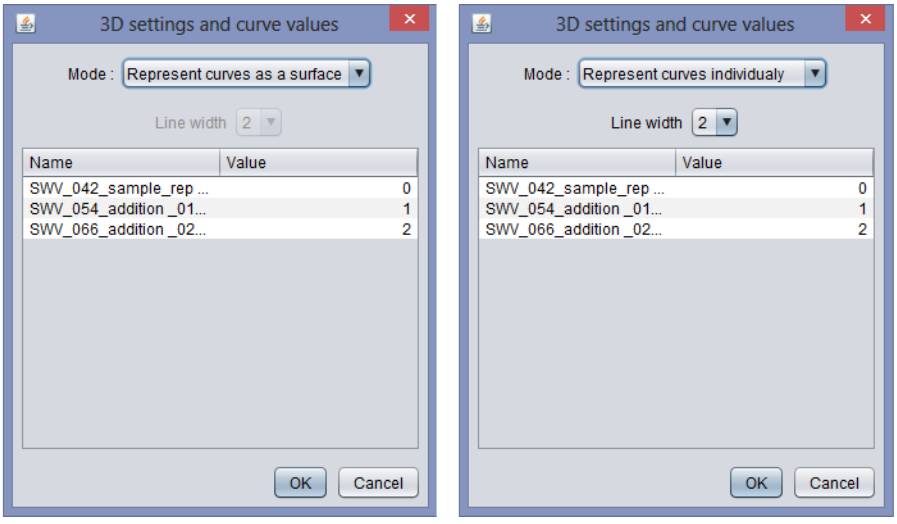


Figure 9 3D settings window options

3
- Select the **Mode** of the 3D plot: **Represent as a surface** or **Represent curves individually**
- If **Represent curves individually** is selected, define the **Line** width.

- Define the sequence of the selected curves by changing the numbers in the **Value** column.

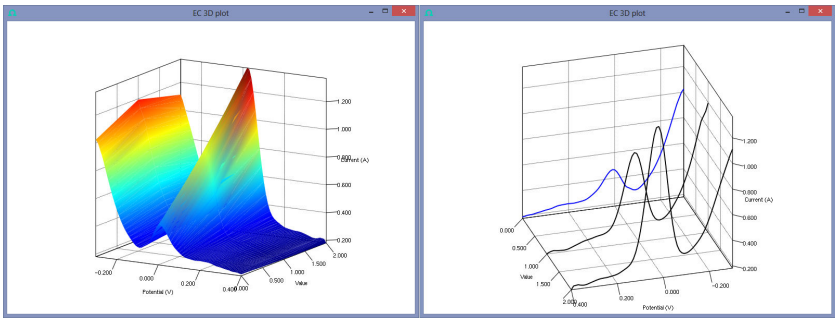


Figure 10 3D plots

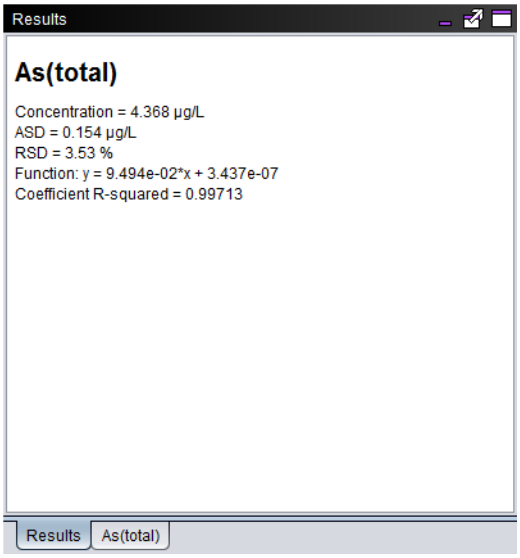
Options for manipulating the plot

- To rotate: Left click and drag mouse
- To scale: Roll mouse wheel
- To Z Shift: Right click and drag mouse
- To animate: Double left click
- To stop animation: Left click
- To save as .png: click “s” on the keyboard

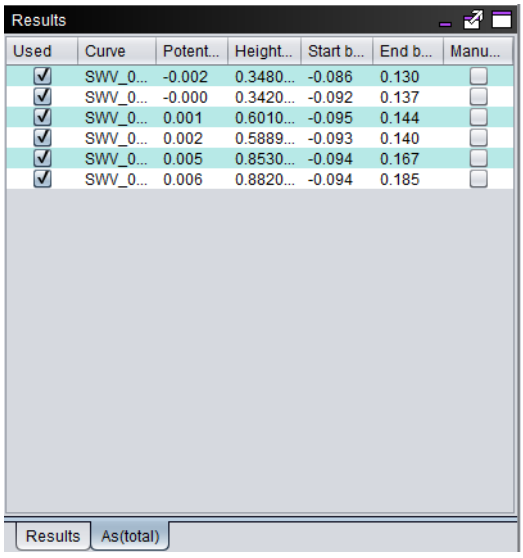
6 Results

The subwindow **Results** contains two different types of tabs:

- **Results**
  Shows the final result and the corresponding regression data used for the calculation. The information is summarized for all substances defined in the method.



- **'Substance name'**
  1 to 4 tabs showing evaluation details, like peak position and peak height of each individual curve. For each substance defined in the method an individual tab with the corresponding evaluation details in a table is available.



During a determination, the evaluation details are continuously updated. The results are refreshed as soon as another sweep is finished.

6.1 Results tab

The **Results** tab shows the concentration and regression data for 1 to 4 substances, depending on the number of substances defined in the method. Concentration(s) and regression data are displayed as soon as a sufficient number of calibration points is available for the calculation. The results are automatically refreshed after each sweep.

For details on the calculation of the linear regression using Least Square Fit method see Chapter 11.8.1, page 72.

For details on the calculation of the concentration from the regression data using standard addition technique see Chapter 11.7.2, page 69.

The following parameters are displayed for each substance:

Concentration

Substance concentration in the sample with respect to the **Sample volume** defined in the method.

ASD

Absolute standard deviation of the substance concentration in the sample.

RSD

Relative standard deviation of the substance concentration in the sample.

Function

Result of the calculation of the linear regression of the standard addition curve, with offset in [A] (Ampere) and slope in [A/(g·L-1)].

Coefficient R-squared

Coefficient R2 of determination calculated from the calibration function.

6.2 Evaluation details

Each sweep is tested for the presence of peaks which can be correlated to a substance defined in the method *(for details on the automatic peak recognition, see Chapter 11.4, page 65)*.

If a peak is detected, the peak height is evaluated using an approximated baseline *(for details see Chapters Peak height, page 66* and *Baseline type, page 67*). The details of this evaluation, such as peak position, peak height and baseline parameters are listed in a table for each substance on an individual tab, tagged with the substance name. In this table, it is also possible to adapt the evaluation of individual curves, either adapting base points or excluding the curve from evaluation.

The following evaluation details can be found in the table:

Used

on | off (Default value: **on**)

If the check box is activated, the curve is used for the result calculation. Individual curves can be excluded from result calculation.

Height (µA)

The peak height with the fixed unit µA.

For the evaluation of the peak height, a perpendicular is dropped from the peak maximum to the baseline and the height between peak maximum and baseline is determined.

Potential (V)

The peak potential with the fixed unit V.

For the evaluation of the peak position, the potential value corresponding with the maximum current value of the peak is determined.

Start base point (V)

The potential value of the Start base point of the baseline in Volt.

End base point (V)

The potential value of the End base point of the baseline in Volt.

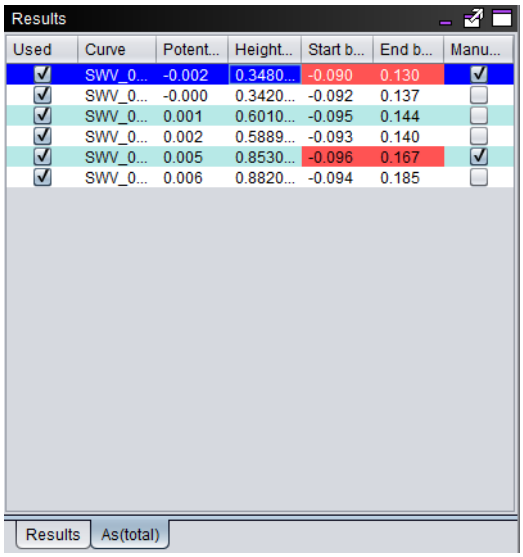
Manual base points

on | off (Default value: **off**)

If the check box is deactivated, the base points are automatically set according to method settings.

If the check box is activated, a manual value for each the start point and end point can be entered.

The manual values are highlighted in red until the determination is reprocessed using or **File ▸ Reprocess the curve evaluation**. After the reprocessing, the start base point and end base point for the baseline of this peak are forced to these manual values and the red cells will be displayed in the normal color.



For more details on reevaluating a determination see Chapter 4.4, page 31.

7 Procedure editor

Dialog window **Method** ▸ **Advanced settings** ▸ **Procedure editor**

The Portable VA Analyzer software allows configuring and programming advanced command sequences that can be mixed with the actual procedure. Open the Procedure editor to program or configure individual sequences.

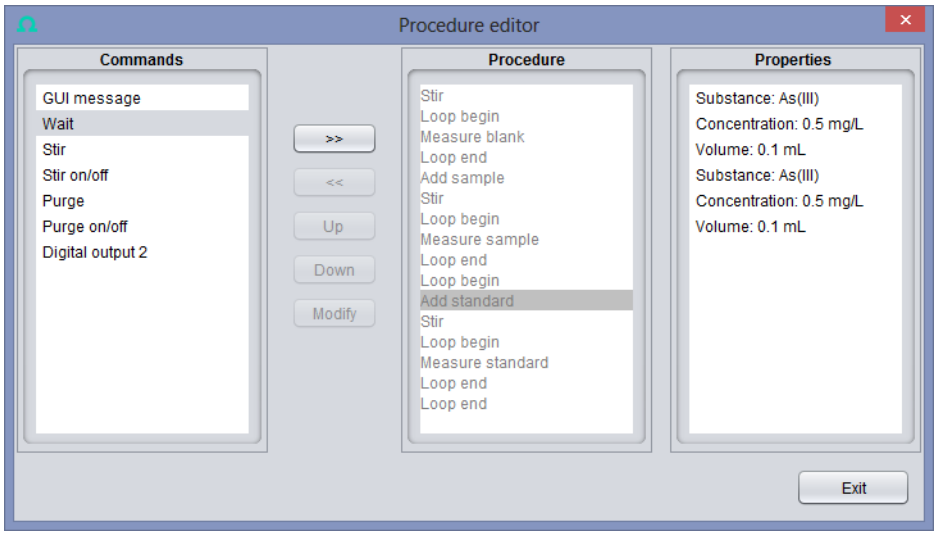


Figure 11 Procedure editor

Commands

Commands available for adding to a procedure.

GUI message

The text of the message will be displayed in the **Messages** subwindow on the workplace according to its position in the command sequence.

Wait

Waiting time (s).

Stir

Stirrer action.

In the **Properties** box, a stirring rate must be selected and a stirring time (s) defined.

Stirring rate

Only available if the command **Stir** is selected.

Input range	**500 - 4000 1/min**

Stirring time

Only available if the command **Stir** is selected.

Stirring time in seconds.

Stir on/off

Stirrer action. Switches the stirrer on or off unless another command says otherwise.

Purge

Purging action (s). The digital output 1 of the DIO cable (not included) is set to a high level (3.3V) for the time defined in the command, in order to control an external purge valve (not included).

In the **Properties** box, a purging time must be selected.

Purge time

Only available if the command **Purge** is selected.

Purging time in seconds.

Purge on/off

Purging action. Sets the digital output 1 of the DIO cable to a high level (3.3V) if on or to a low level (0 V) if off, in order to control an external purge valve (not included).

Digital output 2

Sets the digital output 2 of the DIO cable (not included) to a high level (3.3V) if on or to a low level (0 V) if off, in order to control an external device.

Procedure

Commands originating from the method or determination loaded are displayed in gray and cannot be modified.

Commands added from the **Commands** box are shown in black and can be modified.

Properties

Properties of the command selected in the **Procedure** box.

[>>]

Moves the command selected in the **Commands** box to the **Procedure** box. The command is entered at the top of the list. A dialog window appears reminding the user to enter the properties of the command.

[<<]

Moves the command selected in the **Procedure** box to the **Commands** box.

[Up]

Moves the command selected in the **Procedure** box up one position in the list.

[Down]

Moves the command selected in the **Procedure** box down one position in the list.

[Modify]

Opens the dialog window of the command selected in the **Procedure** box to modify the properties.

NOTE

Only commands inserter from the **Procedure editor** can be modified. All gray commands have to be edited in the **Method parameters** dialog window of the workplace.

[Exit]

Closes the **Procedure editor** dialog. The modified procedure is shown in the **Run** subwindow.

Editing a procedure

1. Select a command from the **Commands** box.
2. To move the command to the **Procedure** box, click on **[>>]**.

   The command is entered at the top of the list.
3. To move the command to the appropriate position in the list, click on **[Down]**.
4. To modify the properties of the command, click on **[Modify]**.
5. Once the procedure is edited, click on **[Exit]**.

   The modified procedure is displayed in the **Run** subwindow. The modified method can be saved and executed like a normal method.

NOTE

Standard method parameters can be edited in the **Method parameters** dialog window *(see Chapter 4.1, page 9)*.

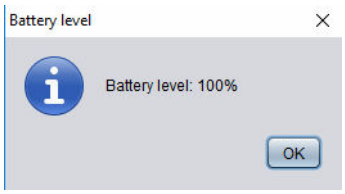
Commands introduced via **Procedure editor** can only be edited in the **Procedure editor**.

8 Other options

8.1 Check battery level

Dialog window: **Tool bar** ▸ **Devices** ▸ **View battery level**

The internal battery level of the instrument can be checked any time except if a determination is running.



If the battery level is lower than 30 %, we recommend to charge the battery using the power adapter.

8.2 Service option

The **Service** option is only available to authorized staff with a password.

8.3 Device info

Dialog window: **Menu bar** ▸ **Help** ▸ **Device info**

The **Device Info** dialog window shows the following information about the instrument connected:

- Device type
- Firmware version
- Serial number

8.4 Change language

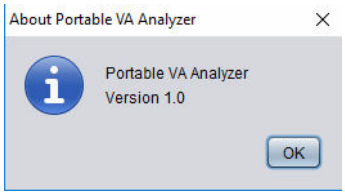
1. ▪ In the menu bar, click on **Language**.
   ▪ Select English or Chinese.

2. To apply the new language, close the software and restart it.

8.5 Help

To open the PDF file of the software manual, in the menu bar click on **Help ▸ Manual**.

To show the name and version of the software, in the menu bar click **Help ▸ About…**.



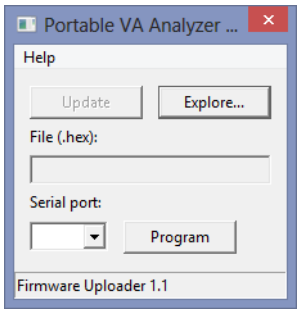
9 Firmware update

The firmware of the instrument can be updated with the *.hex files provided.

Updating the firmware

1
- Connect the 946 Portable VA Analyzer to the computer using the USB cable provided.
- Switch on the potentiostat

2 On the computer, start the **Portable VA Analyzer Firmware uploader**. Click on **Start** ▸ **All programms** ▸ **Metrohm** ▸ **Portable VA Analyzer** ▸ **Portable VA Analyzer Firmware uploader**.



3 Click on **[Explore…]** and navigate to the location of the *.hex file.

4 Select the Serial port to which the instrument is connected. Find more information on the serial port in chapter "Manual driver installation" in the Software installation manual (8.946.8002EN).

5 Click on **[Program]**. Wait until the update is finished successfully.

NOTE

The update can take several minutes. Do not disconnect the 946 Portable VA Analyzer instrument while update is in progress.

When the update is finished:

- The firmware uploader software shows the message **Firmware uploaded** in the footer.
- On the potentiostat the green and yellow status LEDs light up.

6 On the potentiostat, press the **Reset** button.

The upload is completed. The 946 Portable VA Analyzer is ready to be used with the uploaded firmware.

10 Troubleshooting

Problem	Cause	Remedy
Error - Connection error	*The USB cable is not connected.*	▪ Disconnect the software from the instrument. ▪ Connect the USB cable between potentiostat and PC/laptop. ▪ Restart the Software and re-establish the connection *(see "Connecting the instrument after a connection error", page 8)*
	The potentiostat is switched off.	▪ Disconnect the software from the instrument. ▪ Switch on the potentiostat and check for the green status LED which indicates that the power is on. ▪ Restart the Software and re-establish the connection *(see "Connecting the instrument after a connection error", page 8)*
	The connect button is clicked too shortly after switching on the instrument.	▪ Disconnect the software from the instrument. ▪ After the potentiostat is switched on it takes a few seconds before the USB communication is established. Allow 5 s and retry to connect the potentiostat. ▪ Restart the Software and re-establish the connection *(see "Connecting the instrument after a connection error", page 8)*
Error - No device available	*The USB cable is not connected.*	▪ Connect the USB cable between potentiostat and PC/laptop. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*
	The potentiostat is switched off.	▪ Switch on the potentiostat and check for the green status LED which indicates that the power is on. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*

Problem	Cause	Remedy
	The connect button is clicked too shortly after switching on the instrument.	▪ After the potentiostat is switched on it takes a few seconds before the USB communication is established. Allow 5 s and retry to connect the potentiostat. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*
Error - Potentiosat not found	*The USB cable is not connected.*	▪ Connect the USB cable between potentiostat and PC/laptop. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*
	The potentiostat is switched off.	▪ Switch on the potentiostat and check for the green status LED which indicates that the power is on. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*
	The connect button is clicked too shortly after switching on the instrument.	▪ After the potentiostat is switched on it takes a few seconds before the USB communication is established. Allow 5 s and retry to connect the potentiostat. ▪ Connect the instrument manually *(see "Connecting the instrument manually", page 7)*

11 Appendix

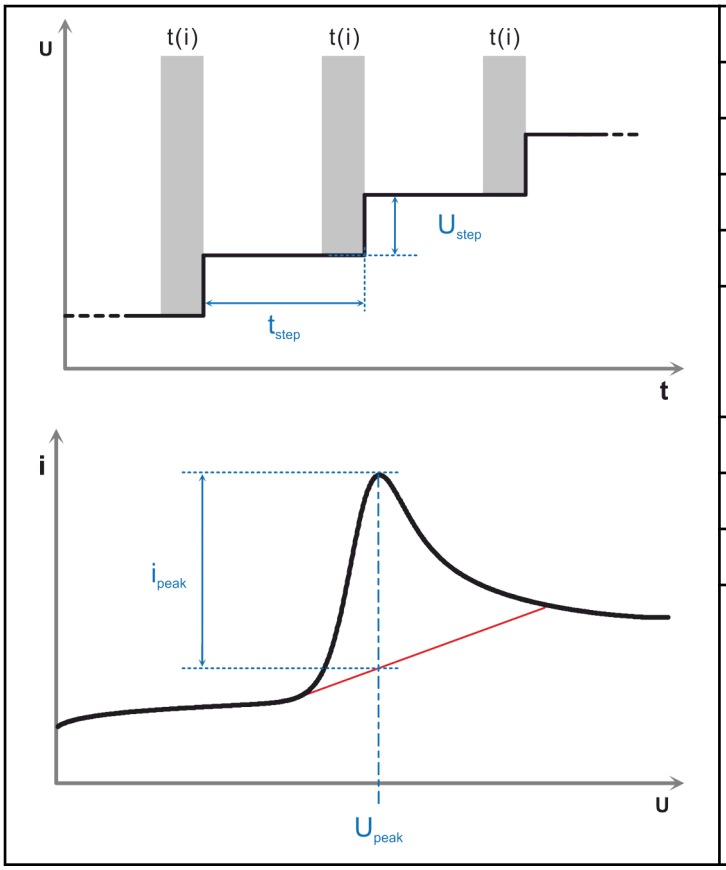
11.1 Linear sweep measuring mode

11.1.1 Principle

Linear sweep measuring mode is the classic, simplest voltammetric measurement mode. The potential applied to the working electrode is continuously changed with the rate defined by the parameters potential step and potential step time, resulting in a potential ramp with the slope of the sweep rate. For each step the resulting current is measured and plotted as a function of the potential U of the potential step. On a static electrode this results in a peak-shaped curve, in accordance with the Cotrell equation:

$$i(t) = \frac{nFA\sqrt{D} \cdot c_a}{\sqrt{\pi \cdot t}}$$

i	Current
t	Time
n	Number of electrones exchanged in the electrochemical reaction
F	Faraday constant $9.648 \cdot 10^4$ A·s/mol
A	Electrode area
D	Diffusion coefficient
c_a	Concentration of analyte
π	Pi (3.14159...)



U	**Potential**
t	**Time**
U_{start}	**Start potential**
U_{step}	**Potential step**
t_{step}	**Potential step time**
t(i)	**Measuring time** (Current measurementat the end of the potential step)
i	Current
i_{peak}	Peak height
U_{peak}	Peak potential

Sequence of individual steps

In the **Linear sweep** measuring mode, the following individual steps are successively executed in the method run:

Linear sweep measuring mode

1 Stirrer on

The stirrer is switched on with the defined **Stirring rate**.

2 Stirring time

Idle until the period defined in the **Stirring time** parameter has expired.

3 Cyclovoltammetric pretreatment

- The **Start potential** is applied.
- The sweep is carried out towards **Vertex potential** with the defined **Potential step** and **Sweep rate**.
- At the **Vertex potential** the sweep direction is reversed and the sweep is continued towards **Start potential** with the defined **Potential step** and **Sweep rate**.

- The sweep ends at **Start potential**.
- The cycle **Start potential** - **Vertex potential** - **Start potential** is repeated in accordance with the **No. of cycles**.

4 Potentiostatic pretreatment

- **Potential 1** is applied to the electrodes during **Waiting time 1** (if **Waiting time 1** > 0 s).
- **Potential 2** is applied to the electrodes during **Waiting time 2** (if **Waiting time 2** > 0 s).

5 Stirrer off

The stirrer is switched off.

6 Start potential

The **Start potential** defined in the sweep is applied to the electrodes.

7 Equilibration time

Idle until the period defined in the **Equilibration time** parameter has expired.

8 Sweep

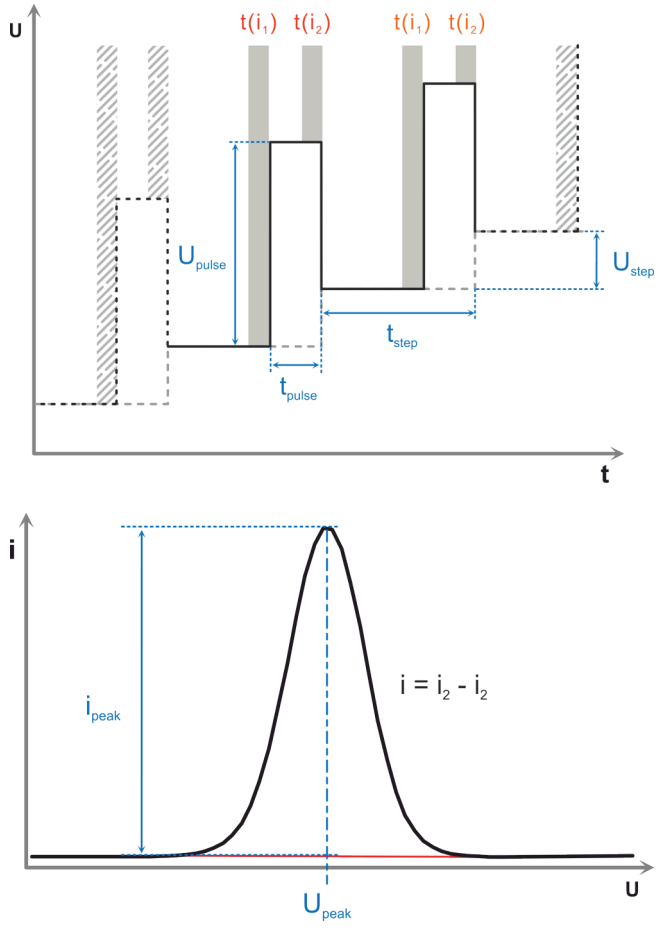
- The measurement is carried out from **Start potential** towards **End potential** with the **Potential step** defining the resolution of the curve and the **Sweep rate** defining the rate of potential change.
- The curve resulting from the sweep is stored and evaluated.

11.2 Differential pulse measuring mode

11.2.1 Principle

In the differential pulse measuring mode, a gradually increasing potential ramp (as in linear sweep voltammetry) is overlaid with rectangular pulses which are applied in sweep direction. The current *i* is measured immediately before the pulse and at the end of the pulse. The difference between the two measured currents is plotted as a function of the potential U of the potential step. This results in a peak-shaped curve.

Differential pulse measuring mode is the most universal and frequently used voltammetric measurement mode. It is equally well suited for irreversible and reversible systems and offers a high sensitivity.



U	**Potential**
t	**Time**
U_{start}	**Start potential** *(see page 18)*
U_{pulse}	**Pulse amplitude** *(see page 20)*
U_{step}	**Potential step** *(see page 18)*
t_{pulse}	**Pulse time** *(see page 20)*
t_{step}	**Potential step time**
$t(i_1)$	**Measuring time** (Current measurement immediately before pulse start)
$t(i_2)$	**Measuring time** (Current measurement immediately before pulse end)
i	Current
i_{peak}	Peak height
$i = i_2 - i_1$	Difference between the two current measurements
U_{peak}	Peak potential

Sequence of individual steps

In the **Differential pulse** measuring mode, the following individual steps are successively executed in the method run:

Differential pulse measuring mode

1 Stirrer on

The stirrer is switched on with the defined **Stirring rate**.

2 Stirring time

Idle until the period defined in the **Stirring time** parameter has expired.

3 Cyclovoltammetric pretreatment

- The **Start potential** is applied.
- The sweep is carried out towards **Vertex potential** with the defined **Potential step** and **Sweep rate**.
- At the **Vertex potential** the sweep direction is reversed and the sweep is continued towards Start potential with the defined **Potential step** and **Sweep rate**.
- The sweep ends at **Start potential**.
- The cycle **Start potential** - **Vertex potential** - **Start potential** is repeated in accordance with the **No. of cycles**.

4 Potentiostatic pretreatment

- **Potential 1** is applied to the electrodes during **Waiting time 1** (if **Waiting time 1** > 0 s).
- **Potential 2** is applied to the electrodes during **Waiting time 2** (if **Waiting time 2** > 0 s).

5 Stirrer off

The stirrer is switched off.

6 Start potential

The **Start potential** defined in the sweep is applied to the electrodes.

7 Equilibration time

Idle until the period defined in the **Equilibration time** parameter has expired.

8 Sweep

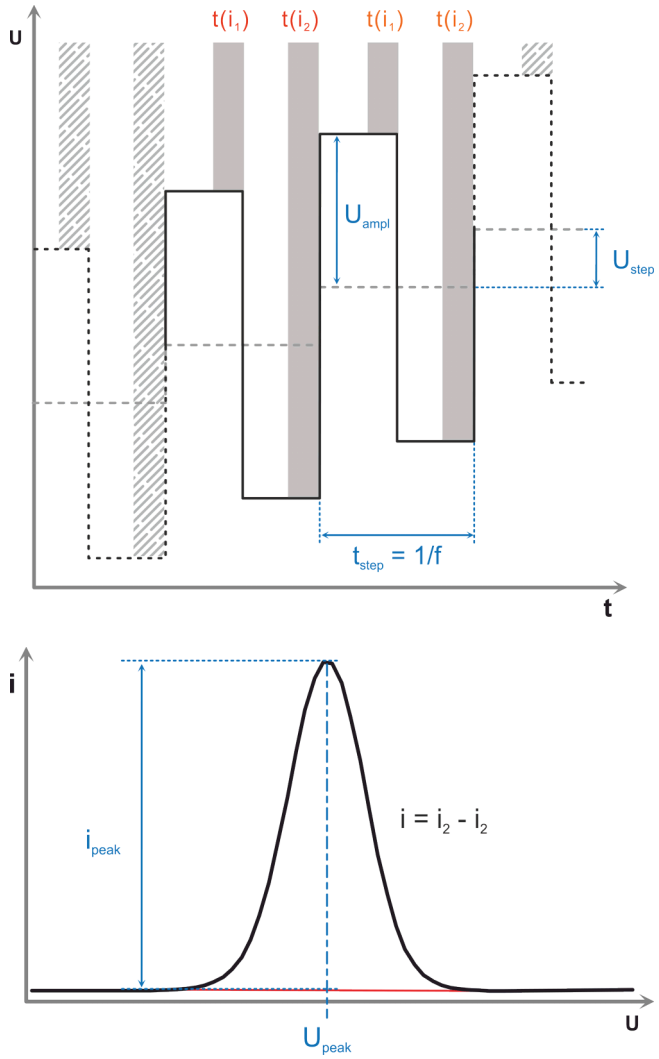
- The measurement is carried out from **Start potential** towards **End potential** with the **Potential step** defining the resolution of the curve and the **Sweep rate** defining the rate of potential change. The parameters **Pulse amplitude** and **Pulse time** define the superimposed rectangular pulse.
- The curve resulting from the sweep is stored and evaluated.

11.3 Square wave measuring mode

11.3.1 Principle

In the square-wave measuring mode (according to Osteryoung), a gradually increasing potential ramp (as in linear sweep voltammetry) is overlaid with rectangular AC potentials with a constant amplitude. For each potential step a rectangular pulse is applied in sweep direction and another one contrary to the sweep direction. The current *I* is measured at the end of each pulse during the measuring time. The difference between the two measured currents is plotted as a function of the potential *U* of the potential step. This results in a peak-shaped curve.

Square-wave measuring mode is primarily suitable for reversible electrode processes. It is used particularly for sensitive stripping voltammetric determinations.



U	**Potential**
t	**Time**
U_{start}	**Start potential** *(see page 16)*
U_{ampl}	Amplitude
U_{step}	**Potential step** *(see page 18)*
$t_{step} = 1/f$ f = Frequency	**Potential step time**
$t(i_1)$	Measuring time (current measurement at the end of the pulse in sweep direction)
$t(i_2)$	Measuring time (current measurement at the end of the pulse contrary to sweep direction)
i	Current
i_{peak}	Peak height
$i = i_1 - i_2$	Difference between the two current measurements
U_{peak}	Peak potential

Sequence of individual steps

In the **Square wave** measuring mode, the following individual steps are successively executed in the method run:

Square wave measuring mode

1 Stirrer on

The stirrer is switched on with the defined **Stirring rate**.

2 Stirring time

Idle until the period defined in the **Stirring time** parameter has expired.

3 Cyclovoltammetric pretreatment

- The **Start potential** is applied.
- The sweep is carried out towards **Vertex potential** with the defined **Potential step** and **Sweep rate**.
- At the **Vertex potential** the sweep direction is reversed and the sweep is continued towards Start potential with the defined **Potential step** and **Sweep rate**.
- The sweep ends at **Start potential**.
- The cycle **Start potential** - **Vertex potential** - **Start potential** is repeated in accordance with the **No. of cycles**.

4 Potentiostatic pretreatment

- **Potential 1** is applied to the electrodes during **Waiting time 1** (if **Waiting time 1** > 0 s).
- **Potential 2** is applied to the electrodes during **Waiting time 2** (if **Waiting time 2** > 0 s).

5 Stirrer off

The stirrer is switched off.

6 Start potential

The **Start potential** defined in the sweep is applied to the electrodes.

7 Equilibration time

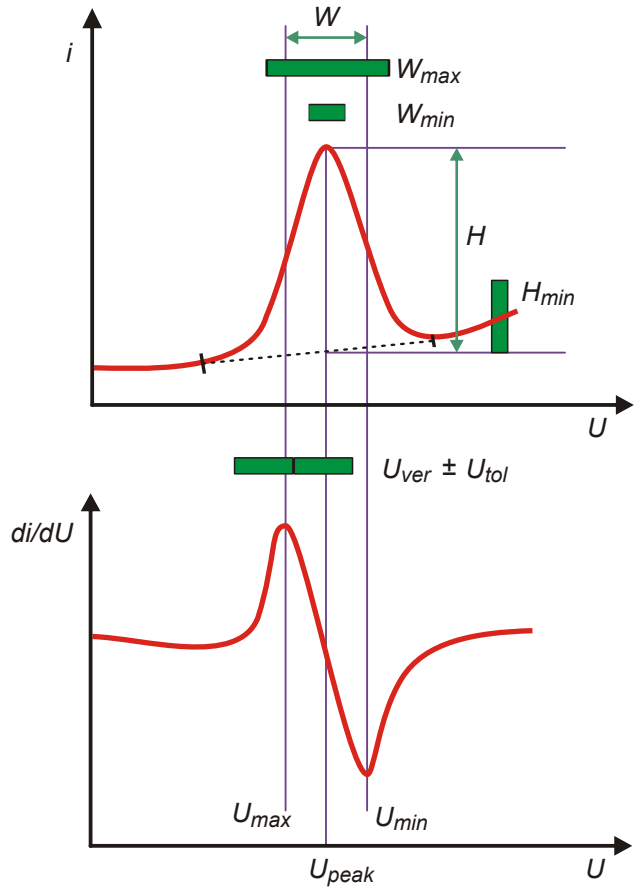
Idle until the period defined in the **Equilibration time** parameter has expired.

8 Sweep

- The measurement is carried out from **Start potential** towards **End potential** with the **Potential step** defining the resolution of the curve and the **Sweep rate** (given by **Sweep rate** = **Potential step** · **Frequency**) defining the rate of potential change. The parameters **Pulse amplitude** and **Frequency** define the superimposed rectangular pulse.
- The curve resulting from the sweep is stored and evaluated.

11.4 Peak recognition

The derived curve is used to search for consecutive minima U_{min} and maxima U_{max}. A maximum followed by a minimum indicates a normal peak, a minimum followed by a maximum a "reversed peak". These values are used to determine the peak potential U_{peak} and the peak width W for each peak. After peak detection, a baseline is constructed and the peak height H is determined from the value of the peak maximum minus the value of the baseline at the position of the peak potential.



i = Current
U = Potential
di/dU = 1st derivative of the current with respect to the potential
W = Peak width = $\lvert U_{min} - U_{max} \rvert$
W_{min} = Minimum peak width = **Min. width**
W_{max} = Maximum peak width = **Max. width**
H = Peak height
H_{min} = Minimum peak height = **Min. measured quantity**
U_{ver} = **Characteristic potential**
U_{tol} = **Tolerance** of the characteristic potential
U_{max} = Maximum potential of the derivative
U_{min} = Minimum potential of the derivative
U_{peak} = Peak potential = (U_{max} + U_{min}) / 2

The detected peaks are assigned to the defined substances based on these estimated values and the parameters defined on the **Recognition** tab in the **Substances** section. In the process, the following tests are carried out:

- **Peak potential**
  $U_{peak} = U_{ver} \pm U_{tol}$

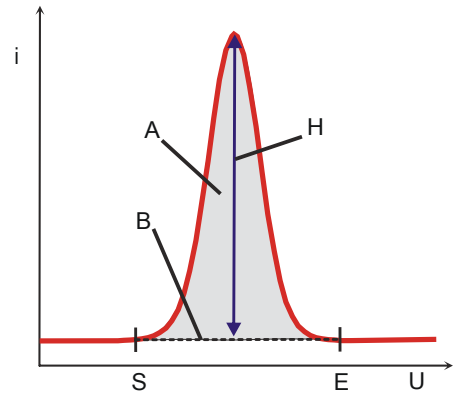
- **Peak width**
  $W > W_{min}$
  $W < W_{max}$
- **Peak height**
  $H > H_{min}$

This peak is assigned to the corresponding substance and thus recognized as substance peak when all test conditions are fulfilled. The peak is labeled with the substance name in the curve display if **Show substance label** is enabled in the menu **View**.

11.5 Peak height

The software can automatically evaluate a peak in a measurement curve. Using the peak height, the software can also perform an automatic calibration.

For the evaluation of the **Peak height**, a perpendicular is dropped from the peak maximum to the baseline and the height between peak maximum and baseline is determined. The peak height is output as current ***i*** [A].

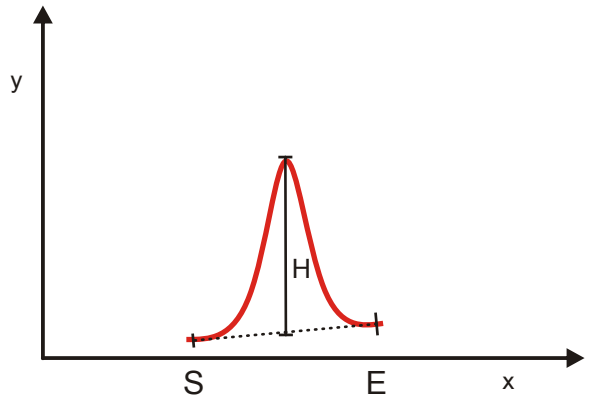
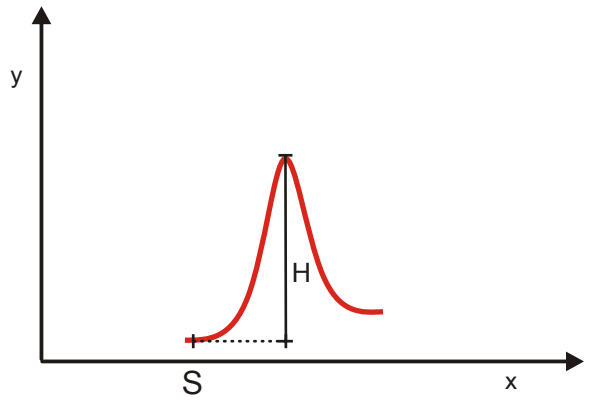
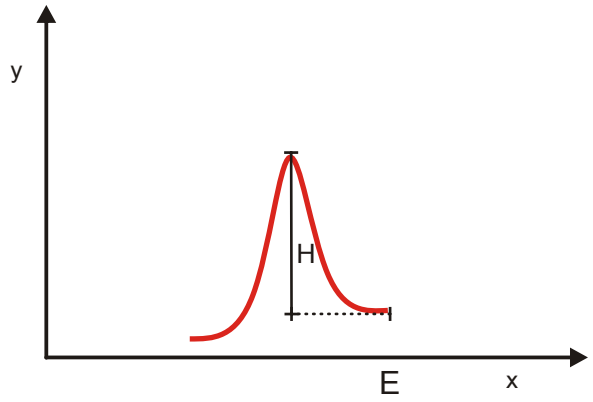


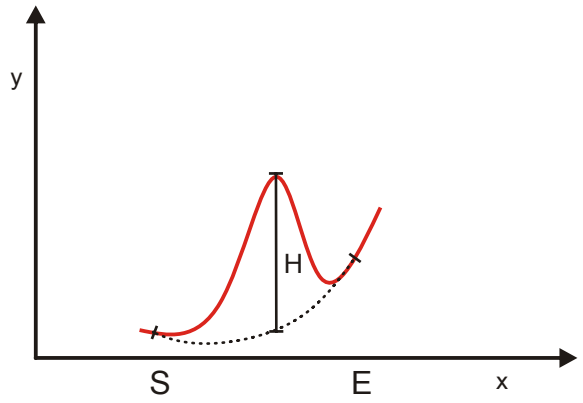
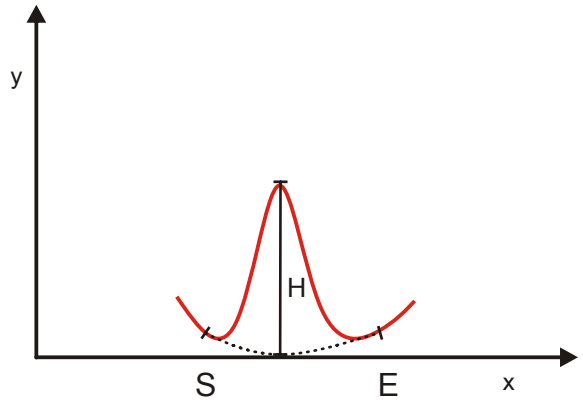
i = Current
U = Potential
S = Start base point
E = End base point
B = Baseline
A = Peak area
H = Peak height

11.6 Baseline type

The evaluation of detected peaks is carried out using approximated baselines.

The following types of baselines are differentiated:

Baseline type	Description
	**Linear** Linear baseline between two automatically determined or manually specified base points.
	**Horizontal start** Horizontal baseline starting from the automatically determined or manually specified start base point. The evaluation of the first peak half is used for asymmetric peaks.
	**Horizontal end** Horizontal baseline starting from the automatically determined or manually specified end base point. The evaluation of the second peak half is used for asymmetric peaks.

Baseline type	Description
	**Exponential** Curved baseline for peaks that are located in the ascending or descending part of another peak or of the background current. The base points can be determined automatically or specified manually.
	**Polynomial** Curved baseline for peaks that are located in a valley between two ascending curve parts. The base points can be determined automatically or specified manually.
Legend: S = Start base point E = End base point H = Peak height	

11.7 Evaluation - Calibration

11.7.1 Rules for the standard addition

Standard addition is the usual calibration method for voltammetric determinations. Its advantage is the high accuracy, as the calibration in the sample takes place under real matrix conditions and all measuring parameters remain unchanged. The following rules should be followed to ensure optimum trueness and minimized scattering:

- **Check linearity range**
  The linearity range should be checked for each substance when developing a method. To do so, spike the substance several times over a big concentration range. From the calibration curve displayed in the **Curves** subwindow, tab **'Substance name'** you can determine in which range the standard addition is linear and in which it is nonlinear.

- **Spiking procedure**
  If the substance content is in the linear range, then repeated spiking only makes sense if you want to check the linearity during each determination. In order to minimize scattering, it is better to spike only once but select the highest possible number of replications.
- **Spiking ratio 1:1 to 1:5**
  The optimum spiking ratio for the entire spiking procedure is 1:1 to 1:5, i.e., the sum of all spiking amounts should be one to five times the sample amount present in the measuring vessel.
- **Keep spiking volume low**
  Every spiking dilutes the measuring solution and thereby reduces the sample signal. The software corrects the resulting error. Nevertheless, the volumes used for the standard addition should be as small as possible. At the end of the determination the volume of all added standard solutions should not be more than 10% of the total volume.
  50 to 200 µL standard solution are usually added per spiking for 10 mL of measuring solution.
- **Evaluation quantity has to be monotonously ascending**
  A regression is only calculated for the standard addition if the evaluation quantity **Peak height** gets bigger with each spiking (monotonously ascending). If the evaluation quantity gets smaller with each spiking (monotonously descending) or the function is not monotonous, i.e. the peak gets bigger after one spiking and smaller after another, no regression and no result will be calculated.

11.7.2 Calculation of the standard addition

With the standard addition procedure (also known as spiking technique), a known amount of the substance(s) to be determined is added to the sample once or more. This addition is carried out manually. The following procedure is used to calculate the substance concentration in the measuring vessel **CONCM**:

1 Measurement of the sample solution

The sample solution with the unknown substance concentration **CONCM** is measured once or more (defined by the number of replications **y**). This results in:

- the evaluation quantity **Peak height** *y* (shown on the workplace in the subwindow **Results** on the tab with the evaluation details (tagged with the substance name) and in the PDF report in the column **Height (µA)** under **Evaluation details**)
- the mean value of all replications of the evaluation quantity *y* for the sample (shown only in the PDF report in the column **Mean height (µA)** under **Evaluation details**)

- the absolute standard deviation of all replications of the evaluation quantity *y* for the sample (shown only in the PDF report in the column **Std deviation (µA)** under **Evaluation details**)

2 Measurement of the spiked sample solutions

The sample solution is spiked n times with a standard solution with a known substance concentration. Each of these spiked solutions is measured once or more (defined by the number of replications **y**). This results in:

- the evaluation quantity *y*(n) of a single measurement for the spiked sample n (shown on the workplace in the subwindow **Results** on the tab with the evaluation details (tagged with the substance name) and in the PDF report in the column **Height (µA)** under **Evaluation details**)
- the mean value of all replications of the evaluation quantity *y*(n) for the spiked sample n (shown only in the PDF report in the column **Mean height (µA)** under **Evaluation details**)
- the absolute standard deviation of all replications of the evaluation quantity *y*(*n*) for the spiked samples (shown only in the PDF report in the column **Std deviation (µA)** under **Evaluation details**)
- the difference *x*(n) between the substance concentration *c*(n) in the spiked sample n and the substance concentration **CONCM** in the original sample solution

3 Calculation of the standard addition curve

For the calculation of the linear standard addition curve, the parameters **CALC0** and **CALC1** of the following linear regression curve are determined by weighted least squares:

$y(n) = \mathbf{CALC0} + \mathbf{CALC1} \cdot x(n)$

with $y(n) =$ **Peak height**

and $x(n) = c(n) -$ **CONCM**

The calibration function y = **CALC1**· x + **CALC0** is displayed in the **Results** subwindow on the tab **Results**. The coefficients have the following meaning:

- **CALC0** = y axis intercept of the standard addition curve
- **CALC1** = slope of the standard addition curve

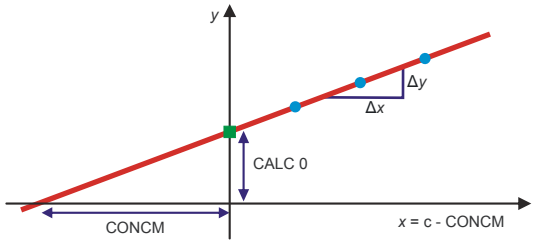
4 Calculation of the substance concentration CONCM

A prerequisite for the application of the standard addition is that for $c = 0$, the evaluation quantity *y* is also = 0. If 0 is entered in the cali-

bration function for these two quantities, the substance concentration **CONCM** can be calculated using the following equation:

$$CONCM = \frac{CALC0}{CALC1}$$

In the graphical display of the standard addition curve, the substance concentration **CONCM** is set by the distance from the point of origin to the intersection point with the regression line.



y = **Peak height**
x = *c* - **CONCM**
Δ*y* / Δ*x* = **CALC1** = slope
CALC0 = y axis intercept
CONCM = the unknown substance concentration
■ = sample
● = spiking

5 Calculation of the total error of the concentration calculation of CONCM

The total error **CONCM.ASD** of the result **CONCM** is determined with a linear error calculation. Irrespective of the number of measurements, the total error is always calculated so that **CONCM** ± **CONCM.ASD** indicates the area in which the true value of **CONCM** may be expected with a probability of 68.3%.

6 Calculation of the substance concentration in the sample CONC

Taking the dilution of the sample by the added auxiliary solutions into account, the substance concentration in the sample is calculated as follows:

$$CONC = \frac{CONCM \cdot V_{TOT}}{V_{SAMPLE}}$$

Variable	Description
CONC	Substance concentration in the sample.
CONCM	Substance concentration in the measuring vessel.

Variable	Description
V_{TOT}	Total volume in the measuring vessel at the moment of the sample measurement.
V_{SAMPLE}	Sample volume.

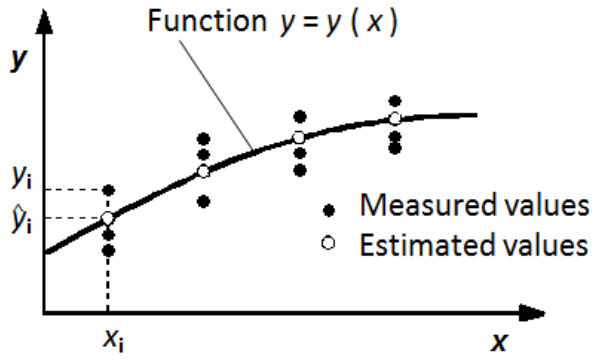
11.8 Evaluation - Calculated results

11.8.1 Result calculation from calibration curves and error calculation

The concentration (e.g. a mass concentration or a molar concentration) in the measuring vessel must be determined with the help of a calibration curve. This calibration curve itself must be determined by the measurement of solutions for which the concentrations are known. The parameters for a specified linear or nonlinear curve function are then calculated from the value pairs **Evaluation quantity / Concentration**. Because, as a general principle, the calculations of the calibration curves and the results based on them as well as the associated error calculation remain the same for all calibration methods, the calculation procedure that is applied is described in general terms below.

The connection between the variables x and y are sought on the basis of the measured values x_i, y_i, for which it is assumed that the following prerequisites apply:

- The variable x is error-free.
- The variable y is dependent on x and can be described by the function $y = y(x)$.
- The error with the measurement of y is distributed normally and is sufficiently small to be able to apply linear error calculation.



Depending on the calibration method selected, the following model functions are available for the calculation of the **calibration curve** $y = y(x)$:

Selected curve type	Calibration function	Description
Linear regression	$y = a + bx$	Line

To calculate the parameters a and b, the Least Squares Fit method is applied, for which the sum of the squared deviations of the measured val-

ues y_i from the estimates $\hat{y}_i$ is minimized. The scatter $\sigma_{y,i}$ of the measured values is usually not constant, however, but rather dependent on their values. Therefore, the deviations can be weighted with the factor g_i. Extremely scattered values should be given less weight, more precisely measured values should be given more weight. It is known from statistics that, under the conditions listed, weighting 1/variance = 1/standard deviation^2 = 1/$(\sigma_{y,i})^2$ yields the best results. In practice, however, the number of repeated measurements is too low to allow estimates from the measured values σ to be made. A general fact is of help here:

In the case of most measuring instruments, the scatter is comprised of a constant basic part and of a part proportional to the measured quantity. Influences that change over time also exist, however, e.g. the electrode status or the temperature. These usually change only slowly, which is why they can be regarded as constant during the measurement. One can therefore take their influence into account by means of an (unknown) factor p, which is multiplied against the basic scatter. Because of the fact that a constant factor has no influence over curve fitting, however, it can be ignored.

$$\sum_{i=1}^{n} g_i (y_i - \hat{y}_i)^2 = Minimum$$

with

$$g_i = \frac{1}{(\sigma_{y,i})^2} = \frac{1}{(p\,\sigma_{0,i})^2}$$

The weighting must adopt a constant value for small measured values in the vicinity of the instrument noise in order to exclude the possibility that small measured values are over-weighted.

The weighting is also appropriate if a calibration curve is acquired across a wide concentration range. Without weighting, the wide scatter of the values with a high concentration would falsify the calibration curve for the small values.

The calculated calibration curve is used with subsequent measurements to determine the associated **result** x_M from the mean value $\bar{y}_M$. The mean value $\bar{y}_M$ and the scattering $\sigma_{y,M}$ of the individual values are defined thereby as follows:

$$\bar{y}_M = \frac{1}{m} \sum_{i=1}^{m} y_{M,i} \qquad \sigma_{y,M} = \sqrt{\frac{\sum_{i=1}^{m} (y_{M,i} - \bar{y}_M)^2}{m - 1}}$$

The estimation of the total error σ_x of the result x_M is carried out with a linear **error calculation** that takes into account not only the error amount from the measurement but also that from the calibration. Because of the fact that the two amounts are statistically independent of one another, it is not the individual errors σ that are added but rather their variances σ^2 (with t = Student factor):

$$(\sigma_x)^2 = t\left[(\sigma_{x,M})^2 + (\sigma_{x,C})^2\right]$$

The error amount from the measurement itself is calculated from the derivative of the calibration function resolved in accordance with *x* in accordance with *y* and the measured scattering $\sigma_{y,M}$ as follows:

$$(\sigma_{x,M})^2 = \left(\frac{\partial x}{\partial y}\right)^2 (\sigma_{y,M})^2$$

The errors of the individual parameters $p_i = a, b$ of the calibration function used are determining for the calculation of the error amount from the calibration. Because of the fact that these parameters are statistically dependent on one another, all covariances $cov(p_i, p_j)$ must be taken into account here:

$$(\sigma_{x,C})^2 = \sum_{i,j} \frac{\partial x}{\partial p_i} \frac{\partial x}{\partial p_j} cov\,(p_i, p_j)$$

Statistically speaking, only small random samples (<10) are determined for voltammetric measurements from a population with Gaussian distribution. These random samples indicate a Student distribution that is taken into account with the Student factor *t*. If the variance is made up of a number of partial variances, then the Student factor is calculated by means of Welch-Satterthwaite formula approximation. The variance acquired with this procedure is multiplied by t^2; the resulting square root yields the standard deviation of the result.

The Student factor *t* depends on the number of measurements *n*, or, to be more precise, on the number of degrees of freedom $n - f$, for which *n* is the number of measuring points and *f* is the number of estimated parameters. The Student factor *t* is defined as follows for a probability of 68.3%:

$n - f$	t	$n - f$	t	$n - f$	t	Curve type	f
2	1.321	7	1.077	20	1.026	$y = a + bx$	2

Even though probabilities of 90% and more are usual in statistics, we select 68.3% in order to ensure compatibility with the conventional specification of normally distributed measured values *Mean value* ± *Standard deviation*. With normally distributed values, a standard deviation corresponds to a probability of 68.3%.

The total error **CONCM.ASD** of the result **CONCM** consequently indicates the **CONCM ± CONCM.ASD** area in which the true value of **CONCM** may be expected with a probability of 68.3%.

11.8.2 Curve results

11.8.2.1 Substance name

Description	Substance name
Decimal places	–
Unit	–

11.8.2.2 Peak potential of a substance

Description	Peak potential
Decimal places	**3**
Unit	**V**

11.8.2.3 Height

Description	Peak height
Decimal places	**6**
Unit	**µA**

11.8.2.4 Mean value of the heights of all replications

Description	Mean value of the peak heights of all replications.
Decimal places	**6**
Unit	**µA**

11.8.2.5 Absolute standard deviation of the heights of all replications

Description	Mean value of the peak heights of all replications.
Decimal places	**6**
Unit	**µA**

11.8.2.6 Delta of the mean values of the heights of all replications

Description	Difference between the mean value of the peak heights of all replications for the variation **{x}** and the mean value of the peak heights of all replications for the variation **{x-1}**.
Decimal places	**6**
Unit	**µA**

11.8.2.7 Start base point of baseline

Description	Start base point, where the peak evaluation baseline begins.
Decimal places	**3**
Unit	**V**

11.8.2.8 End base point of baseline

Description	End base point, where the peak evaluation baseline ends.
Decimal places	**3**
Unit	**V**

11.8.3 Calibration curve results

Standard results of the calibration curve calculation are referred to as **calibration curve results**. They are created once per substance.

The results of the regression (**CALC0** and **CALC1** and **R2**) are calculated as soon as a sufficient number of calibration points of different concentrations is available for the selected calibration curve type. The variables will be recalculated once again and their old value will be overwritten as soon as another calibration point is added.

11.8.3.1 Coefficient CALC 0

Description	Zero-order coefficient of the standard addition curve.
Decimal places	**3**
Unit	**A**

11.8.3.2 Coefficient CALC 1

Description	First-order coefficient of the standard addition curve.	
Decimal places	**3**	
Unit	Concentration unit of the standard solution = **#g/L**	**A · L · g^{-1}**
	Concentration unit of the standard solution = **#mol/L**	**A · L · mol^{-1}**

11.8.3.3 Coefficient of determination R^2

Description	Coefficient of determination R^2.
Decimal places	**5**
Unit	**–**

Calculation

$$R^2 = \frac{\sum_{i=1}^{n}(y_i - \bar{y})^2 - \sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2}$$

Variable	Description
R^2	Coefficient of determination.
y_i	y value of calibration point *i*.
$\bar{y}$	Mean value of all y values of the calibration points.
$\hat{y}_i$	The y value of calibration point *i* calculated with the calibration curve.

11.8.4 Concentration results

11.8.4.1 Substance concentration in the sample

Description	Substance concentration in the sample.		
Decimal places	**3**		
Unit		**Unit of standard solution**	
	Sample volume	**#g/L**	**#mol/L**
	mL	#g/L	#mol/L

Calculation

$$CONC = \frac{CONCM \cdot V_{TOT}}{V_{SAMPLE}}$$

Variable	Description
CONC	Substance concentration in the sample.
CONCM	Substance concentration in the measuring vessel.
V_{TOT}	Total volume in the measuring vessel at the moment of the sample measurement.

Variable	Description
V_{SAMPLE}	Sample volume.

11.8.4.2 Absolute standard deviation of the concentration of the substance in the sample

Description	Absolute standard deviation of the substance concentration in the sample.
Decimal places	**3**
Unit	same as for substance concentration in the sample *(see Chapter 11.8.4.1, page 77)*

11.8.4.3 Relative standard deviation of the concentration of the substance in the sample

Description	Relative standard deviation of the substance concentration in the sample.
Decimal places	**2**
Unit	**%**

Index