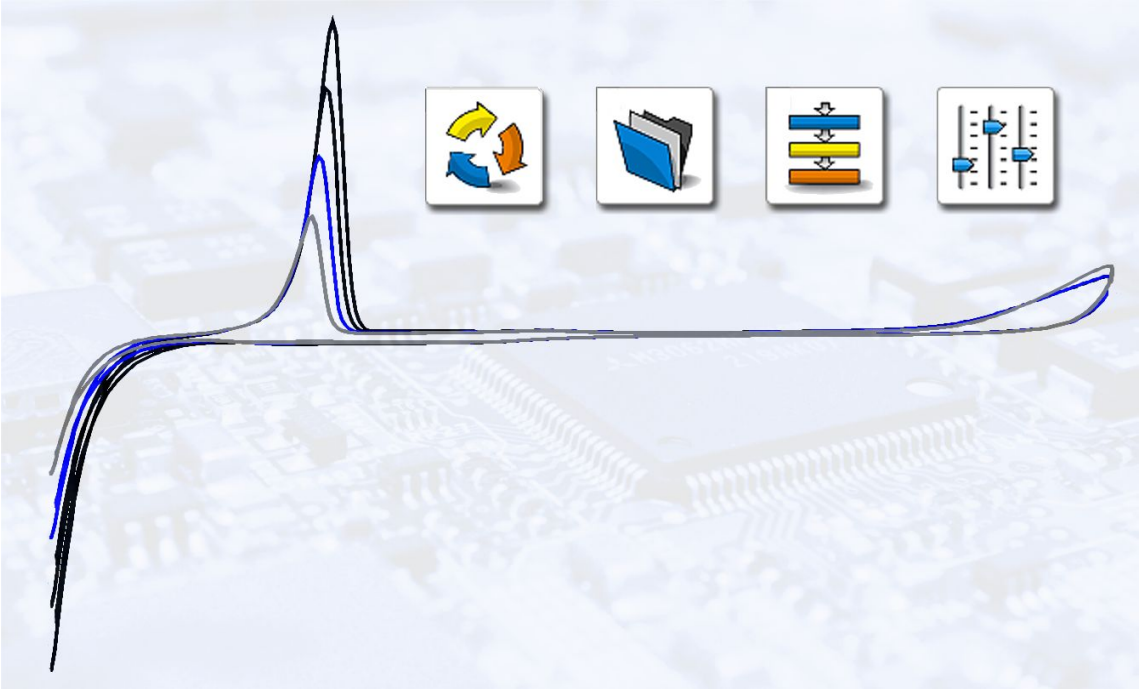
viva



Tutorial CVS

8.103.8010EN

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

Tutorial CVS

8.103.8010EN

04.2013 ek/doe

Teachware
Metrohm AG
CH-9100 Herisau
teachware@metrohm.com

This documentation is protected by copyright. All rights reserved.

Although all the information given in this documentation has been checked with great care, errors cannot be entirely excluded. Should you notice any mistakes please send us your comments using the address given above.

Documentation in additional languages can be found on *http://documents.metrohm.com*.

Table of contents

1 Introduction 1

1.1 Structure of the tutorial ... 1

1.2 Program description ... 1

1.3 Symbols and conventions ... 2

2 Preparations 3

2.1 Equipment ... 3

2.2 Preparing solutions ... 4

3 Configuration 5

3.1 Starting the software ... 5

4 Manual determination 7

4.1 Configuration ... 7
4.1.1 Configuring the instrument ... 7
4.1.2 Configuring electrodes ... 8

4.2 Methods for the manual determination ... 9
4.2.1 Conditioning the Pt working electrode ... 9
4.2.2 Determining the suppressor concentration ... 18
4.2.3 Determining the brightener concentration ... 29

5 Semiautomated determination 38

5.1 Configuration ... 39
5.1.1 Configuring the instrument ... 39
5.1.2 Configuring electrodes ... 39
5.1.3 Configuring dosing units ... 39
5.1.4 Defining solutions ... 42

5.2 Methods for the semiautomated determination ... 44
5.2.1 Conditioning the Pt working electrode ... 44
5.2.2 Determining the suppressor concentration ... 50
5.2.3 Determining the brightener concentration ... 56

6 Automated determination 62

6.1 Configuration ... 63
6.1.1 Configuring the instrument ... 63
6.1.2 Configuring electrodes ... 67
6.1.3 Configuring dosing units ... 67
6.1.4 Defining solutions ... 67

6.2 Methods for the automated determination ... 67
6.2.1 Determining the suppressor concentration ... 67

6.2.2 Determining the brightener concentration 77

7 Editing determinations 87

7.1 Viewing determinations 87

7.2 Viewing results 89

7.3 Reprocessing determinations 91

7.4 Editing a report template 93

7.5 Printing a determination report 97

Index 99

1 Introduction

1.1 Structure of the tutorial

The present tutorial guides you through your first steps using the **viva** software. You will become acquainted with the most important operating elements by way of a manual, a semiautomated and an automated determination of the suppressor and brightener concentration.

The instruments, solutions, electrodes and dosing units are defined in the **Configuration** program part.

Methods are created in the **Method** program part.

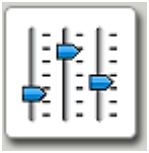
Determinations are carried out and live modifications made in the **Workplace** program part.

Determinations can be edited in the **Database** program part.

1.2 Program description

viva comprises the following program parts:

Configuration



- Configuring instruments, electrodes, solutions, rack data, dosing units and variables
- User administration
- Security settings
- Program administration

Method

- Creating, editing and managing methods
- Defining substances and standards
- Selecting the calibration method and defining the calibration parameters
- Result definition

Workplace

- Opening workplaces, selecting methods
- Entering sample data
- Starting single and multiple determinations
- Displaying live curves

Database

- Opening/closing databases
- Managing determinations
- Reprocessing determinations
- Creating reports

1.3 Symbols and conventions

The following symbols and formatting may appear in this documentation:

*(5-**12**)*	**Cross-reference to figure legend** The first number refers to the figure number, the second to the instrument part in the figure.
1	**Instruction step** Carry out these steps in the sequence shown.
Method	**Dialog text**, **parameter** in the software
File ▸ New	Menu or menu item
[Next]	**Button** or **key**
	WARNING This symbol draws attention to a possible life-threatening hazard or risk of injury.
	WARNING This symbol draws attention to a possible hazard due to electrical current.
	WARNING This symbol draws attention to a possible hazard due to heat or hot instrument parts.
	WARNING This symbol draws attention to a possible biological hazard.
	CAUTION This symbol draws attention to possible damage to instruments or instrument parts.
	NOTE This symbol highlights additional information and tips.

2 Preparations

2.1 Equipment

You will require the following equipment in order to be able to carry out the determinations described in this tutorial:

Devices

- 894 Professional CVS
- 858 Professional Sample Processor
- 807 Dosing Unit (three with a 2 mL and one with a 50 mL glass cylinder)
- 800 Dosino
  - 800 Dosino and 807 Dosing Unit with cylinder size 50 mL for dosing VMS
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing suppressor concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing brightener concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing standard solution or sample
- 843 Pump Station

Electrodes

- Working electrode **WE**
  - Pt electrode tip (e.g. 6.1204.610)
  - Driving axle for rotating disk electrode (RDE) (e.g. 6.1204.510)
- Reference electrode **RE**
  - Reference electrode filled with reference electrolyte (e.g. 6.0728.130)
    Reference electrolyte: c(KCl) = 3 mol/L
  - Electrolyte vessel filled with bridge electrolyte (e.g. 6.1245.010)
    Bridge electrolyte: $c(KNO_3)$ = 1 mol/L
- Auxiliary electrode **AE** (6.0343.100)

Reagents

- **VMS** (Virgin make-up solution)
  $\beta(CuSO_4 \cdot 5H_2O)$ = 60 g/L
  $\sigma(5H_2SO_4)$ = 130 mL/L
  $\beta(Cl^-)$ = 50 mg/L
- **Suppressor concentrate**
  σ(suppressor) = 1,000 mL/L
- **Brightener concentrate**
  σ(brightener) = 1,000 mL/L

Accessories

- Measuring vessel 10 - 90 mL (6.1415.210)
- Measuring vessel 10 - 150 mL (6.1415.250)
- Two 100 mL glass bottles
- One 2 L glass bottle
- Bottle holder (6.2055.110)
- Three thread adapters GL 45 on GL 45
- FEP tubing / M6 / 100 cm (6.1805.120)
- Four FEP tubings / M6 / 200 cm (6.1805.530)

2.2 Preparing solutions

VMS

1 In a 2,000 mL flask, dissolve 120 g of $CuSO_4 \cdot 5H_2O$ in approx. 800 mL of deionized water.

2

WARNING

Solution becomes hot!

Carefully add 260 mL of concentrated H_2SO_4 and 0.165 g of NaCl.

3 After cooling to room temperature, fill up to 2,000 mL with deionized water.

Suppressor standard solution

Suppressor concentrate is used for preparing the suppressor standard solution.

1 Fill VMS in a 50 mL flask, add 0.5 mL of suppressor concentrate and fill up to 50 mL with VMS.

Standard solution: σ(suppressor) = 10 mL/L.

3 Configuration

Metrohm devices connected to the PC via a USB connector are automatically recognized when the program is started, as are devices connected to MSB connectors of USB devices (Dosinos, sample changers).

The elements used in a method and at the workplace are defined in the **Configuration** program part. These include:

- Devices
- Dosing units
- Solutions
- Sensors/electrodes
- Rack data
- Common variables/global variables

3.1 Starting the software

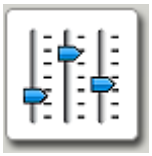
NOTE

Instruments are detected automatically and can be monitored by **viva**.

Proceed as follows to start the **viva** program:

1 Click on the **viva** icon on the desktop.

2 Enter user name and password (if defined) and click on **[OK]**.



3 Click on the **[Configuration]** icon.

The dialog window for the **Configuration** program part opens. Up to six subwindows can be displayed. Available are:

Devices	Shows the automatically detected devices.
Dosing units	Shows the automatically recognized dosing units.
Solutions	Shows the data of the defined solutions.
Sensors/Electrodes	Shows the data for all defined sensors and electrodes.
Rack data	Shows the data of the automatically recognized Metrohm sample racks.
Common Variables	Shows the data of all common variables.

Global Variables Shows the data of all global variables.

4 Manual determination

A manual determination is carried out with the following instrument:

- 894 Professional CVS

4.1 Configuration

4.1.1 Configuring the instrument

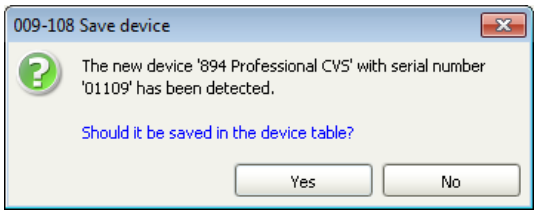
894 Professional CVS

Proceed as follows to start up the 894 Professional CVS for the first time:

1 Connecting the instrument

- Connect the 894 Professional CVS to the power supply by means of the power supply cable (6.2122.0x0).
- Connect the controller cable (6.2151.000) to the "Controller" connector of the 894 Professional CVS.
- Connect the USB plug of the controller cable to a USB connector of the PC.

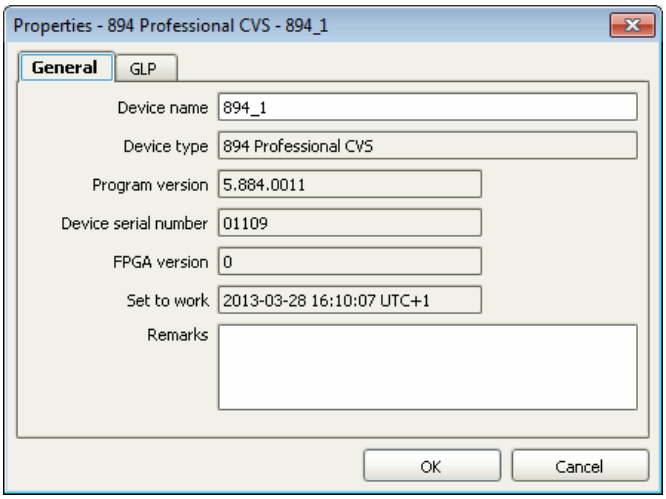
When the USB connection is active, then the 894 Professional CVS will be started and automatically detected by **viva**.



2 Saving the instrument in the table

Confirm the message with **[Yes]**.

The **Properties - 894 Professional CVS - 'Device name'** dialog window opens.



3 Entering an instrument name (optional)

On the **General** tab, enter a new name for the instrument in the **Device name** field and close the dialog window with **[OK]**.

The newly recognized instrument is entered in the device table in the **Devices** subwindow.

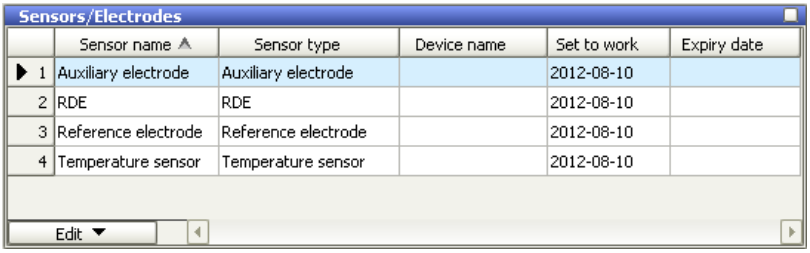
NOTE

In order to ensure a high measuring accuracy, the calibrator has to be activated (see Manual - Short Instructions 894 Professional CVS).

4.1.2 Configuring electrodes

The electrodes are configured in the **Sensors/Electrodes** subwindow.

The electrodes that are listed by default are used for the method templates applied here.



4.2 Methods for the manual determination

A method is a run instruction for processing a sample. It comprises all components necessary to record a voltammogram. These include:

- Devices and their start parameters
- Defining the sequence of a method. This consists of tracks that are themselves made up of various commands.
- Parameters for the evaluation of the voltammograms
- Result definitions

In this chapter, you will use method templates to create the following methods:

- A method for the manual conditioning of the Pt working electrode
- A method for the manual determination of the suppressor concentration (single determination)
- A method for the manual determination of the brightener concentration (single determination)

4.2.1 Conditioning the Pt working electrode

Prior to the analysis, the Pt working electrode needs to be conditioned. When used regularly, the electrode needs to be conditioned at least once a day.

4.2.1.1 Creating a method

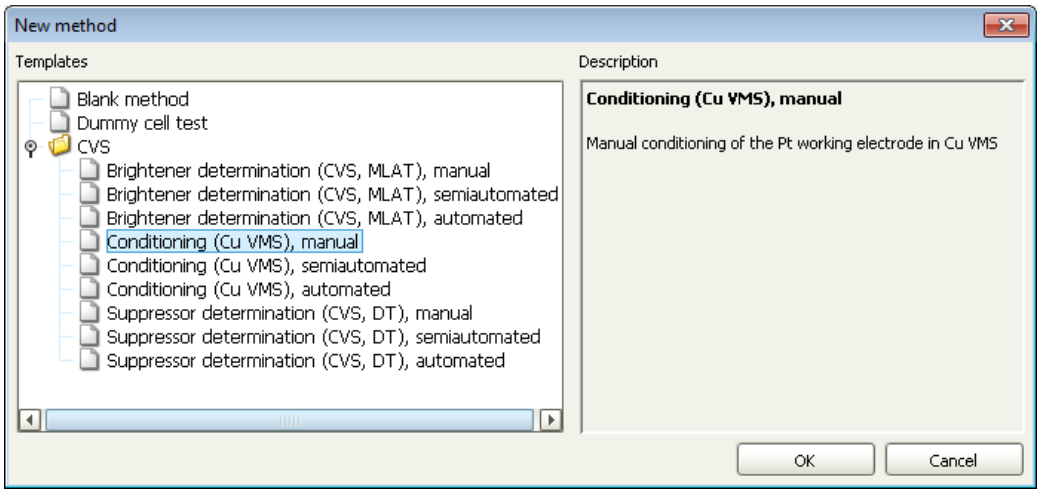
viva comprises method templates that contain all commands required to perform a determination. These method templates can be customized. You can, for instance, change parameters, select a different database to store determinations or add further commands.

It is advisable to use a method template; you can, however, also create a new method from scratch. To do so, select the method template **Blank method**.

Loading a method template

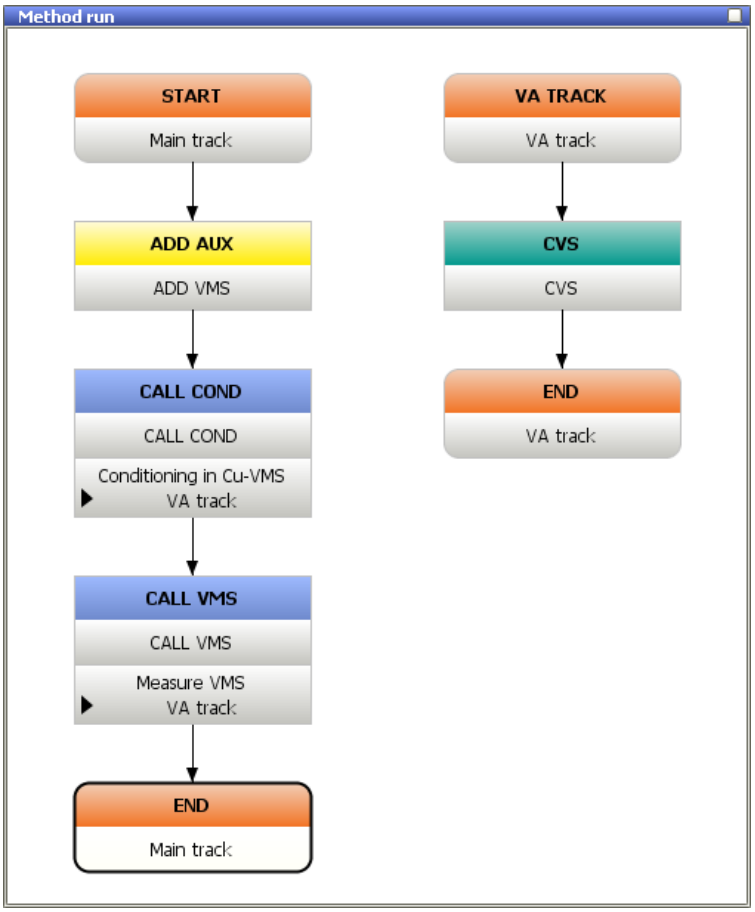
1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File** ▸ **New...** menu.



3 Under **Templates ▸ CVS**, select **Conditioning (Cu VMS), manual** in the left-hand part of the window and click on **[OK]**.

The method template opens.



The method consists of a main track and a VA track. The **CVS** command is transposed to a separate VA track in order to ensure that the

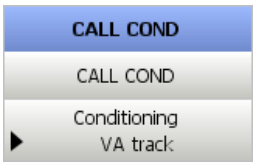
same voltammetric parameters are used every time the command is called.

Meaning of the single commands

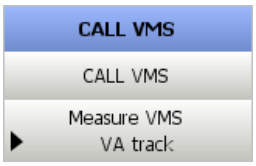
The following commands are required for conditioning the Pt working electrode:

Main track

The addition of an auxiliary solution is defined with the **ADD AUX** command. The volume that is to be added, the way in which the addition takes place (manually or with a dosing device) and the messages that are to be displayed can be specified.



The VA track is called with the **CALL COND** command. It is carried out until one of the defined stop criteria has been met. This command is used for conditioning the working electrodes in the Cu VMS.



The VA track is called again with the **CALL VMS** command. The data acquired in the called VA track is used for the calculation of the VMS value for the standardization of the calibration curves in the calibration method DT (Dilution Titration).

VA track

CVS measurements (Cyclic Voltammetric Stripping) are carried out with the **CVS** command.

Defining command parameters

Various parameters specific to the application have to be set in the method templates. You can find these parameters in the application documentation. To set the application-specific parameters, proceed as follows:

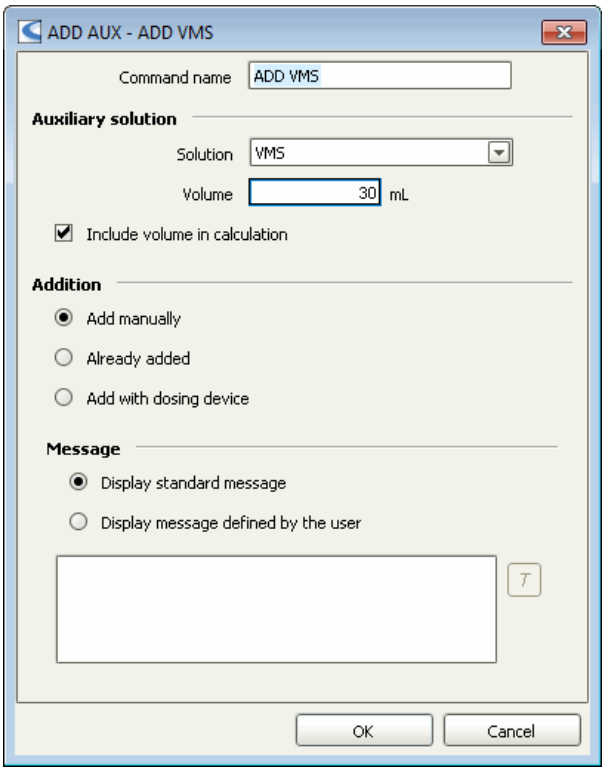
1. Double-click on the **ADD AUX** command.

   The **ADD AUX - Add VMS** dialog window opens.

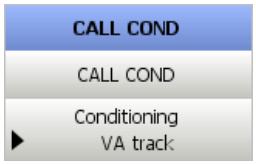
2. In the **Auxiliary solution** section, enter the application-specific volume in the **Volume** field.

   The solution **VMS** is preset in the **Auxiliary solution** section.

   The option **Add manually** is selected in the **Addition** section.



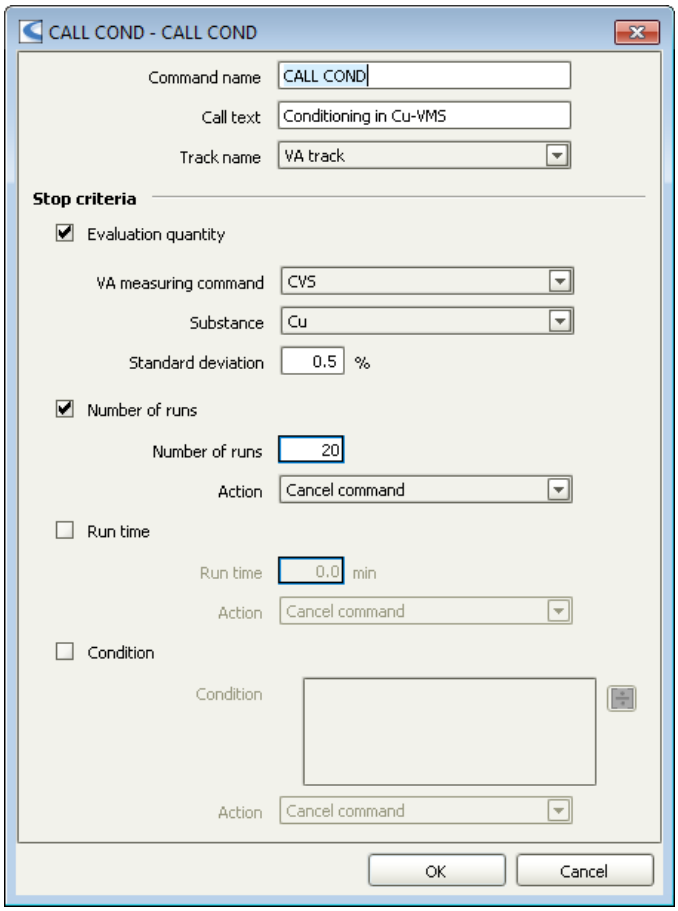
3 Close the dialog window with **[OK]**.

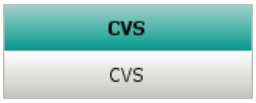


4 Double-click on the **CALL COND** command.

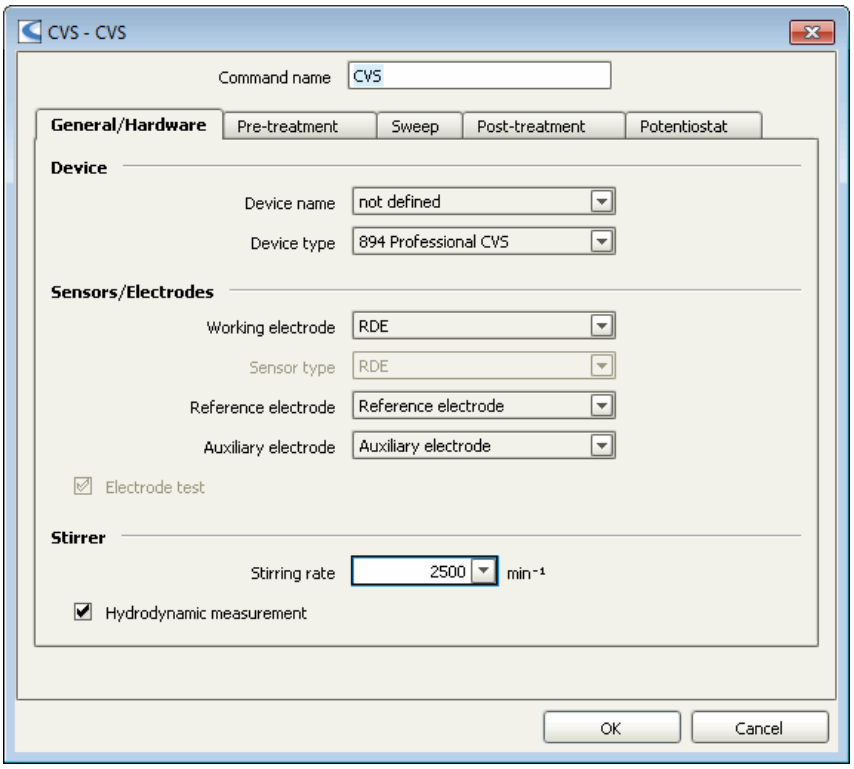
The **CALL COND - CALL COND** dialog window opens.

The application-specific stop criteria are defined for the VA track in this window. When a defined standard deviation of the measured charge Q has been reached (or after a specified number of runs) the VA track is finished.



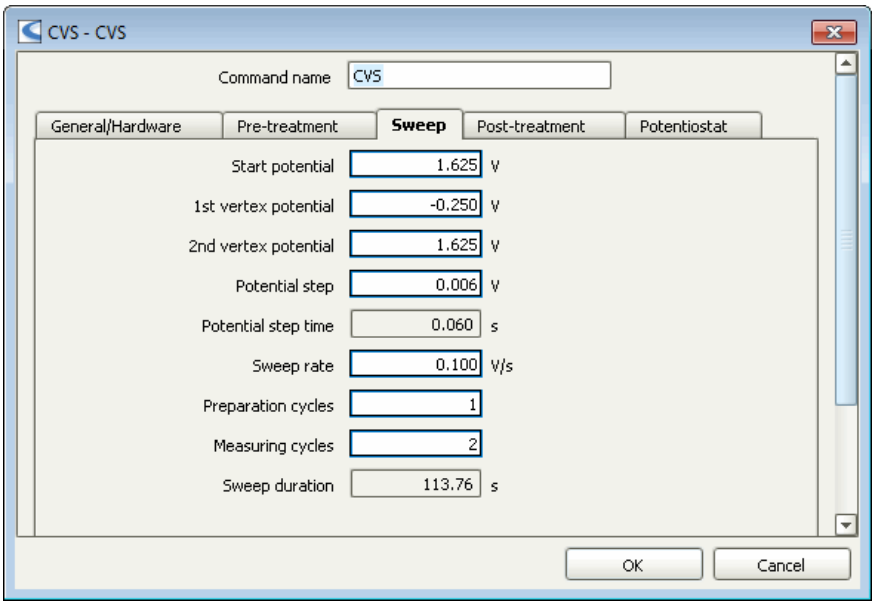


5 Double-click on the **CVS** command and select the **General/Hardware** tab.



6 In the **Device** section, assign a measuring instrument that is present in the configuration to the method (the instrument must be present in the device table of the configuration).

7 Select the **Sweep** tab.



8 Enter the application-specific parameters from the application documentation.

9 Close the dialog window with **[OK]**.

Method check

Proceed as follows to test the method for plausibility before saving:

1 Click on the **File** ▸ **Method check** menu or the icon.

2 Confirm the message with **[OK]**.

Correct any errors.

Saving a method

After having entered and checked all relevant parameters for the method, save the method as follows:

1 Open the **Save method** dialog window using the **File** ▸ **Save as...** menu.

2 Enter the name **Conditioning (Cu VMS), manual** for the method in the **Method name** field.

3 Click on **[Save]**.

4.2.1.2 Carrying out the conditioning

These steps are performed in the **Workplace** program part.

Conditioning the Pt working electrode

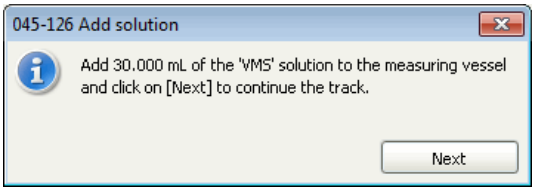
1 Click on the icon of the **Workplace** program part.

2 Select the **Single determination** tab in the **Run** subwindow.

3 In the **Method** field, select the **Conditioning (Cu VMS), manual** method created from the method template.

4 Click on **[Start]**.

The prompt for adding VMS appears.



NOTE

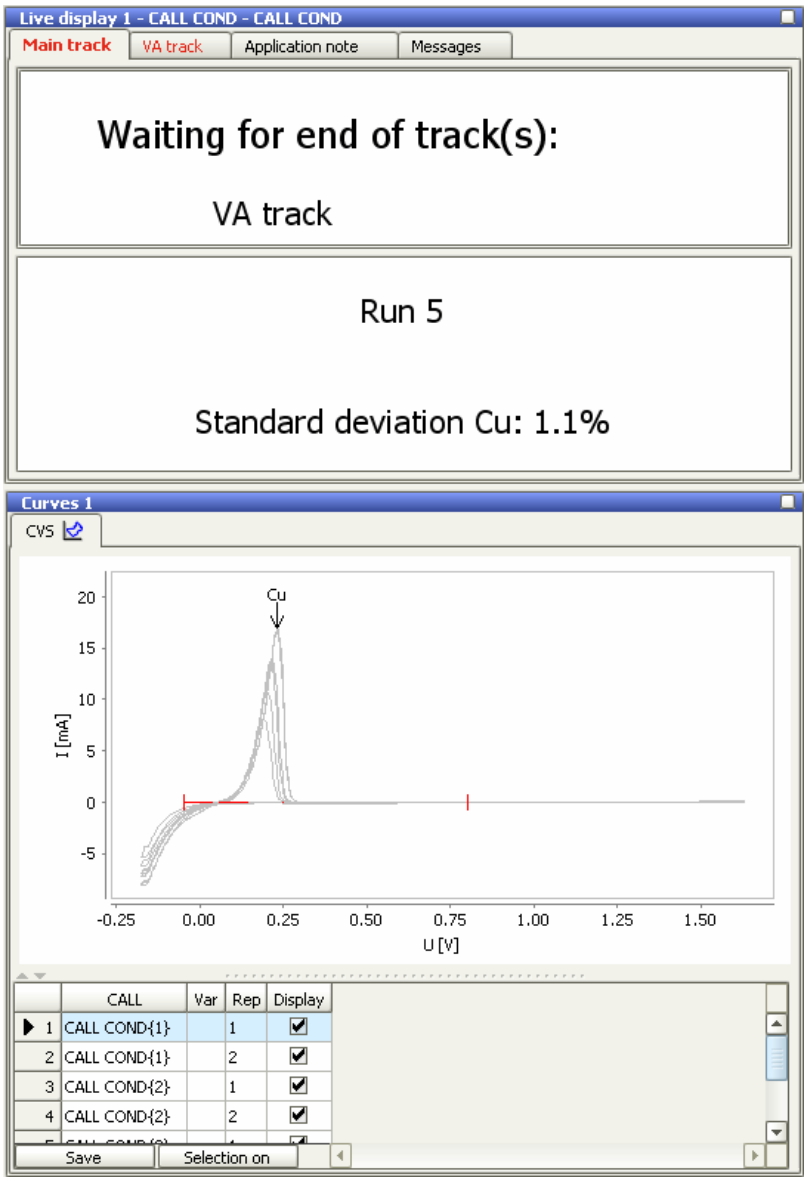
All solutions are added to the measuring vessel via the pipetting opening so as to prevent the electrodes from being exposed to atmospheric oxygen during the measurement.

5 Pipette the volume of VMS displayed in the message into the measuring vessel.

6 Click on **[Next]**.

Conditioning commences.

The number of runs and the actual value for the standard deviation is displayed on the **Main track** tab in the **Live display** subwindow. The **Curve** subwindow shows the voltammograms and the tables of the measurement curve.



When a stop criterion has been reached, conditioning is finished. Then the VA track is called again with the **CALL VMS** command and the VMS is measured again. The signal measured in the VMS (the conditioned area x [C]) is stored as the result in the default database **viva**.

In this method, one run corresponds to three sweeps. The first sweep (preparation cycle) is discarded; the second and third sweeps (measuring cycle, replication) are used for the calculation of the relative standard deviation.

The first calculation takes place after the second run has finished.

The number of preparation and measuring cycles is defined on the **Sweep** tab *(see "Defining command parameters", page 11)*.

4.2.2 Determining the suppressor concentration

The addition of suppressor to a copper solution reduces the deposition of Cu on the electrode surface. The suppressor concentration in an electroplating bath is determined with the calibration method **DT** (Dilution Titration).

The method for the manual determination of the suppressor concentration comprises:

- the recording of a calibration curve with a suppressor standard solution
- the determination of the suppressor concentration in a sample

4.2.2.1 Creating a method

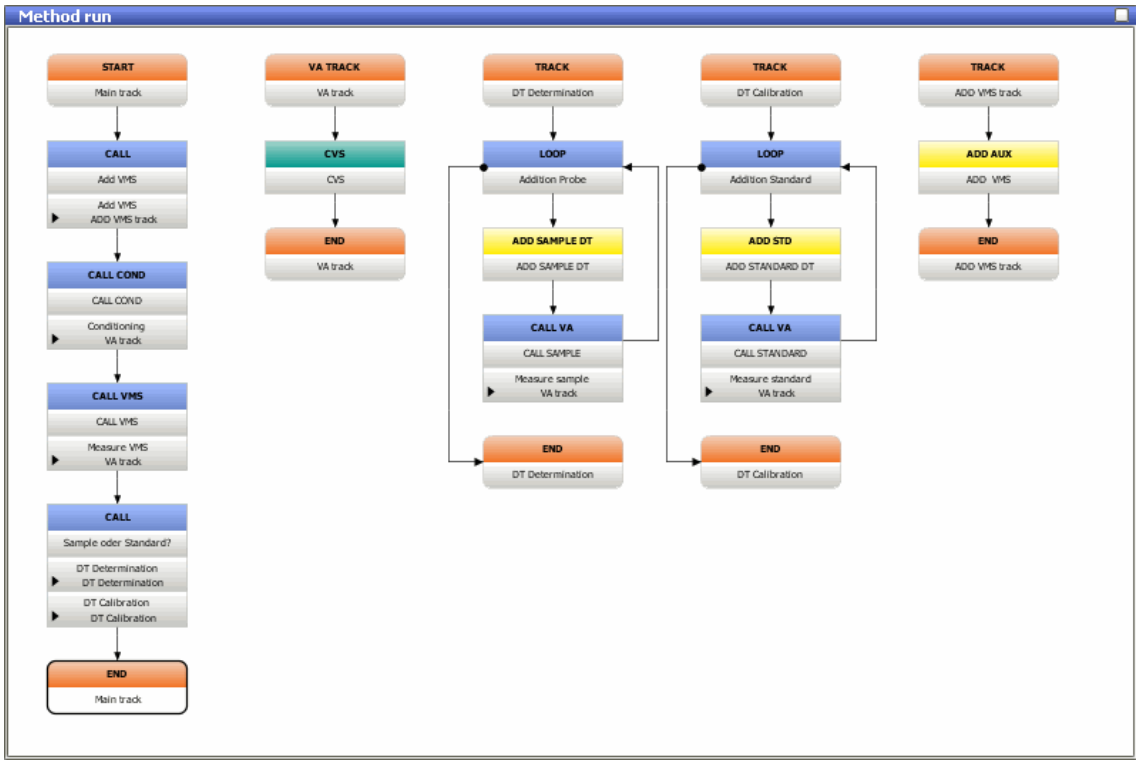
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New…** menu.

3 Under **Templates ▸ CVS**, select **Suppressor determination (CVS, DT), manual** in the left-hand part of the window and confirm with **[OK]**.

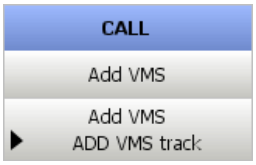
The method template opens.



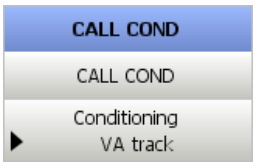
Meaning of the single commands

The following commands are required for a manual determination of the suppressor concentration:

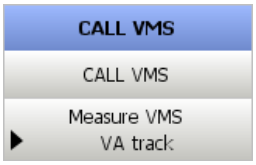
Main track



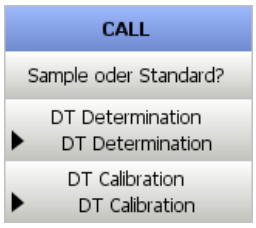
Calls the track **ADD VMS track**.



(see "Meaning of the single commands", page 11)



Calls the VA track *(see "Meaning of the single commands", page 11)*.



Depending on the sample type selected in the workplace (**Sample** or **Standard**) the track **DT Determination** or **DT Calibration** is called.

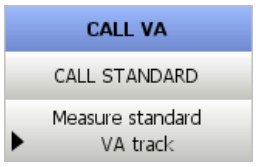
VA track

CVS measurements (Cyclic Voltammetric Stripping) are carried out with the **CVS** command.

DT Calibration

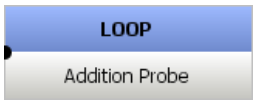
After the **DT Calibration** track has been called by the **CALL** command, the prompt **Add standard** appears after each measuring cycle until the stop criterion defined in the command has been fulfilled.

The addition of standard solution is defined in this command (number and size of the volume increment).



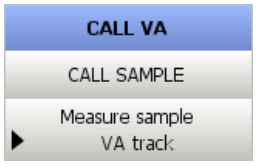
Calls the VA track in which the CVS measurements are carried out after the manual addition of suppressor standard solution.

DT Determination



After the **DT Determination** track has been called by the **CALL** command, the prompt **Add sample** appears after each measuring cycle until the stop criterion defined in the command has been fulfilled.

The addition of sample is defined in this command (number and size of the volume increment).



Calls the VA track in which the CVS measurements are carried out after the manual addition of sample.

ADD VMS track

The addition of VMS (volume and addition type for dosing the auxiliary solution) is defined in this command.

4.2.2.2 Defining the evaluation

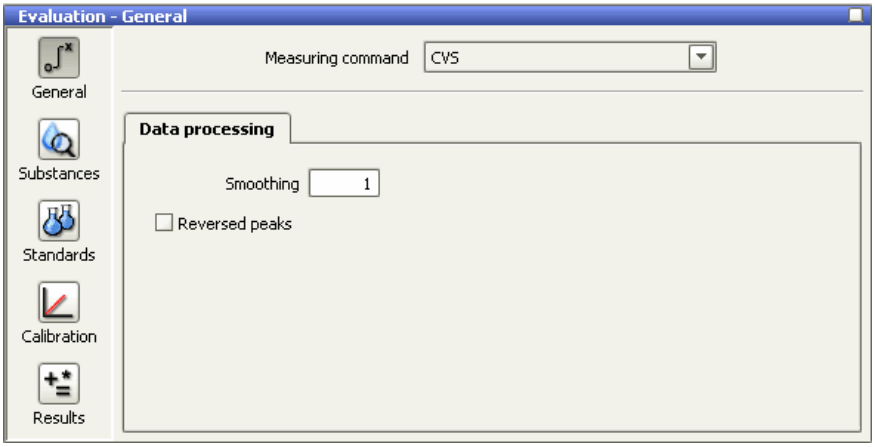
The parameters for the evaluation of the voltammograms are defined in the **Evaluation** subwindow of the **Method** program part. Each analysis has its own set of evaluation parameters.

All relevant evaluation parameters are predefined in the method templates. The evaluation parameters can be defined individually, and the modified method template can then be saved again.

General

The parameters that are to be used for the processing of the acquired data and the display of the measuring curves for all substances are defined in the **General** section.

1 Click on the **General** button.



The VA measuring command defined in the method template is automatically indicated for data acquisition in the list box.

The entries on the **Data processing** tab are adopted.

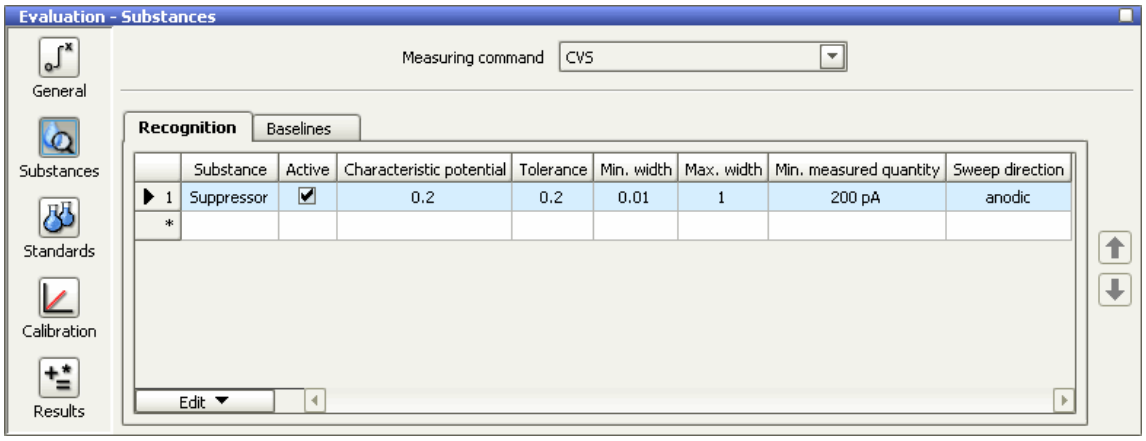
Substances

The substance that is to be determined is defined in the **Substances** section.

The substance name, the peak position and the tolerances for the peak recognition are parameterized on the **Recognition** tab.

The baseline type as well as the start and end base points are defined on the **Baselines** tab.

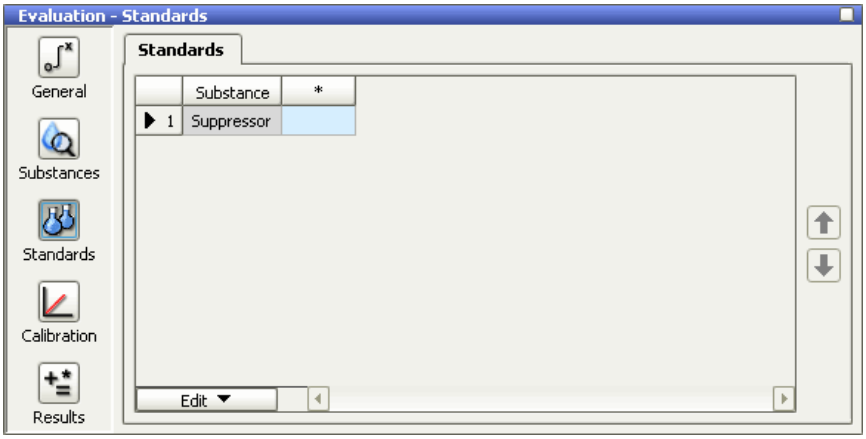
1 Click on the **Substances** button.



Standards

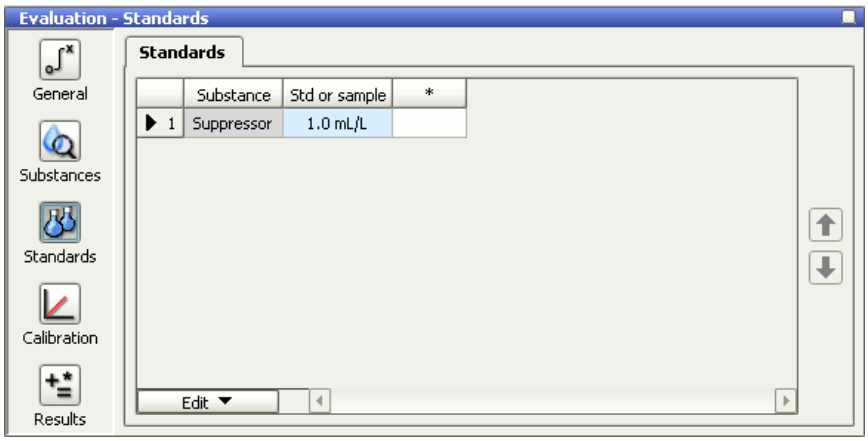
The standard solutions for the calibration are defined in the **Standards** section.

1 Click on the **Standards** button.



2 Click on the **Edit ▸ Apply from ADD STD** menu.

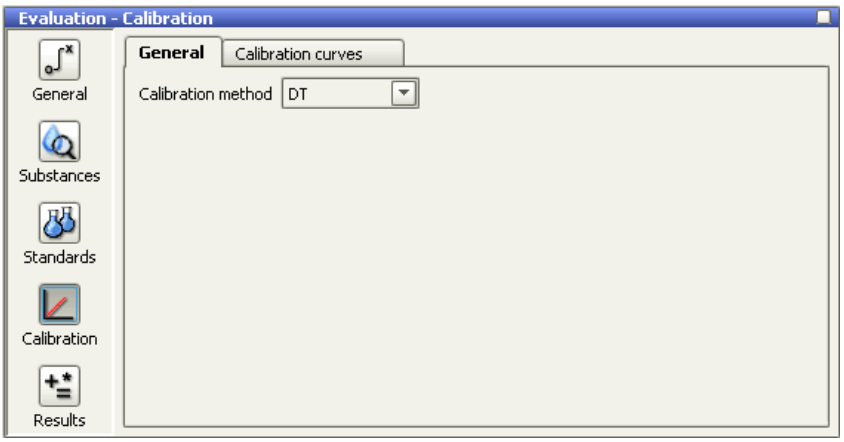
The solution name entered in the **Solutions** field in the **ADD STD** command is entered in the ✺ column.

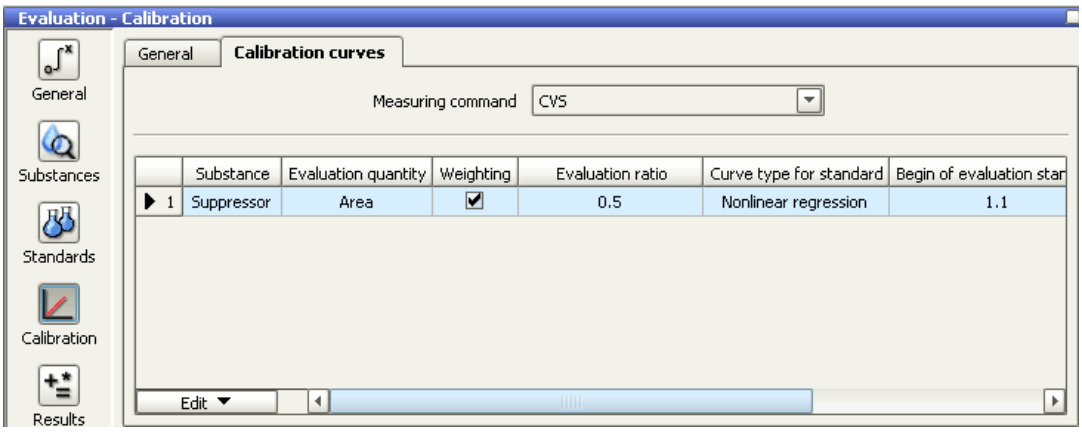


Calibration

The calibration method is selected in the **Calibration** section. The calibration curve type, the evaluation quantity (peak area or peak height), the required evaluation ratio and the evaluation start for the calibration and the determination are defined on the **Calibration curves** tab.

1 Click on the **Calibration** button.



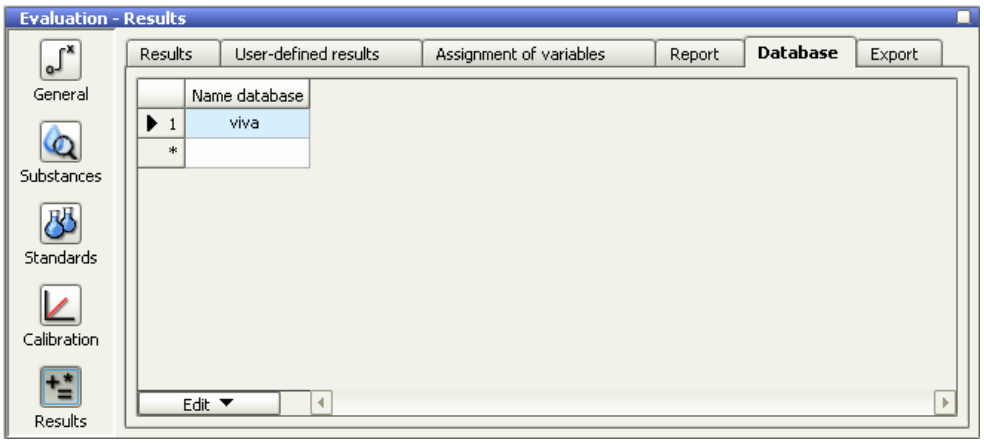


Results

The database in which the results are to be stored is indicated in the **Results** section. The output, the export and additional results can be defined by the user.

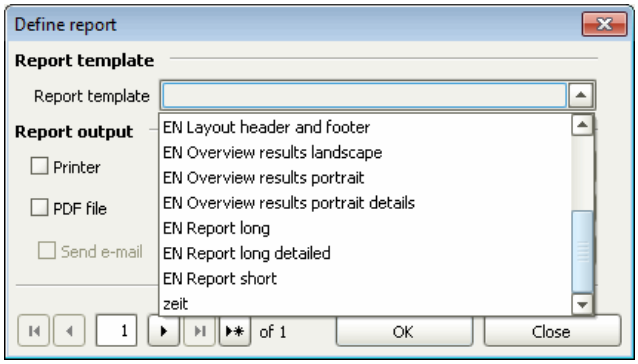
1 Selecting the database

- Click on the **Results** button.
- Select the **Database** tab.
- Open the **Select database** dialog window using the **Edit ▸ Properties...** menu.
- Select the database in which the results are to be stored in the **Database** list box.
- Click on **[OK]**.



2 Defining reports

- Select the **Report** tab.
- Open the **Output** dialog window using the **Edit ▸ New...** menu.
- Select a report template to be used for printing a report in the **Report template** list box.



- Click on **[OK]**.

Method check

(see "Method check", page 15).

Saving a method

After having checked or entered all relevant parameters for the method, save the method as follows:

1. Open the **Save method** dialog window using the **File ▸ Save as...** menu.
2. Enter the name **Suppressor determination (CVS, DT), manual** for the method in the **Method name** field.
3. Click on **[Save]**.

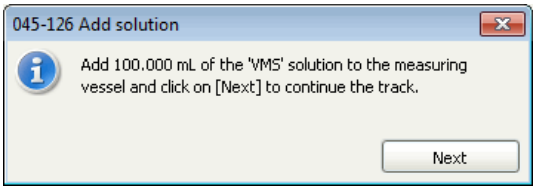
4.2.2.3 Carrying out a determination

These steps are performed in the **Workplace** program part.

Recording a calibration curve

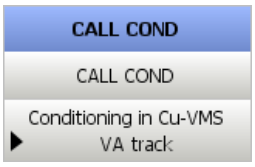
1. Click on the icon of the **Workplace** program part.
2. Select the **Single determination** tab in the **Run** subwindow.
3. In the **Method** field, select the **Suppressor determination (CVS, DT), manual** method created from the method template.
4. Select the **Standard** entry in the **Sample type** list box.

5. Click on **[Start]**.
   - The prompt for adding VMS appears.



6 Pipette the volume of VMS indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

7 The following command is carried out after the addition:



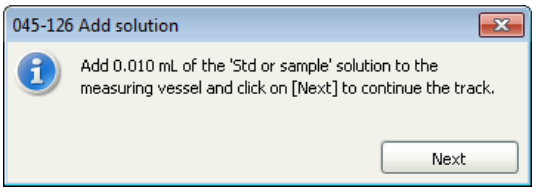
Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

NOTE

If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel have to be thoroughly rinsed with distilled water.

8 Now the VMS signal is measured.

9 The prompt for adding the solution **Std or sample** appears.



10 Pipette the volume of suppressor standard solution in accordance with the message through the pipetting opening into the measuring vessel and click on **[Next]**.

11 Step **10** is repeated until the stop criterion has been fulfilled. The stop criterion is defined in the following command:

12 The calibration curve is stored in the database.

13 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

14 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

Determining the suppressor concentration

1 Click on the icon of the **Workplace** program part.

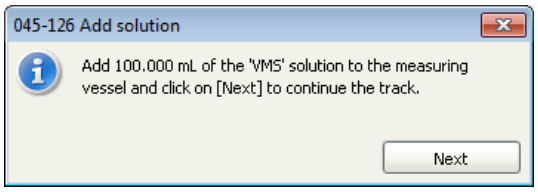
2 Select the **Single determination** tab in the **Run** subwindow.

3 In the **Method** field, select the **Suppressor determination (CVS, DT), manual** method created from the method template.

4 Select the **Sample** entry in the **Sample type** list box.

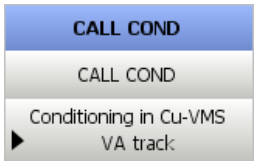
5 Click on **[Start]**.

The prompt for adding VMS appears.



6 Pipette the volume of VMS indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

7 The following command is carried out after the addition:



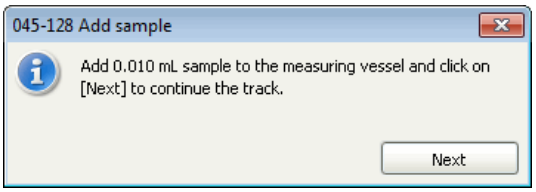
Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

NOTE

If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel have to be thoroughly rinsed with distilled water.

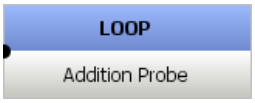
8 The VMS signal is now measured.

9 The prompt for adding the sample appears.



10 Pipette the volume of sample in accordance with the message through the pipetting opening into the measuring vessel and click on **[Next]**.

11 Step **10** is repeated until the stop criterion has been fulfilled. The stop criterion is defined in the following command:



12 When the measurement is finished, the determination is stored in the database.

13 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

14 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

4.2.3 Determining the brightener concentration

The addition of brightener to a copper solution increases the deposition of Cu on the electrode surface. The brightener concentration in an electroplating bath is determined with the calibration method **MLAT** (Modified Linear Approximation Technique).

First, the so-called **intercept solution** (VMS + suppressor excess) is measured. From this, the charge Q_0 is calculated and stored as intercept value. The intercept value (blank value) is then subtracted from the measured value in subsequent measurements.

The method for the manual determination of the brightener concentration comprises:

- the recording of the cyclovoltammogram of the intercept solution (charge Q_0 of intercept solution. Q_0 = intercept value)
- the recording of the cyclovoltammogram of the intercept solution + sample (charge Q of sample)
- the recording of the cyclovoltammogram of the intercept solution + sample + standard addition 1 (charge Q of standard 1)
- the recording of the cyclovoltammogram of the intercept solution + sample + standard addition 2 (charge Q of standard 2)

This can be used to calculate a calibration curve by means of a linear regression.

4.2.3.1 Creating a method

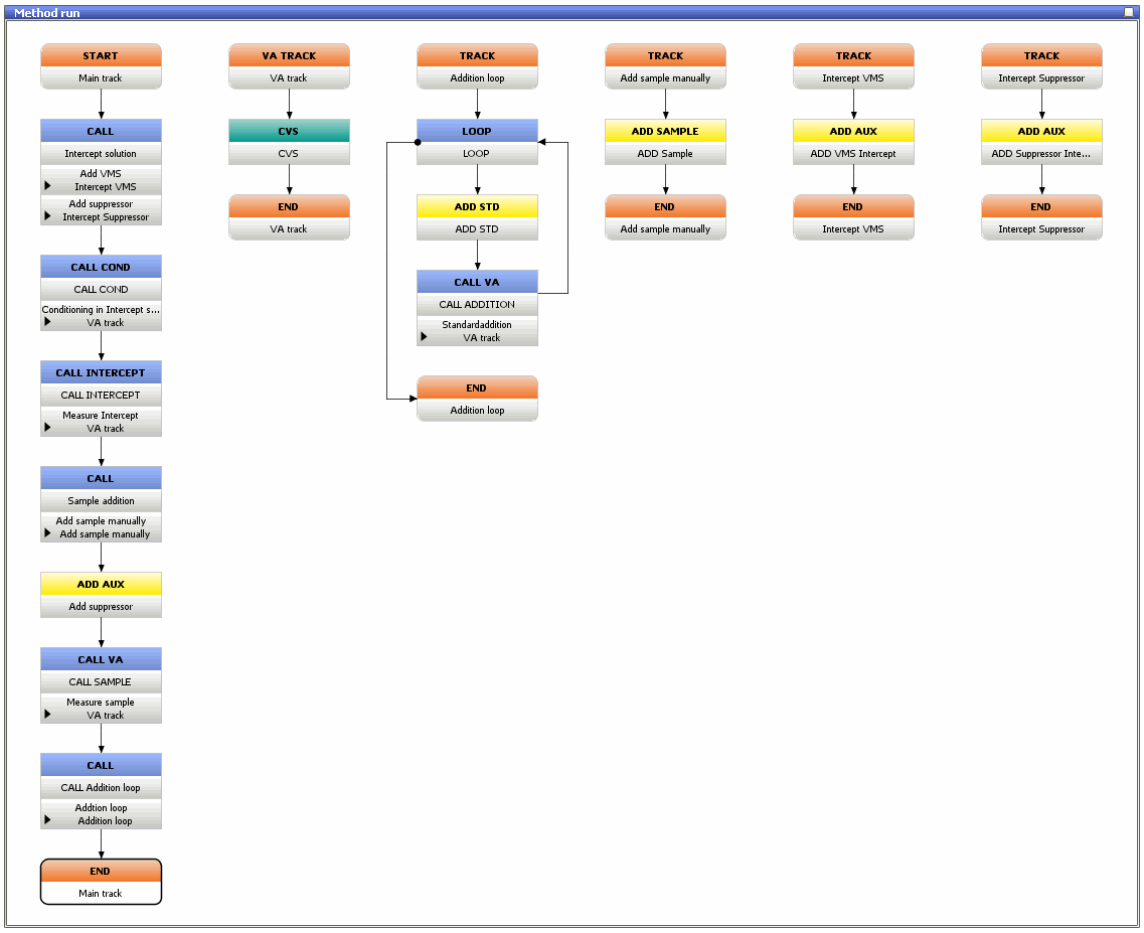
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New…** menu.

3 Under **Templates ▸ CVS**, select **Brightener determination (CVS, MLAT), manual** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.



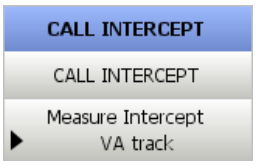
Meaning of the single commands

The following commands are required for a manual determination of the brightener concentration:

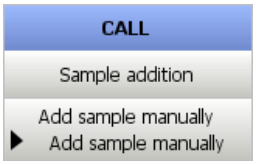
Main track

Simultaneously calls the **track** for dosing VMS (**Intercept VMS**) and the **track** for dosing suppressor concentrate (**Intercept Suppressor**).

The **VA track** is called with the **CALL COND** command. It is carried out until one of the defined stop criteria has been met. This command is used for conditioning electrodes in the intercept solution.

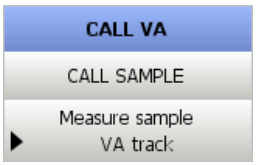


Calls the **VA track** to measure the charge Q_0 in the intercept solution.

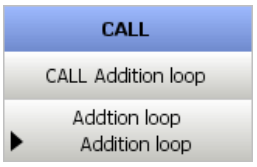


Calls the track **Add sample manually**.

Command for the addition of suppressor concentrate to the intercept solution + sample. Suppressor concentrate is added again, so that the Q_0 value is not increased.



Calls the VA track in which the CVS measurements are carried out after the addition of sample.

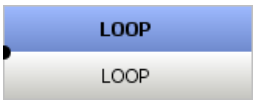


Calls the **Addition loop** track, in which the addition of brightener standard solution is defined.

VA track

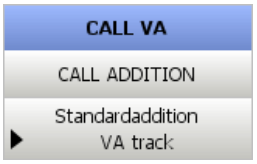
(see "VA track", page 11).

Addition loop



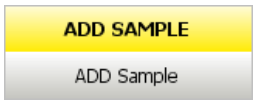
After the **Addition loop** track has been called by the **CALL Addition Loop** command, the prompt for adding brightener standard solution appears before each measuring cycle until the stop criterion defined in the command has been fulfilled.

The addition of the brightener standard solution is defined in this command (volume increment number and size).



Calls the **VA track** in which the CVS measurements are carried out after the addition of brightener standard solution to measure the charge Q of standard addition 1 and the charge Q of standard addition 2.

Add sample manually



Command for dosing the sample manually.

Intercept VMS

Command for dosing VMS of the intercept solution manually.

Intercept Suppressor

Command for dosing suppressor concentrate of the intercept solution manually.

4.2.3.2 Defining the evaluation

Apart from the predefined parameters, the specific parameters for the evaluation of the voltammograms of the brightener determination are also defined.

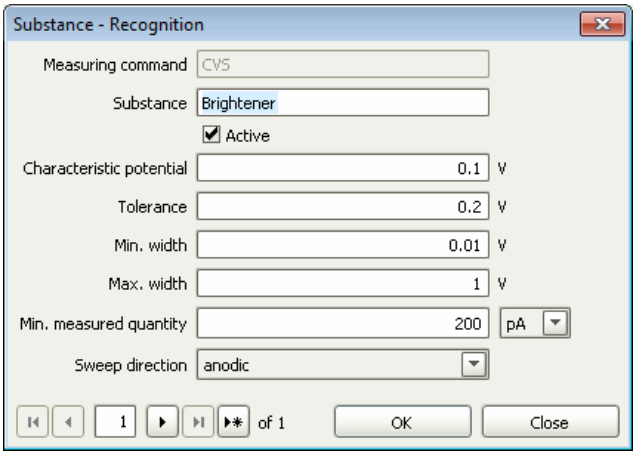
Substances

The characteristic potential specific to the application is defined in the **Substances** section.

1 Click on the **Substances** button.

2 Open the **Substance - Recognition** dialog window using the **Edit ▸ Properties...** menu.

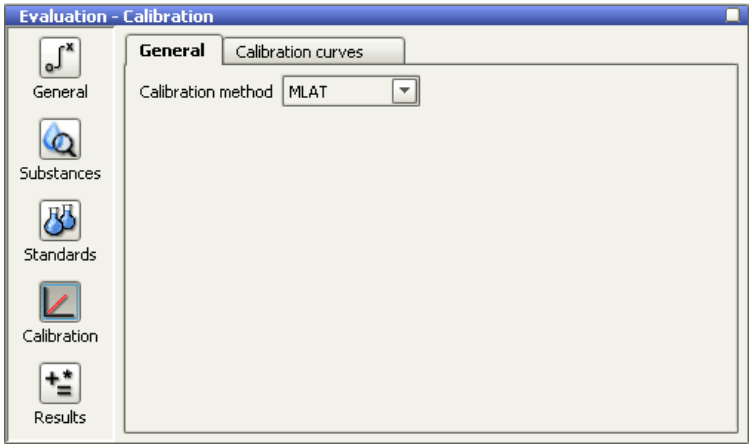
3 Enter the application-specific value in the **Characteristic potential** field.



Calibration

In the **Calibration** section, select the calibration method **MLAT** for the brightener determination.

1 Click on the **Calibration** button.

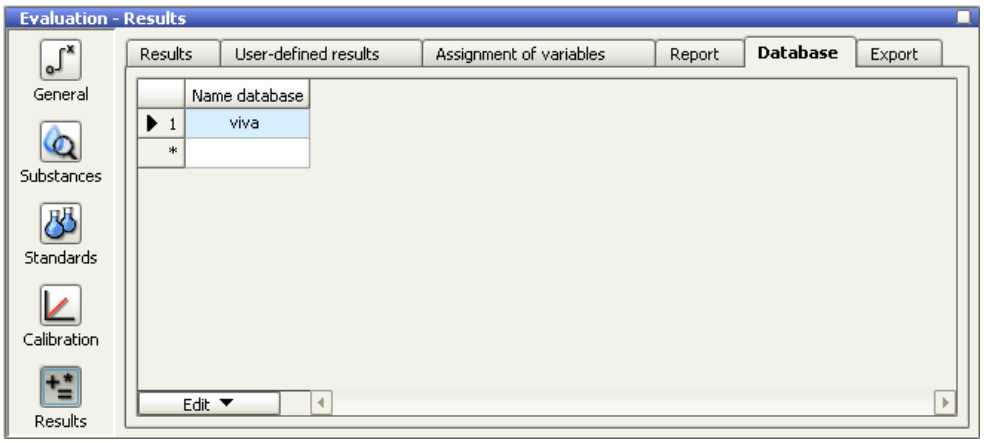


Results

The database in which the results are to be stored is indicated in the **Results** section. The output, the export and additional results can be defined by the user.

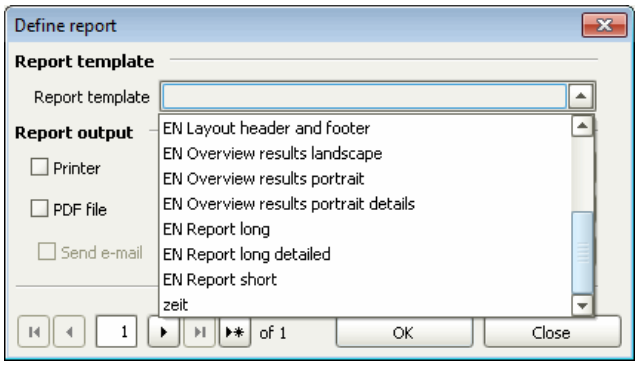
1 **Selecting the database**

- Click on the **Results** button.
- Select the **Database** tab.
- Open the **Select database** dialog window using the **Edit ▸ Properties...** menu.
- Select the database in which the results are to be stored in the **Database** list box.
- Click on **[OK]**.



2 **Defining reports**

- Select the **Report** tab.
- Open the **Output** dialog window using the **Edit ▸ New...** menu.
- Select a report template to be used for printing a report in the **Report template** list box.



- Click on **[OK]**.

Method check

(see "Method check", page 15).

Saving a method

After having entered and checked all relevant parameters for a method, save the method as follows:

1 Open the **Save method** dialog window using the **File ▸ Save as...** menu.

2 Enter the name **Brightener determination (CVS, MLAT), manual** for the method in the **Method name** field.

3 Click on **[Save]**.

4.2.3.3 Carrying out a determination

These steps are performed in the **Workplace** program part.

Carrying out the brightener determination

1 Click on the icon of the **Workplace** program part.

2 Select the **Single determination** tab in the **Run** subwindow.

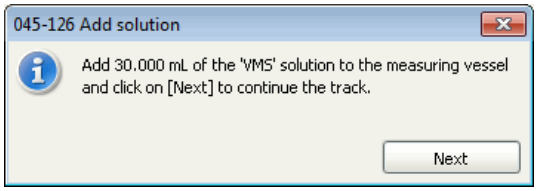
3 In the **Method** field, select the **Brightener determination (CVS, MLAT), manual** method created from the method template.

4 Select the **Sample** entry in the **Sample type** list box.

5 Enter the application-specific value for the sample amount in the **Sample amount** field.

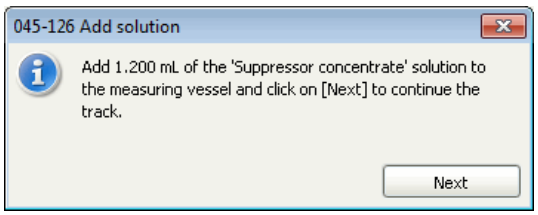
6 Click on **[Start]**.

The prompt for adding VMS appears.



7 Pipette the volume of VMS indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

The prompt for adding suppressor concentrate appears.



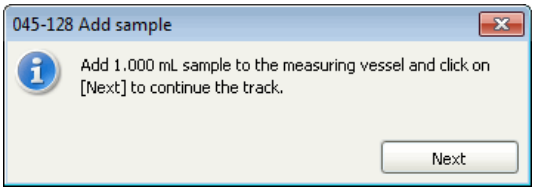
8 Pipette the volume of suppressor concentrate indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

9 The following command is carried out after the additions:

Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

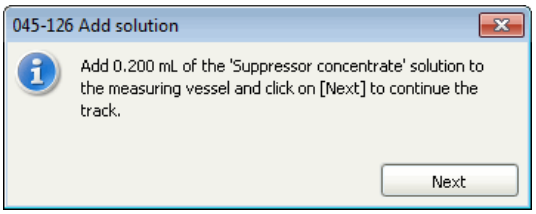
10 Now the intercept value is measured.

After the measurement of the intercept value has been completed, the prompt for adding the sample appears.



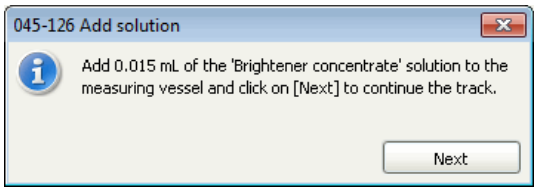
11 Pipette the volume of sample indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

The prompt for adding additional suppressor concentrate appears.



12 Pipette the volume of suppressor concentrate indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

After the sample has been measured, the prompt for adding brightener concentrate appears.



13 Pipette the volume of brightener concentrate indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

The addition volume is defined in the following command:

14 Step **13** is repeated a second time. The number of cycles is defined in the following command:

15 When the measurement is finished, the determination is stored in the database.

16 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

17 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

5 Semiautomated determination

In a semiautomated determination, sample, additives and the VMS can be added either automatically via dosing units or manually via the pipetting opening.

The following equipment is required for a semiautomated determination:

- 894 Professional CVS
- 807 Dosing Unit (three with a 2 mL and one with a 50 mL glass cylinder)
- 800 Dosino
  - 800 Dosino and 807 Dosing Unit with cylinder size 50 mL for dosing VMS
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing suppressor concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing brightener concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing sample

5.1 Configuration

5.1.1 Configuring the instrument

894 Professional CVS

(see Chapter 4.1.1, page 7).

5.1.2 Configuring electrodes

(see Chapter 4.1.2, page 8).

5.1.3 Configuring dosing units

The four 807 Dosing Units connected to the 894 Professional CVS are detected by **viva** after the start. After you have confirmed the corresponding messages with **[Yes]**, they will be entered in the table of dosing units.

NOTE

If several dosing units are connected, then all dosing devices with dosing units have to be connected to the corresponding MSB first and the 894 Professional CVS must then be initialized again.

Connecting an 800 Dosino with dosing unit

Proceed as follows to connect an 800 Dosino to an 894 Professional CVS:

1. Connect the connection cable of the 800 Dosino with 807 Dosing Unit and 50 mL cylinder to the MSB connector 1 of the 894 Professional CVS.

   The following dialog window appears:

2. Confirm with **OK**.

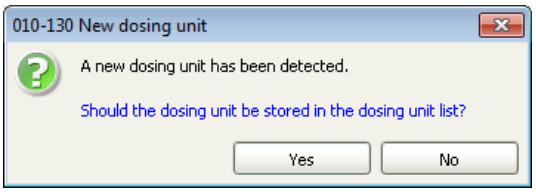
Initializing a dosing unit

Proceed as follows:

1. Select the 894 Professional CVS in the device table of the **Configuration** program part.

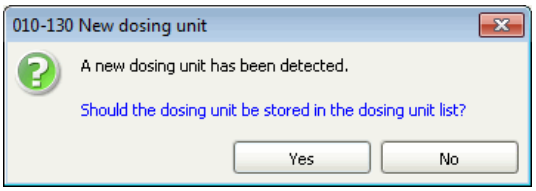
2. In the device table, click on the **Edit** button and select **Initialize**.

   If you have connected a brand-new dosing unit, the following dialog window is displayed:



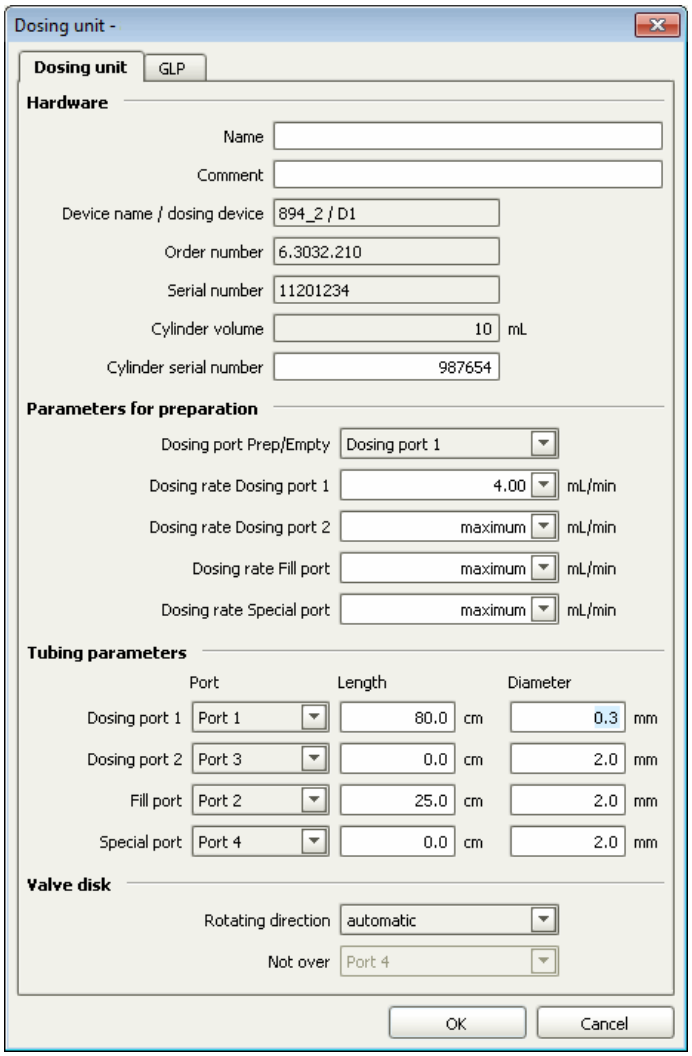
   Or:

   If you have connected a dosing unit that has been previously configured, then the following dialog window is displayed:



3. Click on **OK** if you are using the brand-new dosing unit.

   The following dialog window is displayed:



4 Enter the name **894/D1 50mL VMS** in the field **Name**.

5 Enter the length and the diameter of the tubings and capillaries that are actually connected in the section **Tubing parameters** (see *Manual 894 Professional CVS*).

6 Click on **OK**.

The dosing unit will be automatically displayed in the **Dosing units** subwindow of the **Configuration** program part.

7 Connect and name the other dosing units with a 2 mL cylinder as follows:

Dosing unit	Connector	Solution name	Name of dosing unit
2	MSB 2	Brightener concentrate	894/D2 2mL Brightener
3	MSB 3	Suppressor concentrate	894/D3 2mL Suppressor
4	MSB 4	Std or sample	894/D4 2mL Std or sample

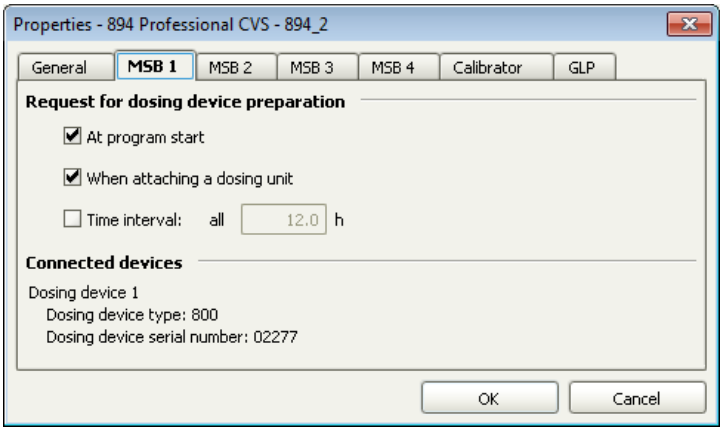
Preparing the dosing unit

For semiautomated determinations, you can additionally define in the configuration that the user is to be reminded to prepare the dosing unit when **viva** is started.

1 In the device table in the **Devices** subwindow, select the device name **894_1** and double-click on it.

The **Properties - 894 Professional CVS - 894_1** dialog window opens.

2 Apply the default settings in the **Request for dosing device preparation** section on the tabs **MSB 1 to MSB 4**.



5.1.4 Defining solutions

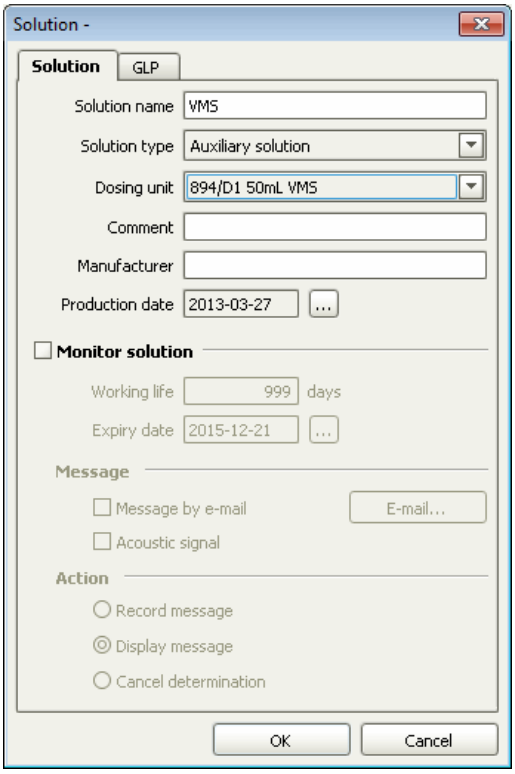
In the semiautomated or automated recording of a calibration curve and the determination of the suppressor concentration in a sample, the solutions are added to the measuring vessel with a dosing unit. The solutions are defined in the **Solutions** subwindow.

1 Open the **Solution** dialog window using the **Edit ▸ New** menu.

2 Edit the **Solution** tab.

- Enter the name **VMS** in the **Solution name** field.

- Select the **Auxiliary solution** entry in the **Solution type** list box.
- In the **Dosing unit** list box, select the entry **894/D1 50mL VMS**.



- Close the dialog window by clicking on **[OK]**.

3 Add the other three solutions in the same way:

Solution name	Dosing unit	Solution type
Brightener concentrate	894/D2 2mL Brightener	Auxiliary solution
Suppressor concentrate	894/D3 2mL Suppressor	Auxiliary solution
Std or sample	894/D4 2mL Std or sample	Standard solution

4 Editing the GLP tab (optional)

- Select the **GLP** tab.
- In the **GLP test date** field, click on the ... button and select the date of the last GLP test.
- Activate the **Monitoring of GLP validity** check box.
- Enter a value in the **GLP test interval** field.
  The date is automatically entered in the **Expiry date** field if you click on the ... button.
- In the **Message** section, activate the **Acoustic signal** check box.
- In the **Action** section, enable the **Display message** option.

- Click on **[OK]** and close the **Solution** dialog window.

5.2 Methods for the semiautomated determination

A method is a run instruction for processing a sample. It comprises all components necessary to record voltammograms. These include:

- Devices and their parameters
- Defining the sequence of a method. This consists of tracks that are themselves made up of various commands.
- Parameters for the evaluation of the voltammograms
- Result definitions

In this chapter, you will use method templates to create the following methods:

- A method for the semiautomated conditioning of the Pt working electrode
- A method for the semiautomated determination of the suppressor concentration (single determination)
- A method for the semiautomated determination of the brightener concentration (single determination)

5.2.1 Conditioning the Pt working electrode

Prior to the analysis, the Pt working electrode needs to be conditioned. When used regularly, the electrode needs to be conditioned at least once a day.

5.2.1.1 Creating a method

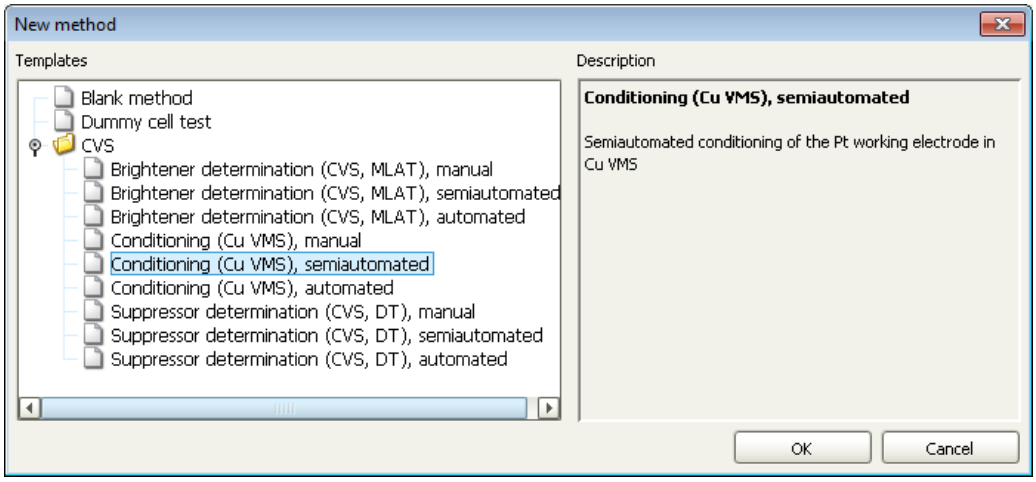
viva comprises method templates that contain all commands required to perform a determination. These method templates can be customized. You can, for instance, change parameters, select a different database to store determinations or add further commands. The selected or modified method template has to be saved.

You also have the possibility to create a new method from scratch. To do so, select the method template **Blank method**.

Loading a method template

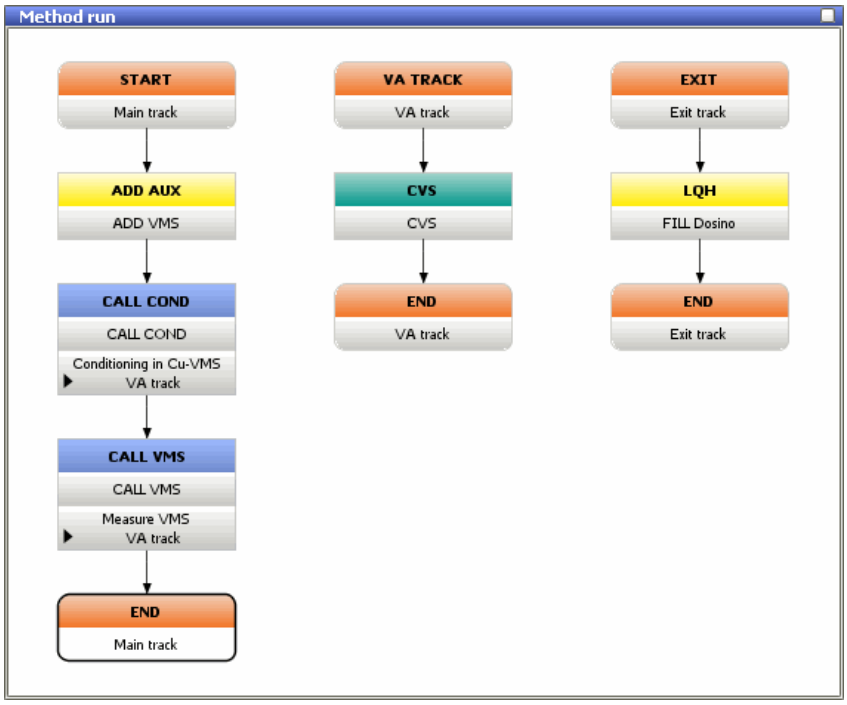
1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New...** menu.



3 Under **Templates** select **Conditioning (Cu VMS), semiautomated** in the left-hand part of the window and click on **[OK]**.

The method template opens.



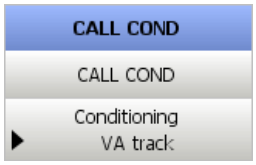
The method consists of a main track, a VA track and an exit track. The **CVS** command is transposed to a separate VA track in order to ensure that the same voltammetric parameters are used every time the command is called.

Meaning of the single commands

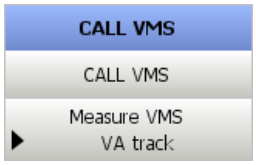
The following commands are required for a semiautomated conditioning of the Pt working electrode:

Main track

The automated addition of VMS with the dosing unit **894/D1 50mL VMS** is defined with the **ADD AUX** command.



(see page 11).

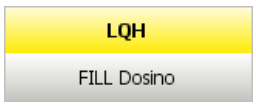


(see page 11).

VA track

(see page 11).

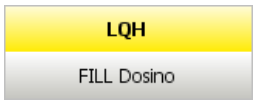
Exit track



The exit track is run at the end of the method. The **LQH** command fills the dosing unit when the determination is finished.

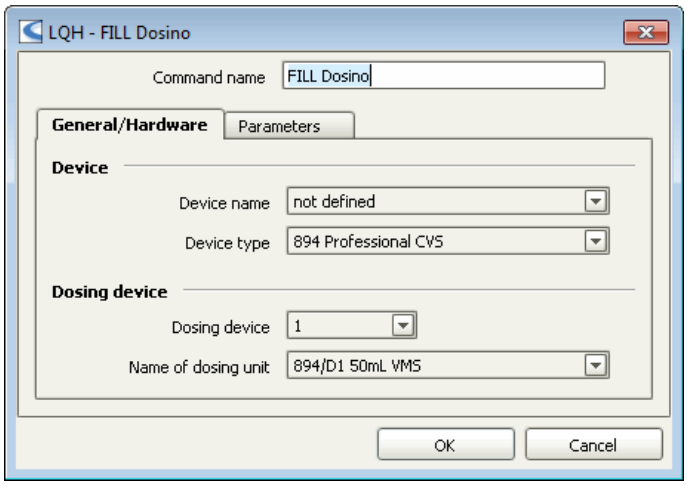
Defining command parameters

In contrast to the manual determination, the VMS is dosed into the measuring vessel with a Dosino.



1 Double-click on the **LQH** command.

The **LQH - Fill Dosino** dialog window opens.



2 Enter the instrument and the dosing device used in the method on the **General/Hardware** tab.

Method check

(see "Method check", page 15).

Saving a method

After having entered and checked all relevant parameters for the method, save the method as follows:

1 Open the **Save method** dialog window using the **File ▸ Save as...** menu.

2 Enter the name **Conditioning (Cu VMS), semiautomated** for the method in the **Method name** field.

3 Click on **[Save]**.

5.2.1.2 Carrying out the conditioning

Preparing the dosing unit

The **Prepare** function is used to rinse the cylinder and tubings of the dosing unit and fill them air bubble-free. You should carry out this function before the first determination or once a day.

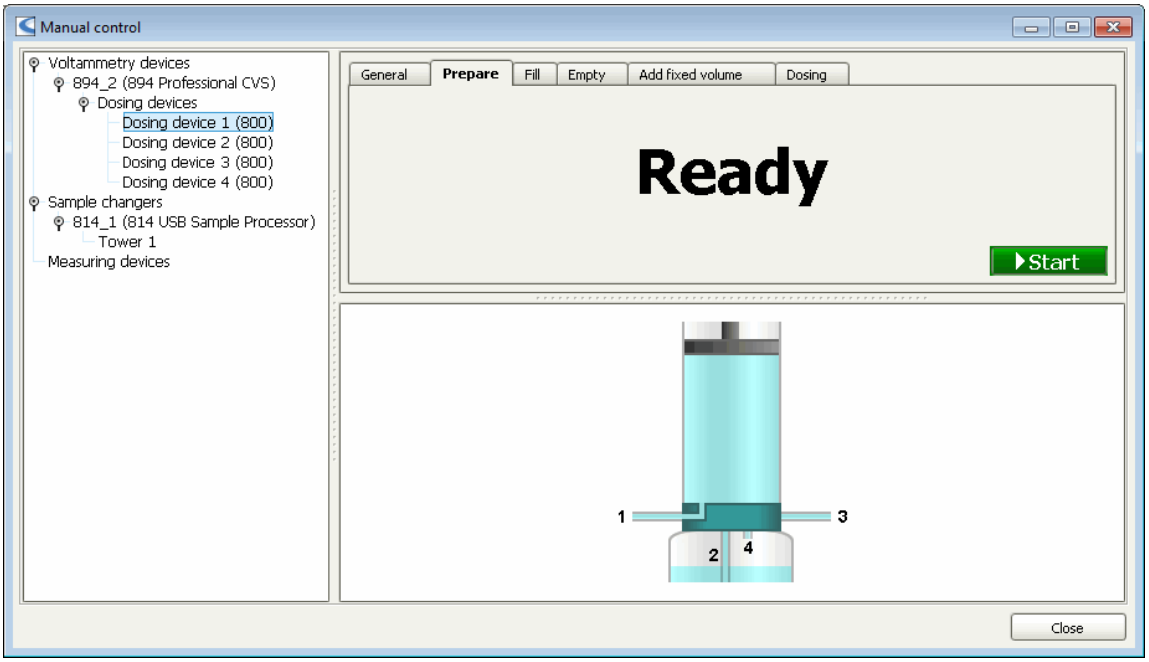
Proceed as follows to do this:

1 Click on the icon of the **Manual control** program part.

The **Manual control** dialog window opens.

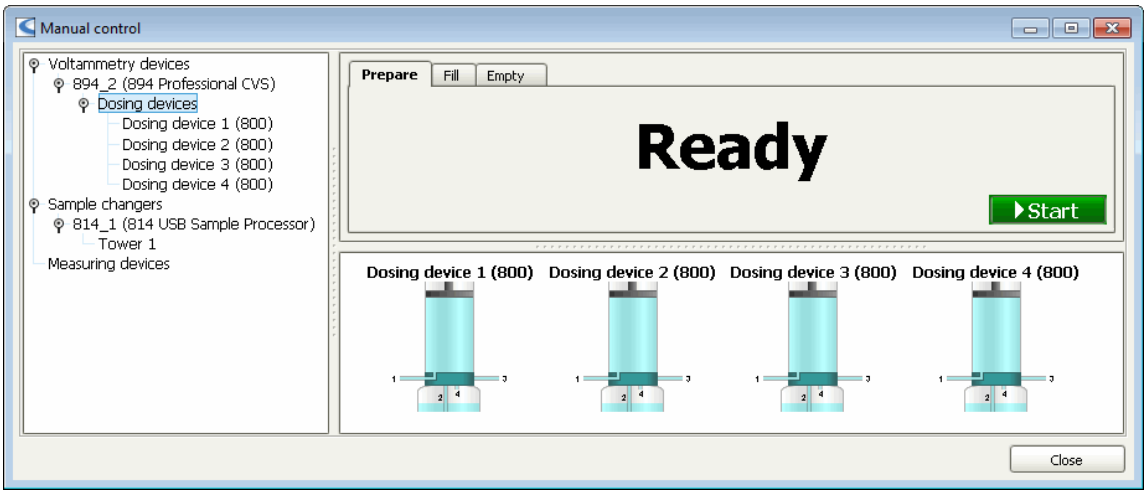
The connected devices are displayed with their peripheral devices in the left-hand part of the window. In the right-hand part of the window, the functions of the selected device are displayed. In the following example, they are shown for Dosing device 1 (800), which corresponds to the dosing unit **894/D1 50mL VMS**.

2 Select **Dosing device 1 (800)** to prepare the selected dosing device.



or

Select **Dosing device** to prepare all connected dosing devices.



3 Place a waste beaker under the measuring head in the drip pan.

4 Select the **Prepare** tab and click on **[Start]**.

5 Repeat step **4**.

6 After the preparation has finished, place the measuring vessel in the holder of the instrument and lower the measuring head arm.

Conditioning the Pt working electrode

1 Click on the icon of the **Workplace** program part.

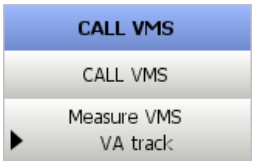
2 Select the **Single determination** tab in the **Run** subwindow.

3 Select the **Conditioning (Cu VMS), semiautomated** method in the **Method** field.

4 Click on **[Start]**.

The VMS volume defined in the **ADD** command is dosed by the dosing unit **894/D1 50mL VMS** into the measuring vessel. Then, the Pt working electrode is conditioned. When the first of the two defined stop criteria (standard deviation < 0.5% or 20 runs) has been fulfilled, conditioning is finished.

5 The VA track is called again and the signal of the VMS is measured with the following command.



The conditioning method is finished.

Empty the measuring vessel and rinse the electrodes and the measuring vessel with distilled H_2O.

5.2.2 Determining the suppressor concentration

The suppressor concentration is determined with the calibration method **DT**.

The method for the semiautomated determination of the suppressor concentration comprises:

- the recording of a calibration curve with a suppressor standard solution
- the determination of the suppressor concentration in a sample

5.2.2.1 Creating a method

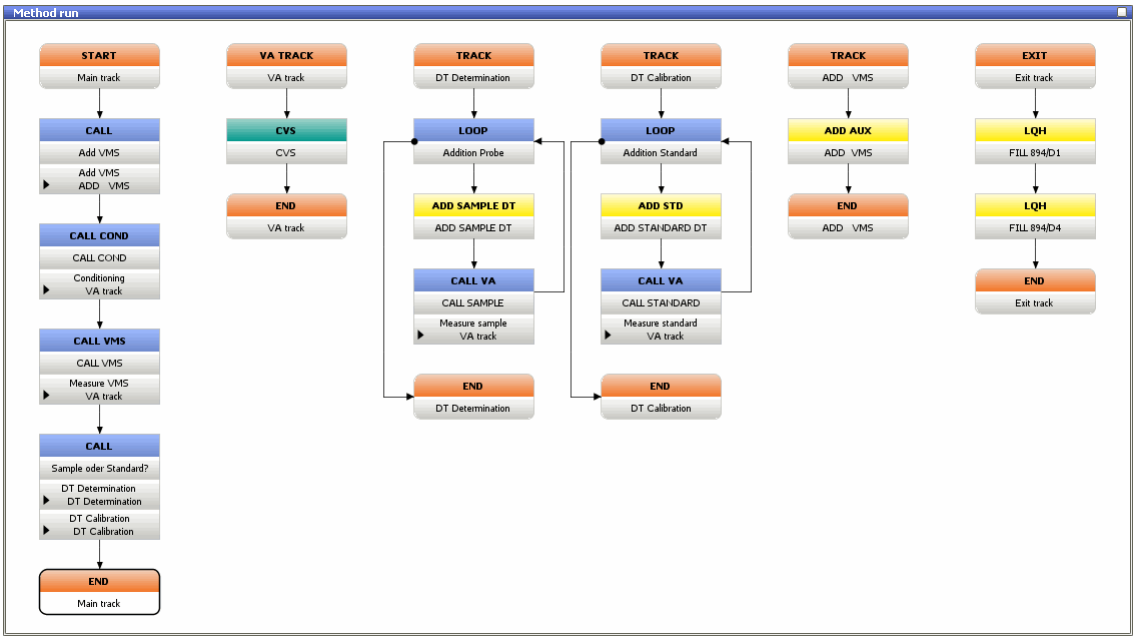
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File** ▸ **New...** menu.

3 Under **Templates**, select **Suppressor determination (CVS, DT), semiautomated** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.

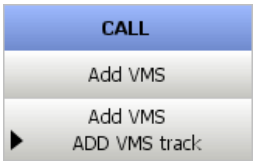


Meaning of the single commands

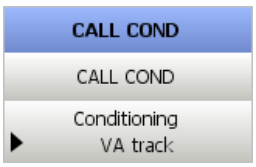
Apart from the **ADD** commands, the method sequence of the semiautomated determination of the suppressor concentration corresponds to the procedure used for the manual determination. The **Add with dosing device** option is selected for the parameter **Addition** in these commands.

The following commands are required to perform a semiautomated determination of the suppressor concentration:

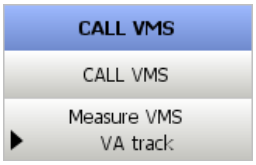
Main track



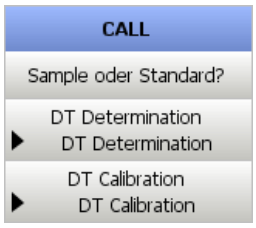
(see page 19).



(see page 11).



(see page 19).

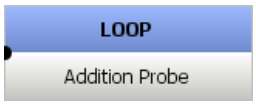


Depending on the sample type selected in the workplace, **Sample** or **Standard**, the track **DT Determination** or **DT Calibration** is called.

VA track

(see page 11).

DT Determination



(see page 20).

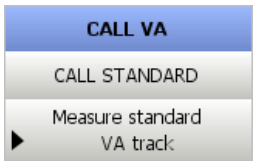
The automated addition of sample with a dosing device is defined in this command.

(see page 20).

DT Calibration

(see page 20).

The automated addition of standard with a dosing device is defined in this command.



(see page 20).

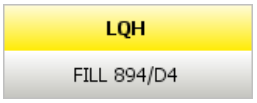
ADD VMS

The automated addition of VMS with a dosing device is defined in this command.

Exit track

The exit track is run at the end of the method.

The **LQH** command fills the dosing unit **894/D1 50mL VMS** when the determination is finished.



The **LQH** command fills the dosing unit **894/D4 2mL Std or sample** when the determination is finished.

Method check

(see "Method check", page 15).

Saving a method

After having entered and checked all relevant parameters for the method, save the method as follows:

1. Open the **Save method** dialog window using the **File ▸ Save as...** menu.
2. Enter the name **Suppressor determination (CVS, DT), semiautomated** for the method in the **Method name** field.
3. Click on **[Save]**.

5.2.2.2 Carrying out a determination

These steps are performed in the **Workplace** program part.

Recording a calibration curve

1. Prepare the dosing unit **894/D4 2mL Std or sample** with suppressor standard solution and the dosing unit **894/D1 50mL VMS** with VMS *(see "Preparing the dosing unit", page 48)*.

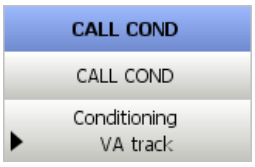
2. Click on the icon of the **Workplace** program part.
3. Select the **Single determination** tab in the **Run** subwindow.
4. In the **Method** field, select the **Suppressor determination (CVS, DT), semiautomated** method created from the method template.

5 Select the **Standard** entry in the **Sample type** list box.

6 Click on **[Start]**.

The volume of VMS defined in the **ADD AUX** command is automatically dosed into the measuring vessel through the dosing unit **894/D1 50mL VMS**.

7 The following command is carried out after the addition:



Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

NOTE

If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel have to be thoroughly rinsed with distilled water.

8 The VMS signal is now measured.

9 The automatic standard addition is carried out.

The volume of suppressor standard solution defined in the **ADD STD** command is automatically dosed into the measuring vessel through the dosing unit **894/D4 2mL Std or sample**.

10 Step **9** is repeated until the stop criterion has been fulfilled. The stop criterion is defined in the following command:

11 When the exit track is reached, all dosing units used are filled.

12 When the measurement is finished, the determination is stored in the database.

13 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

14 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

Determining the suppressor concentration

1 Prepare the dosing unit **894/D4 2mL Std or sample** with sample and, if necessary, the dosing unit **894/D1 50mL VMS** with VMS *(see "Preparing the dosing unit", page 48)*.

2 Click on the icon of the **Workplace** program part.

3 Select the **Single determination** tab in the **Run** subwindow.

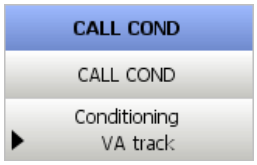
4 In the **Method** field, select the **Suppressor determination (CVS, DT), semiautomated** method created from the method template.

5 Select the **Sample** entry in the **Sample type** list box.

6 Click on **[Start]**.

The volume of VMS defined in the **ADD AUX** command is automatically dosed into the measuring vessel through the dosing unit **894/D1 50mL VMS**.

7 The following command is carried out after the addition:



Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

NOTE

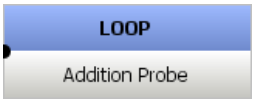
If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel have to be thoroughly rinsed with distilled water.

8 The VMS signal is now measured.

9 The automatic standard addition is carried out.

The volume of sample defined in the **ADD STD** command is automatically dosed into the measuring vessel through the dosing unit **894/D4 2mL Std or sample**.

10 Step **9** is repeated until the stop criterion has been fulfilled. The stop criterion is defined in the following command:



11 When the exit track is reached, all dosing units used are filled.

12 When the measurement is finished, the determination is stored in the database.

13 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

14 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

5.2.3 Determining the brightener concentration

The procedure for the semiautomated brightener determination corresponds to the manual procedure *(see Chapter 4.2.3, page 29)*. For the semiautomated determination, however, VMS, brightener concentrate and suppressor concentrate are dosed into the measuring vessel with Dosinos. Sample is added manually.

5.2.3.1 Creating a method

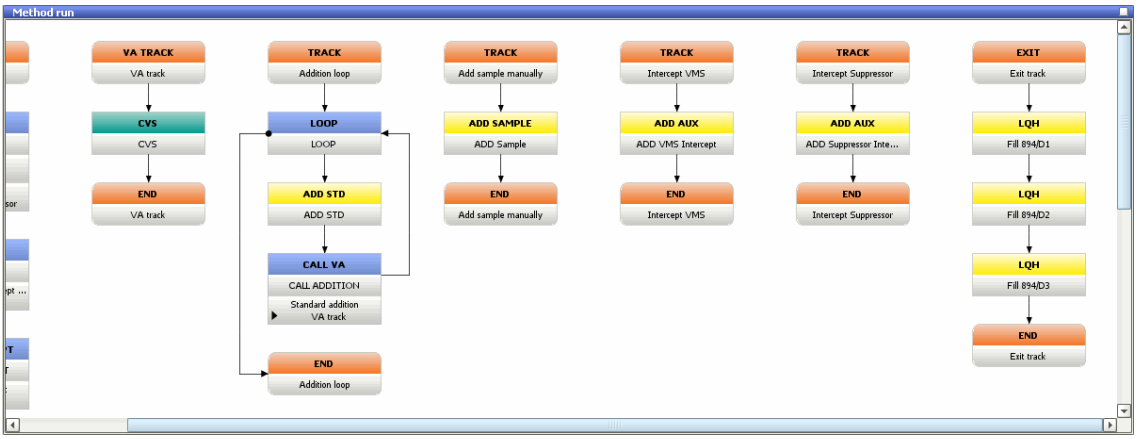
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New...** menu.

3 Under **Templates**, select **Brightener determination (CVS, MLAT), semiautomated** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.

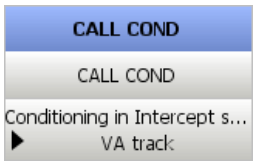


Meaning of the single commands

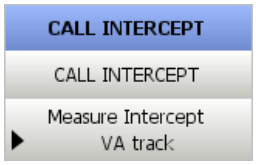
The following commands are required for a semiautomated determination of the brightener concentration:

Main track

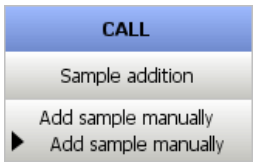
Simultaneously calls the track **Intercept VMS** for the automated dosing of VMS with the dosing unit **894/D1 50mL VMS** and the track **Intercept Suppressor** for the automated dosing of suppressor concentrate with the dosing unit **894/D2 2mL Suppressor**.



(see page 30).



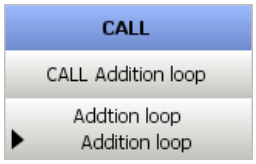
(see page 31).



(see page 31).

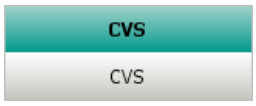
(see page 31).

Calls the **VA track** in which the CVS measurements are carried out after the addition of sample *(see page 11)*.



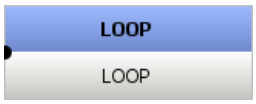
Calls the track **Addition loop**.

VA track



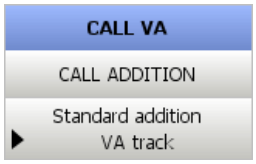
(see page 11).

Addition loop



After the track **Addition loop** has been called by the **CALL Addition Loop** command, brightener standard solution is dosed until the stop criterion defined in the command has been fulfilled after a measuring cycle.

(see page 31).



Calls the **VA track** in which the CVS measurement is carried out after the automated addition of brightener standard solution *(see page 31)*.

Add sample manually

Command for dosing the sample manually.

Intercept VMS

Command for the automated dosing of VMS of the intercept solution.

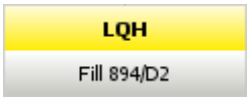
Intercept Suppressor

Command for the automated dosing of suppressor concentrate of the intercept solution.

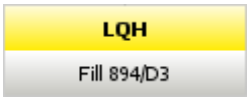
Exit track

The exit track is run at the end of the determination.

The **LQH** command fills the **894/D1 50mL VMS** dosing unit.



The **LQH** command fills the dosing unit **894/D2 2mL Suppressor**.



The **LQH** command fills the dosing unit **894/D3 2mL Brightener**.

5.2.3.2 Carrying out a determination

These steps are performed in the **Workplace** program part.

Carrying out the brightener determination

1 Click on the icon of the **Workplace** program part.

2 Select the **Single determination** tab in the **Run** subwindow.

3 Select the **Brightener determination (CVS, MLAT), semiautomated** method in the **Method** field.

4 Prepare the following dosing units *(see "Preparing the dosing unit", page 48)*:

- **894/D1 50mL VMS** with VMS

- **894/D2 2mL Brightener** with brightener concentrate
- **894/D3 2mL Suppressor** with suppressor concentrate

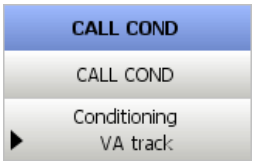
5 Select the **Sample** entry in the **Sample type** list box.

6 Enter the application-specific value for the sample amount in the **Sample amount** field.

7 Click on **[Start]**.

- The volume of VMS defined in the **ADD VMS Intercept** command is automatically dosed into the measuring vessel through the dosing unit **894/D1 50mL VMS**.
- The volume of suppressor concentrate defined in the **ADD Suppressor Intercept** command is automatically dosed into the measuring vessel through the dosing unit **894/D3 2mL Suppressor**.

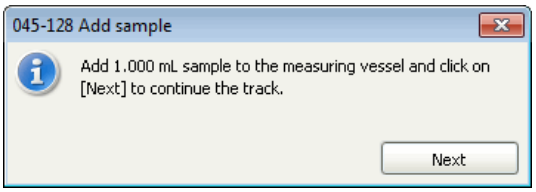
8 The following command is carried out after the additions:



Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

9 Now the intercept value is measured.

10 After the measurement of the intercept value has been completed, the prompt for adding the sample appears.



11 Pipette the volume of sample indicated in the message through the pipetting opening into the measuring vessel and click on **[Next]**.

The volume of suppressor concentrate defined in the **ADD Suppressor Intercept** command is automatically dosed into the measuring vessel through the dosing unit **894/D3 2mL Suppressor**.

12 After the sample has been measured, the volume of brightener concentrate defined in the **ADD STD** command is automatically dosed into the measuring vessel through the dosing unit **894/D2 2mL Brightener**.

13 Step **12** is repeated a second time. The number of cycles is defined in the following command:

14 When the exit track is reached, all dosing units used are filled.

15 When the measurement is finished, the determination is stored in the database.

16 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel with H_2O.

17 Place the measuring vessel back in the holder of the 894 Professional CVS and lower the measuring head arm.

6 Automated determination

The following equipment is required for an automated determination:

- 894 Professional CVS
- 858 Professional Sample Processor
- 843 Pump Station
- 807 Dosing Unit (three with a 2 mL and one with a 50 mL glass cylinder)
- 800 Dosino
  - 800 Dosino and 807 Dosing Unit with cylinder size 50 mL for dosing VMS
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing suppressor concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing brightener concentrate
  - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing sample

6.1 Configuration

6.1.1 Configuring the instrument

894 Professional CVS

(see Chapter 4.1.1, page 7).

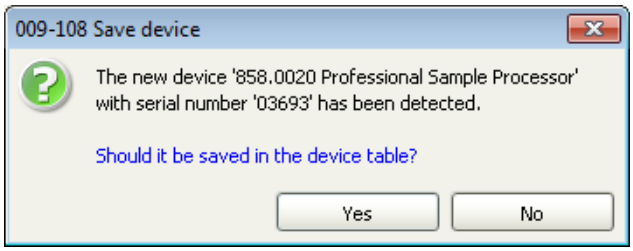
858 Professional Sample Processor

1 Connecting the instrument

Connect the instrument to the PC using the controller cable 6.2151.000.

2 Switching on the instrument

The device parameters of the **858 Professional Sample Processor** are automatically recognized.



3 Saving the instrument in the table

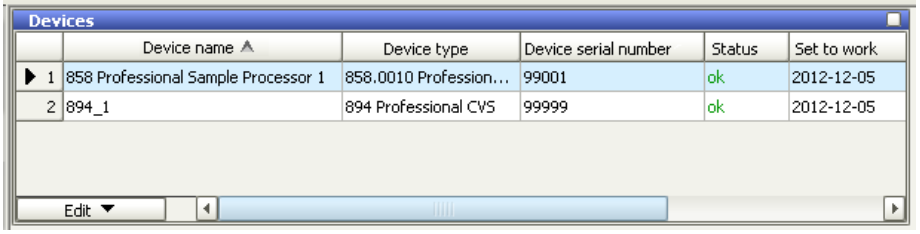
Confirm the message with **[Yes]**.

The **Properties - 858 Professional Sample Processor - 'Device name'** dialog window opens.

4 Entering an instrument name (optional)

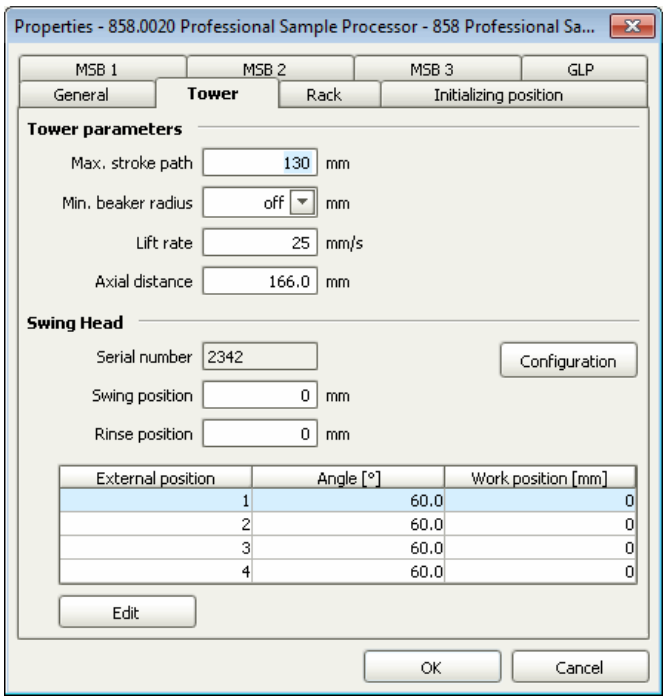
On the **General** tab, enter a new name for the instrument in the **Device name** field and close the dialog window with **[OK]**.

The newly recognized instrument is entered in the device table in the **Devices** subwindow.



5 Defining tower parameters

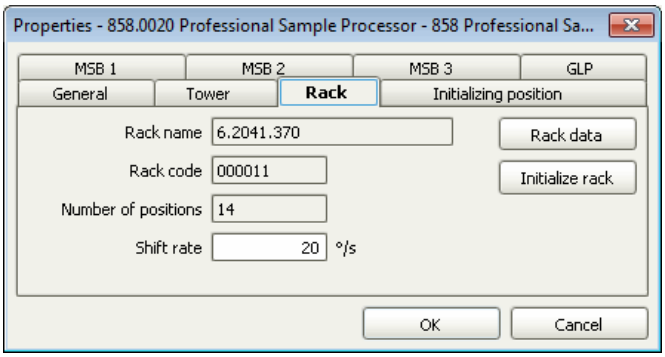
- In the device table in the **Devices** subwindow, select the newly entered instrument and double-click on it.
  The **Properties - 858 Professional Sample Processor - 'Device name'** dialog window opens.
- Select the **Tower** tab.



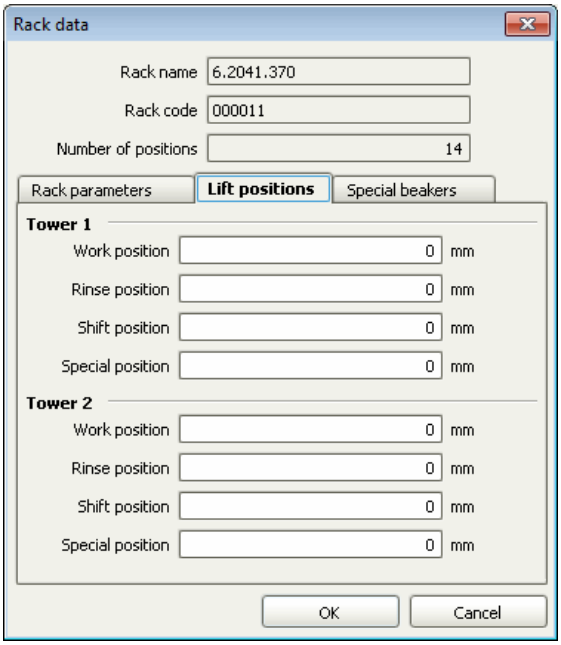
- Enter the value **130 mm** in the **Max. stroke path** field.

6 Defining rack parameters

- Select the **Rack** tab.
  The number of the default rack, 6.2041.450, is entered in the **Rack name** field.



- Click on the **[Rack data]** button.
- Select the **Lift positions** tab.



- Enter the value **125 mm** for **Tower 1** in the **Work position** field.

Close all dialog windows with **[OK]**.

Readjusting the work position

For the determination of the brightener concentration, the entire sample is transferred to the measuring vessel with the peristaltic pump built into the 858 Professional Sample Processor. To ensure that this transfer is completed to 100%, the PEEK needle has to be correctly adjusted. Proceed as follows to do this:

1 Setting the lift position

- Place an empty 10 mL sample vial in the desired position (57 to 126) on the rack.
- Click on the **Manual** program part.
- Select **Tower 1** in the device selection window.
- Open the **Move** tab.
- In the **Target position** field in the **Rack position** section, enter the number of the position in which you have placed the sample vial.
- Click on **[Start]** in the **Rack position** section. The rack position that is set is approached.
- In the **Lift position** section, enter the value **125 mm** in the **Target position** field.
- Click on **[Start]** in the **Lift position** section. The lift position that is set is approached.
- In the **Lift position** section, use the arrow key to move the PEEK needle slowly downwards until it is located no more than 0.5 mm above the floor of the sample vial.
- When the PEEK needle is correctly positioned, open the **Assign position** tab.
  In the **Lift position** section, the new value is entered in the **Current position** field.
- In the **Rack position** section, enable the **Work position for** option and select **Tower**.
- Click on **[Assign]** in the **Rack position** section.

Connecting an 800 Dosino with 807 Dosing Unit

(see "Connecting an 800 Dosino with dosing unit", page 39).

Initializing a dosing unit in 894 Professional CVS

(see "Initializing a dosing unit", page 40).

6.1.2 Configuring electrodes

(see Chapter 4.1.2, page 8).

6.1.3 Configuring dosing units

(see Chapter 5.1.3, page 39).

6.1.4 Defining solutions

(see Chapter 5.1.4, page 42).

6.2 Methods for the automated determination

In this chapter, you will create methods from a method template for:

- an automated determination of the suppressor concentration with a Sample Processor (determination series)
- an automated determination of the brightener concentration with a Sample Processor (determination series)

6.2.1 Determining the suppressor concentration

The suppressor concentration is determined with the calibration method **DT**.

The method for the automated determination of the suppressor concentration comprises:

- the recording of a calibration curve with a suppressor standard solution
- the determination of the suppressor concentration in a sample

6.2.1.1 Creating a method

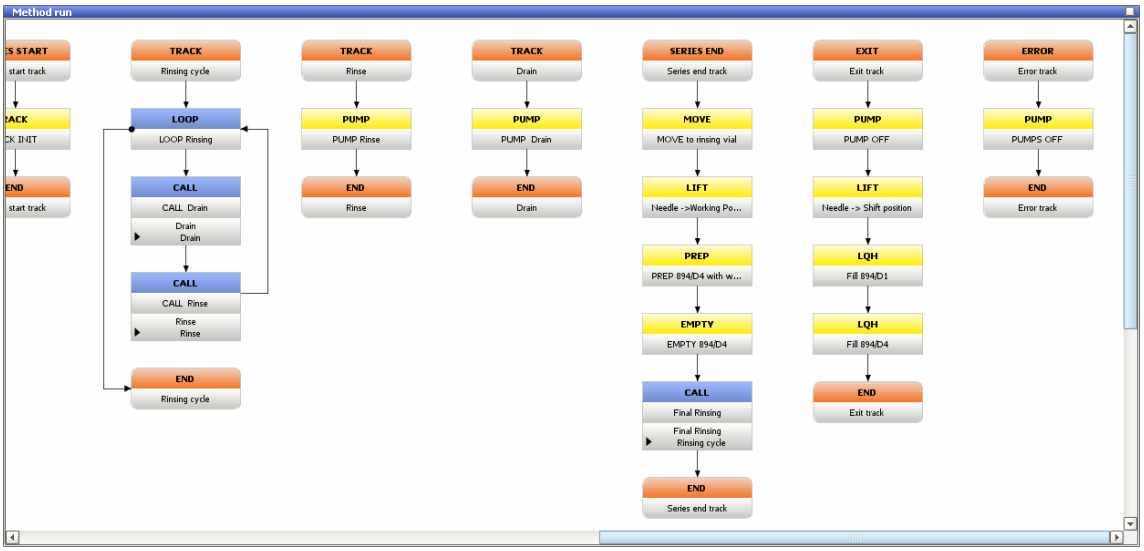
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New...** menu.

3 Under **Templates**, select **Suppressor determination (CVS, DT), automated** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.

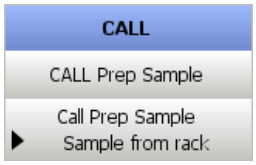


Meaning of the single tracks and commands

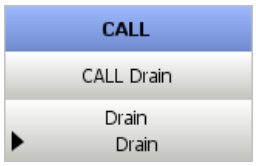
The method run of the automated determination of the suppressor concentration largely corresponds to the procedure used for the semiautomated determination. However, additional automation and rinsing tracks are used for controlling the sample changer. The automatic rinsing of the measuring cell is achieved by means of PUMP commands.

Main track

Compared with the semiautomated determination *(see page 51)*, the method run contains the following additional commands:



Calls the track in which the dosing unit is rinsed with sample.



Calls the track in which the measuring vessel is emptied.

Calls the track in which the measuring vessel is rinsed.

VA track *(see page 52).*

DT Determination *(see page 52).*

DT Calibration *(see page 52).*

ADD VMS *(see page 52)*.

Collecting the sample from the rack In this track, the sample is collected from the rack and the dosing unit is rinsed with sample.

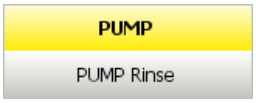
Next sample In this track, the PEEK needle of the sample changer is lowered into the next sample.

Series start track In this track, the sample rack is initialized. This means that the rack, the lift and the robotic arm (if present) are reset, the rack code is read out and the respective rack data is transferred to the sample changer.

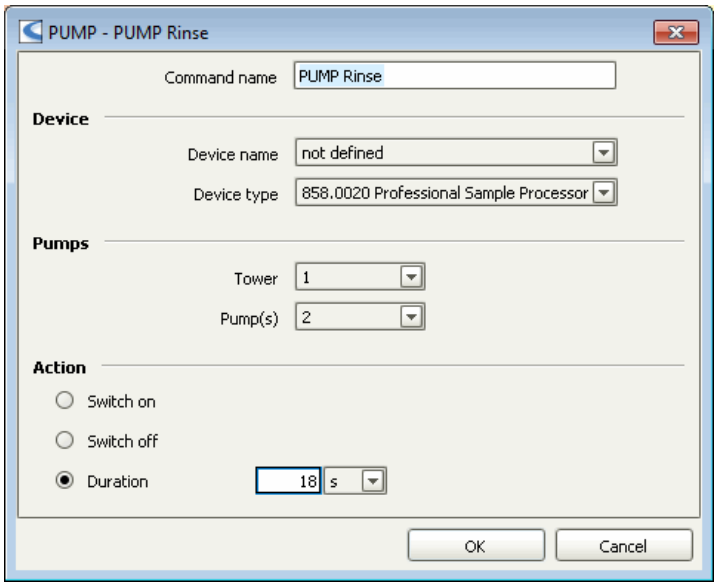
The series start track is executed in the run only once at the beginning of the first determination of a series and before the main track.

Rinsing cycle You can define how often the measuring vessel is to be rinsed and its contents aspirated in this track.

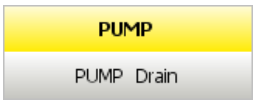
Rinse You can define how the measuring vessel is to be rinsed in this track.



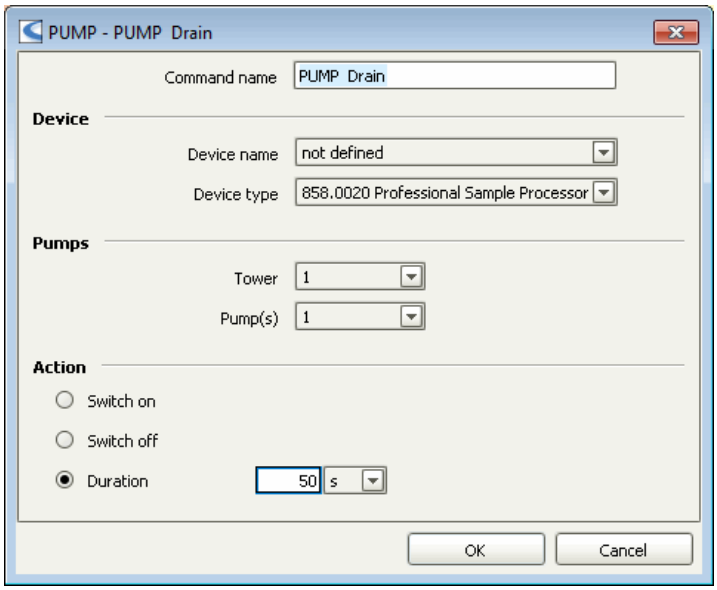
When doing so, adjust the application-specific pump time for rinsing to the measuring vessel volume in the **Duration** field.



Aspirate You can define how the contents of the measuring vessel are to be aspirated in this track.



When doing so, adjust the application-specific pump time for aspirating to the measuring vessel volume in the **Duration** field.



Series end track

In this track, the sample changer moves to the last sample position + 1, where a container with water has to be located. The dosing unit for the sample is then rinsed with water and emptied, and the measuring vessel is also emptied.

The series end track is executed in the run only once at the end of the last determination of a series after the main track.

Exit track

In this track, the pumps are switched off, the PEEK needle is lifted and the dosing units **894/D1 50mL VMS** and **894/D4 2mL Std or sample** are filled.

The exit track is run at the end of the method or when a determination is canceled manually.

Error track

The pumps are switched off in this track.

The error track is run if an error occurs in the run.

Method check

(see "Method check", page 15).

Saving a method

After having entered and checked all relevant parameters for the method, save the method as follows:

1. Open the **Save method** dialog window using the **File ▸ Save as...** menu.

2 Enter the name **Suppressor determination (CVS, DT), automated** for the method in the **Method name** field.

3 Click on **[Save]**.

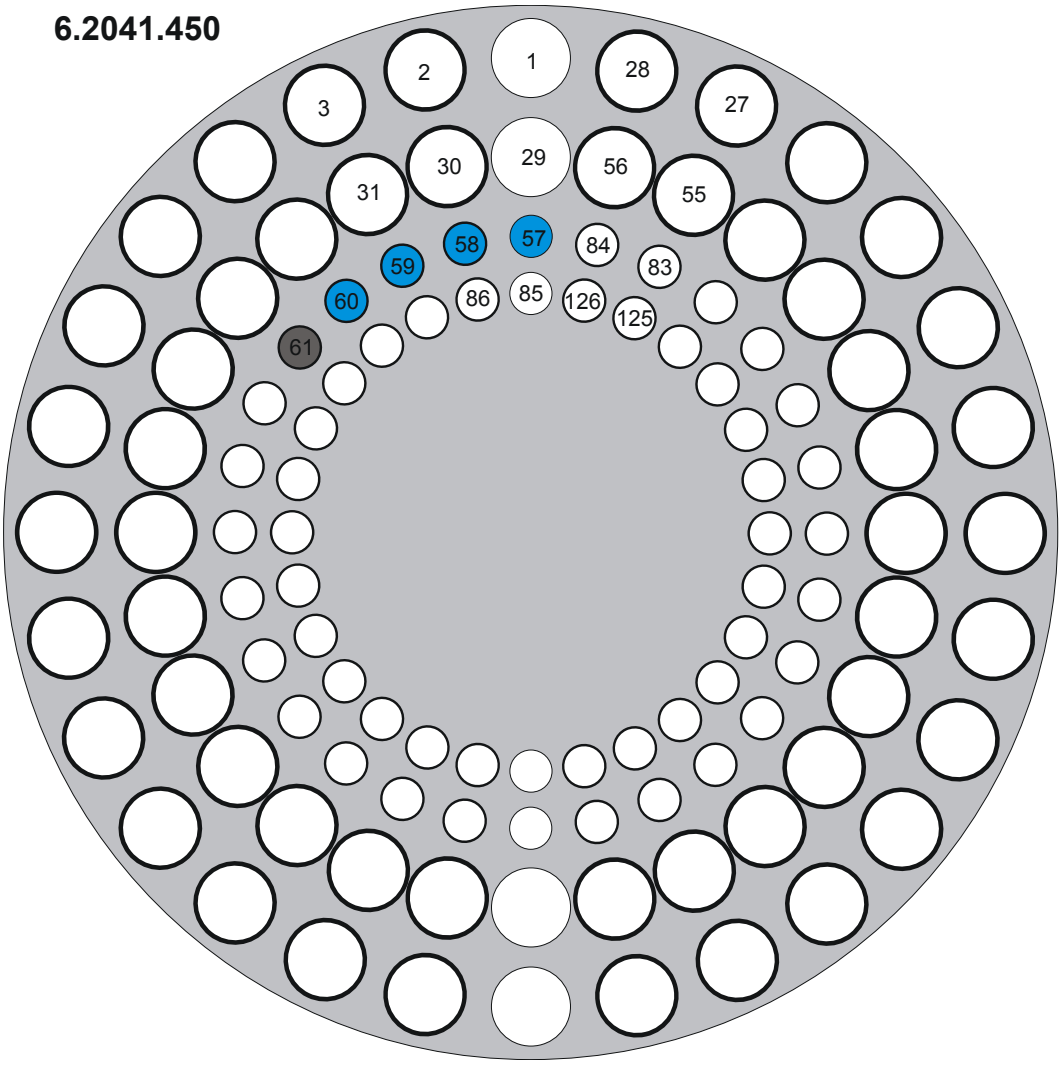
6.2.1.2 Sample table

Filling the sample rack

The 6.2041.450 sample rack used comprises two sets of 56 positions. The two outer rings are intended for 50 mL sample vials and the two inner rings for 11 mL sample vials.

The method template has been devised for the 6.2041.450 rack in conjunction with 11 mL sample vials. Any sample position may be used. For a better understanding, however, the samples or standard solutions are placed in consecutive sample positions. A vial with water always has to be placed in the last sample position so that the dosing unit used can be rinsed with water at the end of a sample series.

- standard solution or first sample in position **57**
- samples in positions **58** to **60**
- rinsing solution (distilled water) in position **61**



Standard or sample

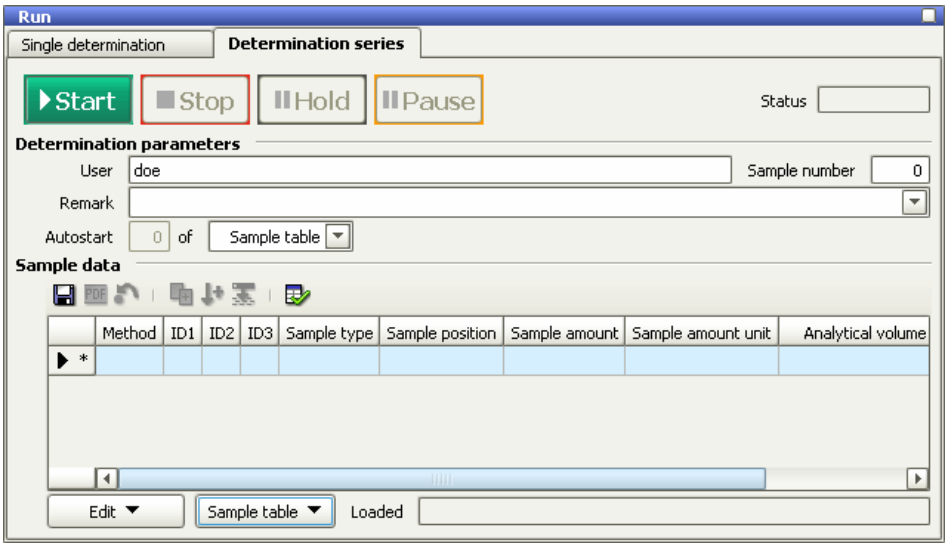
Rinsing solution (distilled water)

Not used

Creating a sample table

1 Switch to the **Workplace** program part.

2 Select the **Determination series** tab in the **Run** subwindow.



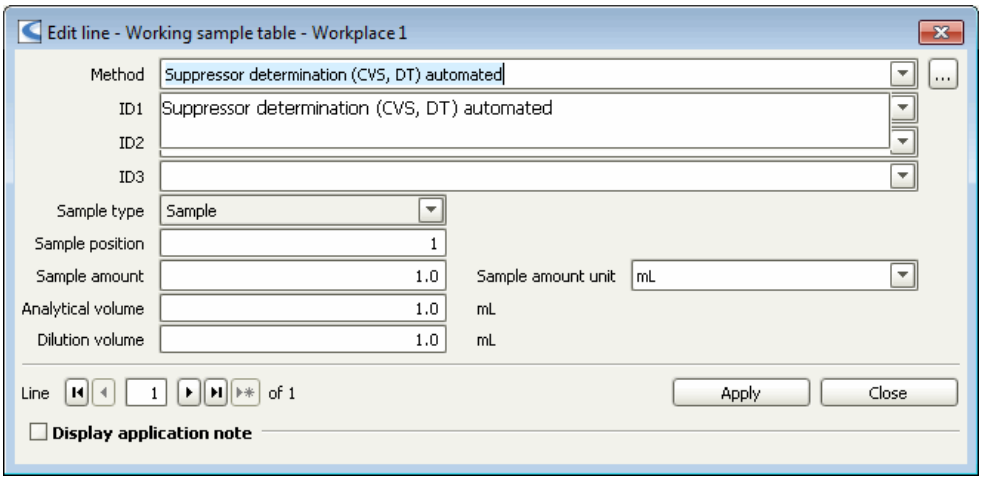
3 Open the **Edit line - Working sample table - Workplace 'Name'** dialog window using the **[Edit]** ▸ **Edit line** button.

4 Click on the button in the **Method** field.

Select the method name **Suppressor determination (CVS, DT), automated** in the table and click on **[Open]**.

If several method groups already exist, the group to which the method belongs must first be selected in the **Method groups** list box.

Suppressor determination (CVS, DT), automated is automatically entered in the **Method** field.



5 **Defining the sample position for standard and samples**

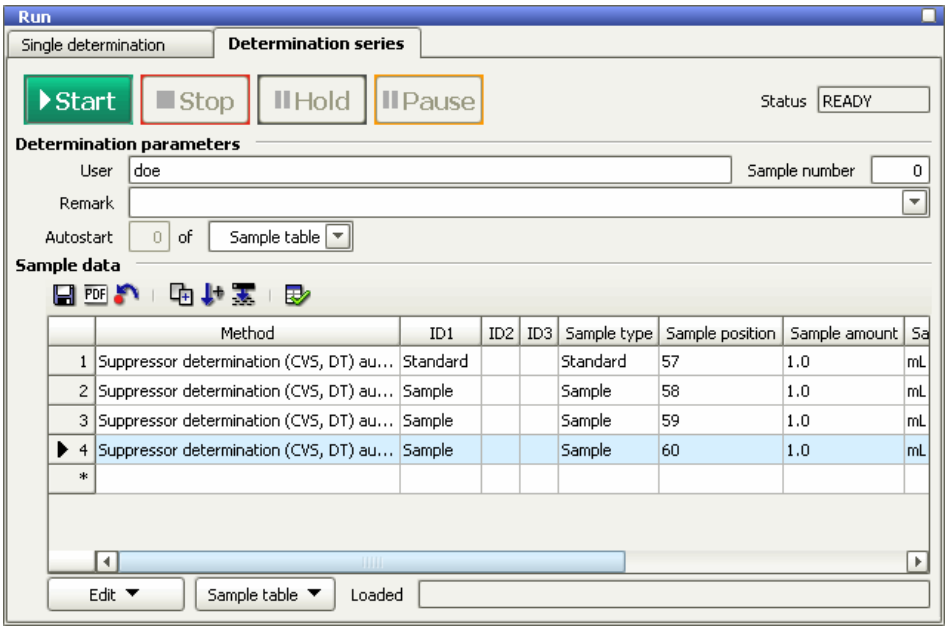
Enter the following values in the fields:

- Enter **Standard** as description in the **ID1** field.
- Select the **Standard** entry in the **Sample type** list box.
- Enter the value **57** in the **Sample position** field.
- The fields **Sample amount**, **Sample amount unit**, **Analytical volume** and **Dilution volume** are not required and can be left unchanged.
- Click on **[Apply]**.
  The parameters for the standards are written into the first line of the sample table and saved.
- Click on the ▸ button in the **Line** field and edit the next line.
- Enter **Sample** as description in the **ID1** field.
- Select the **Sample** entry in the **Sample type** list box.
- Enter the value **58** in the **Sample position** field.
- The fields **Sample amount**, **Sample amount unit**, **Analytical volume** and **Dilution volume** are not required and can be left unchanged.
- Click on **[Apply]**.
  The parameters for the sample are written into the second line of the sample table and saved.
- Click on the ▸ button in the **Line** field and edit the next line.
- The **Sample** sample type is also defined for the samples located in the positions **59** and **60**.

6 Saving the sample table

- Open the **Save sample table** dialog window using the **Sample table ▸ Save as...** button.
- Enter the name **Suppressor determination** in the **Name** field.
- Click on **[Save]**.

The complete table with standard, samples and rinsing solutions looks as follows:



6.2.1.3 Carrying out a determination

These steps are performed in the **Workplace** program part.

Sequence of the determination series

1. Prepare the dosing unit **894/D1 50mL VMS** with VMS *(see "Preparing the dosing unit", page 48)*.

2. Click on the icon of the **Workplace** program part.

3. Select the **Determination series** tab in the **Run** subwindow.

4. Load the previously saved sample table **Suppressor determination** using the **Sample table ▸ Load...** button.

5. Click on **[Start]**.

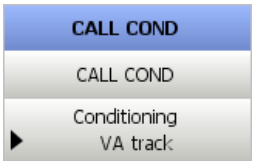
6. The **series start track** is carried out and the rack is initialized.

7. The track **Collect sample from rack** is called.
   - The measuring vessel is emptied.

- The PEEK needle is moved to the first sample position and lowered to the working position into the vial.
- The dosing unit **894/D4 2mL Std or sample** is automatically prepared twice.
- The measuring vessel is automatically rinsed twice with rinsing solution and then emptied.

8 The volume for the solution **VMS** defined in the **ADD AUX** command is automatically dosed into the measuring vessel through the dosing unit **894/D1 50 mL VMS**.

9 The following command is carried out after the addition:



Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

NOTE

If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel have to be thoroughly rinsed with distilled water.

10 The VMS signal is now measured.

11 The automatic standard addition is carried out.

The volume of suppressor standard solution defined in the **ADD STD** command is automatically dosed into the measuring vessel through the dosing unit **894/D4 2mL Std or sample**.

12 Step **11** is repeated until the stop criterion has been fulfilled. The stop criterion is defined in the following command:

13 The measuring vessel is automatically rinsed twice with rinsing solution.

14 When the measurement is finished, the determination is stored in the database.

15 When the exit track is reached, all dosing units used are filled.

16 Steps **7** to **15** are repeated for each position defined in the sample table.

17 When the **series end track** is reached (after the last sample in the sample table), the dosing unit **894/D4 2mL Std or sample** will be automatically prepared twice with distilled water and the PEEK needle will be lifted to the shift position.

18 The **error track** is only run if an error occurs. To prevent the measuring vessel from overflowing, the membrane pumps are switched off.

6.2.2 Determining the brightener concentration

The procedure for the automated brightener determination corresponds to the semiautomated procedure *(see Chapter 5.2.3, page 56)*. For the automated determination, VMS, brightener concentrate and suppressor concentrate are dosed into the measuring vessel with Dosinos. Sample is added by means of a peristaltic pump.

6.2.2.1 Creating a method

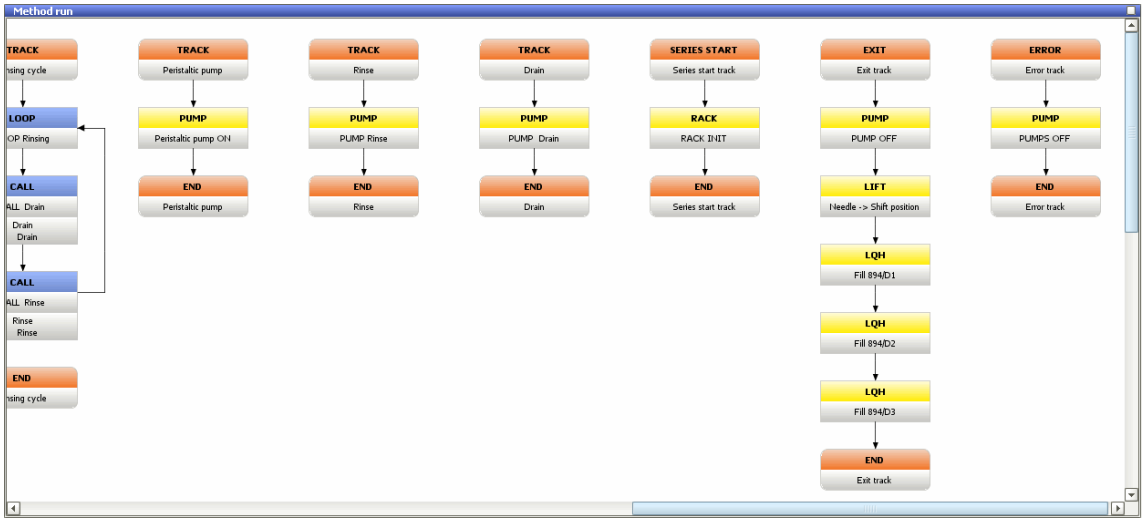
Loading a method template

1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog window using the **File ▸ New...** menu.

3 Under **Templates**, select **Brightener determination (CVS, MLAT), automated** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.

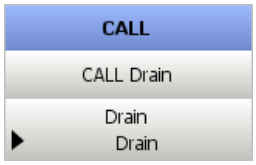


Meaning of the single tracks and commands

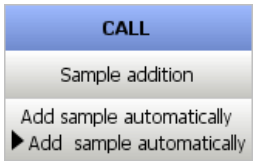
The method run of the automated determination of the brightener concentration largely corresponds to the procedure used for the semiautomated determination. However, additional automation and rinsing tracks are used for controlling the sample changer. The automatic rinsing of the measuring cell is achieved by means of PUMP commands.

Main track

Compared with the semiautomated determination *(see page 51)*, the method run contains the following additional commands:



Calls the track in which the measuring vessel is emptied.



Calls the track in which the sample is automatically added to the measuring vessel.

Calls the track in which the PEEK needle is rinsed.

Calls the track in which the measuring vessel is rinsed.

VA track *(see page 58)*.

Addition loop *(see page 58)*.

Add sample automatically In this track, the sample is automatically added to the measuring vessel.

Next sample In this track, the PEEK needle of the sample changer is lowered into the next sample.

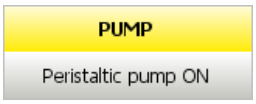
Go to rinse position In this track, the measuring vessel is emptied and the PEEK needle of the sample changer is moved to the rinse position and rinsed.

Intercept VMS In this track, VMS is added to the measuring vessel.

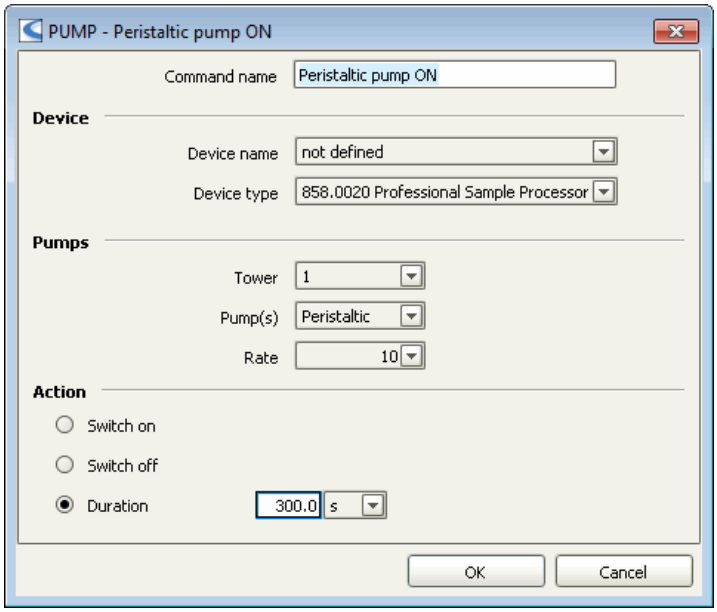
Intercept Suppressor In this track, suppressor concentrate is added to the measuring vessel.

Rinsing cycle You can define how often the measuring vessel is to be rinsed and its contents aspirated in this track.

Peristaltic pump In this track, you can define how long the peristaltic pump will run.



When doing so, adjust the the application-specific operation time of the peristaltic pump in the **Duration** field.



Rinse You can define how the measuring vessel is to be rinsed in this track. When doing so, adjust the pump time for rinsing to the measuring vessel volume.

Aspirate

You can define how the contents of the measuring vessel are to be aspirated in this track. When doing so, adjust the pump time for aspirating to the measuring vessel volume.

Series start track

In this track, the sample rack is initialized. This means that the rack, the lift and the robotic arm (if present) are reset, the rack code is read out and the respective rack data is transferred to the sample changer.

The series start track is executed in the run only once at the beginning of the first determination of a series and before the main track.

Exit track

In this track, the pumps are switched off, the PEEK needle is lifted and the dosing units **D1**, **D2** and **D3** are filled.

The exit track is run at the end of the method or when a determination is canceled manually.

Error track

The pumps are switched off in this track.

The error track is run if an error occurs in the run.

Method check

(see "Method check", page 15).

Saving a method

After having entered and checked all relevant parameters for the method, save the method as follows:

1. Open the **Save method** dialog window using the **File ▸ Save as...** menu.
2. Enter the name **Brightener determination (CVS, MLAT), automated** for the method in the **Method name** field.
3. Click on **[Save]**.

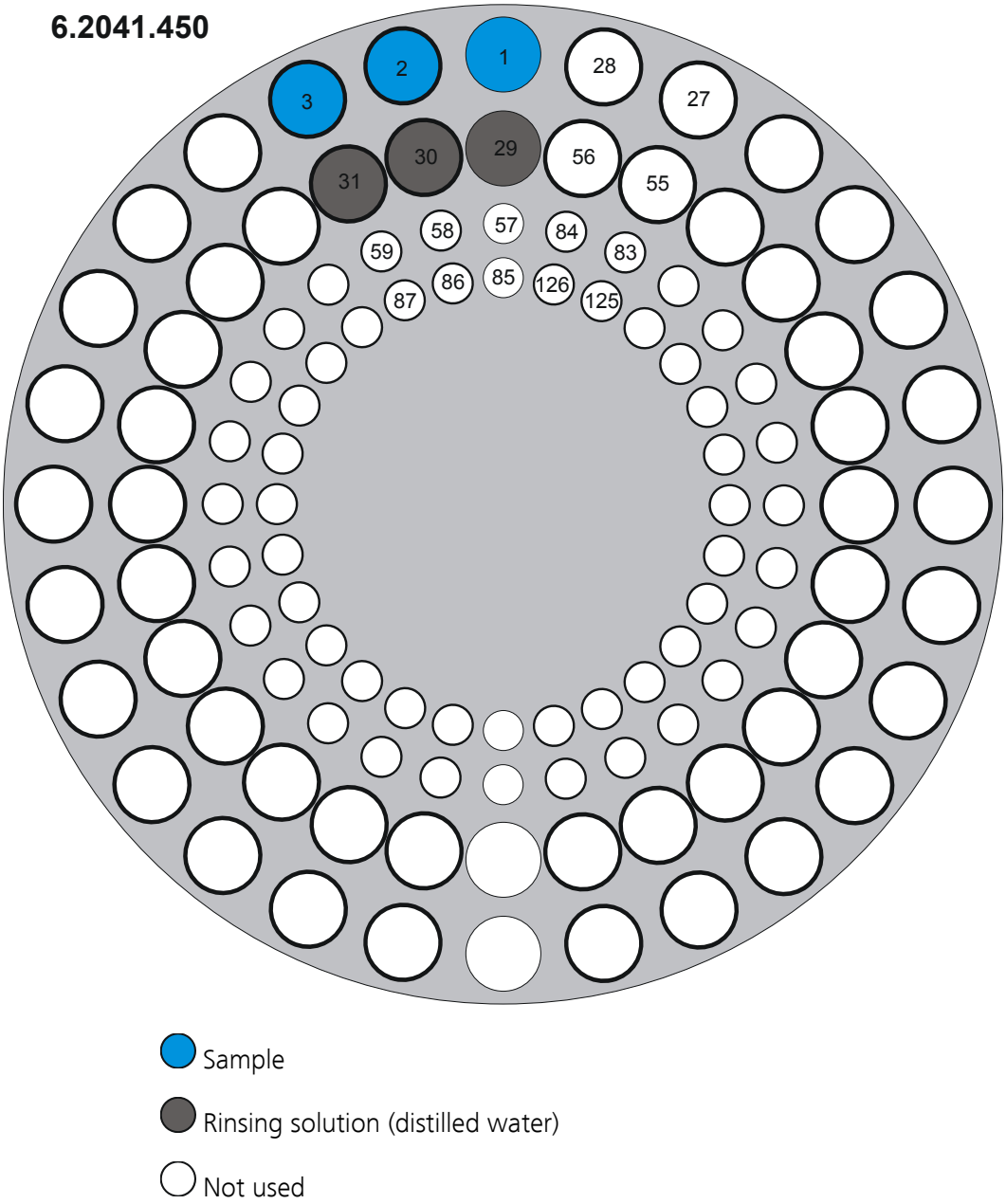
6.2.2.2 Sample table

Filling the sample rack

The 6.2041.450 sample rack used comprises two sets of 56 positions. The two outer rings are intended for 50 mL sample vials and the two inner rings for 11 mL sample vials.

The method template has been devised for the 6.2041.450 rack in conjunction with 50 mL sample vials. The samples have to be placed in the outer ring. For a better understanding, however, the samples are placed in consecutive sample positions. A rinsing vessel has to be placed on the adjacent position in the inner ring for each sample.

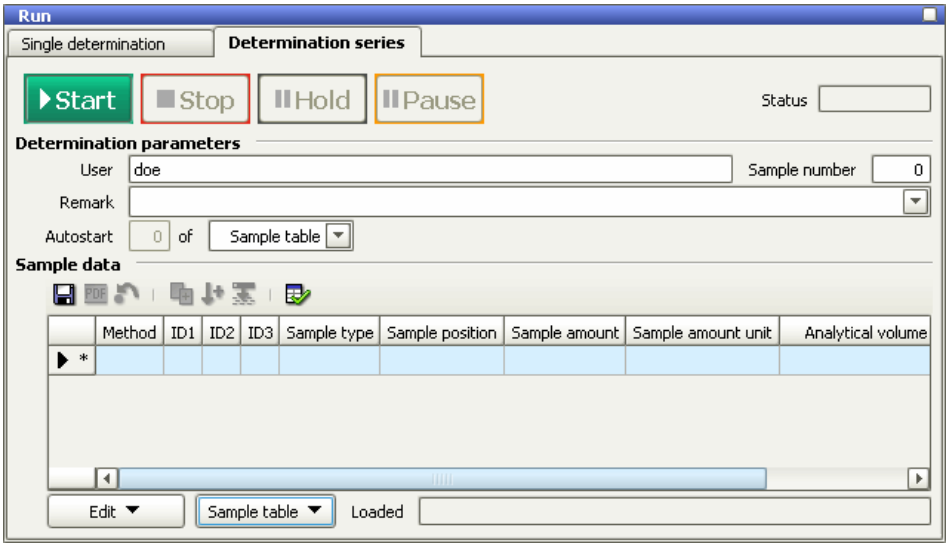
- sample in positions **1**, **2** and **3**
- rinsing solution (distilled water) in positions **29**, **30** and **31**



Creating a sample table

1 Switch to the **Workplace** program part.

2 Select the **Determination series** tab in the **Run** subwindow.



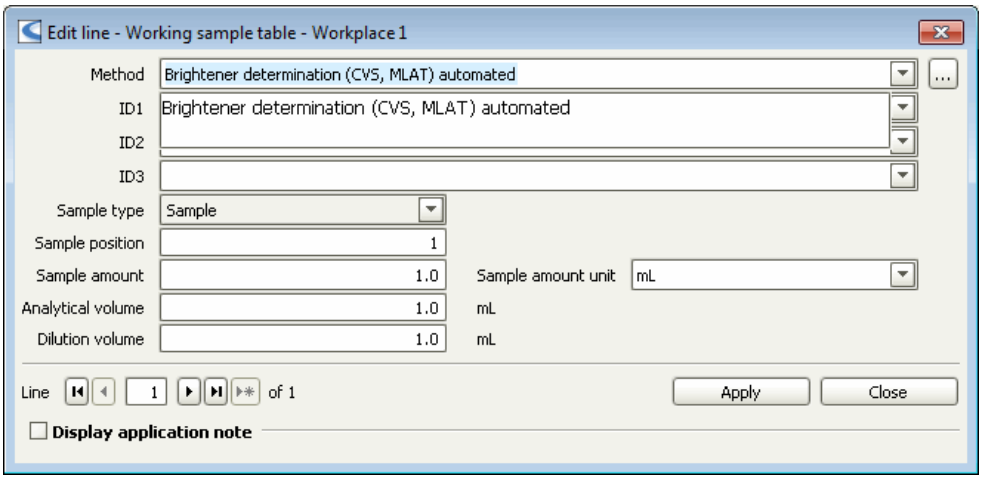
3 Open the **Edit line - Working sample table - Workplace 'Name'** dialog window using the **[Edit]** ▸ **Edit line** button.

4 Click on the ... button in the **Method** field.

Select the method name **Brightener determination (CVS, MLAT), automated** in the table and click on **[Open]**.

If several method groups already exist, the group to which the method belongs must first be selected in the **Method groups** list box.

Brightener determination (CVS, MLAT), automated is automatically entered in the **Method** field.



5 Defining the sample position for samples

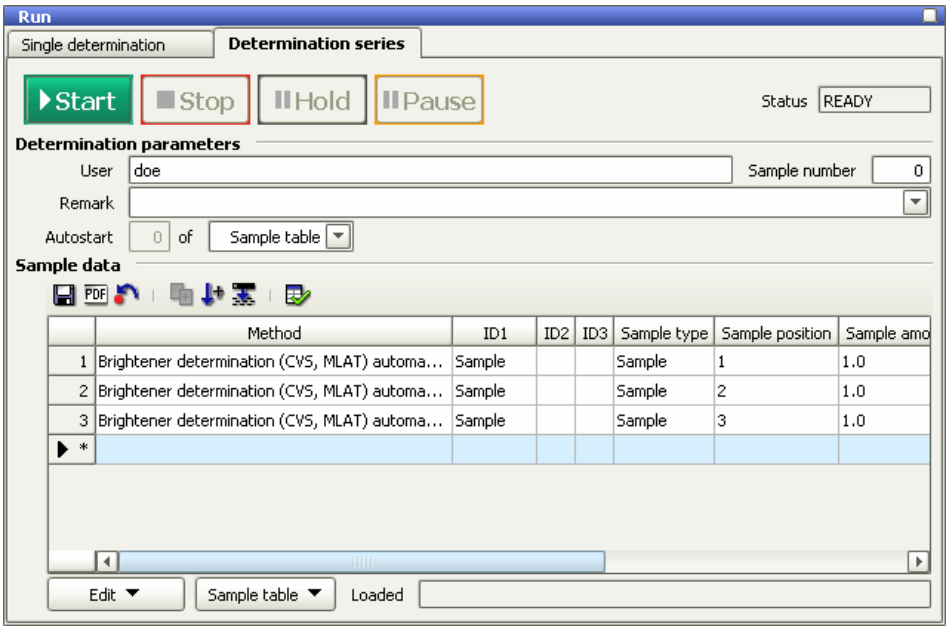
Enter the following values in the fields:

- Enter **Sample** as description in the **ID1** field.
- Enter the value **1** in the **Sample position** field.
- Enter the sample volume in the **Sample amount** field and select the suitable sample amount unit in the **Sample amount unit** list box.
- The fields **Analytical volume** and **Dilution volume** are not required and can be left unchanged.
- Click on **[Apply]**.
  The parameters for the first sample are written in the first line of the sample table and saved.
- Click on the ▸ button in the **Line** field and edit the next line.
- Proceed in the same manner for positions **2** and **3** and create each time a new line in the sample table.

6 Saving the sample table

- Open the **Save sample table** dialog window using the **Sample table ▸ Save as...** button.
- Enter the name **Brightener determination** in the **Name** field.
- Click on **[Save]**.

The complete table looks as follows:



6.2.2.3 Carrying out a determination

These steps are performed in the **Workplace** program part.

Sequence of the determination series

1. Prepare the dosing units: **894/D1 50mL VMS** with VMS, **894/D2 2mL Brightener** with brightener concentrate and **894/D3 2mL Suppressor** with suppressor concentrate *(see "Preparing the dosing unit", page 48)*.

2. Click on the icon of the **Workplace** program part.

3. Select the **Determination series** tab in the **Run** subwindow.

4. Load the previously saved sample table **Brightener determination** using the **Sample table ▸ Load...** button.

5. Click on **[Start]**.

6. The **series start track** is carried out and the rack is initialized.

7 The **PUMP Aspirate** command is carried out and the measuring vessel is emptied.

8 The intercept solution is added automatically:

- The volume of VMS defined in the **ADD VMS Intercept** command is automatically dosed into the measuring vessel through the dosing unit **894/D1 50mL VMS**.
- The volume of suppressor concentrate defined in the **ADD Suppressor Intercept** command is automatically dosed into the measuring vessel through the dosing unit **894/D3 2mL Suppressor**.

9 The following command is carried out after the addition:

Conditioning is finished when one of the stop criteria defined in the method has been fulfilled.

10 Now the intercept value is measured.

11 The automatic sample addition is carried out.

- The PEEK needle is moved to the first sample position and lowered to the working position into the vial.
- The peristaltic pump on the sample changer transfers the entire sample to the measuring vessel.
- The volume of suppressor concentrate defined in the **Add suppressor** command is automatically dosed into the measuring vessel through the dosing unit **894/D3 2mL Suppressor**.

12 After the sample has been measured, the volume of brightener concentrate defined in the **ADD STD** command is automatically dosed into the measuring vessel through the dosing unit **894/D2 2mL Brightener**.

13 Step **12** is repeated a second time. The number of cycles is defined in the following command:

14 The tubings used for sample transfer are rinsed:

- The PEEK needle is moved to the rack position across from the current sample position (sample position + 28) and lowered to the working position.
- The peristaltic pump on the sample changer transfers the entire rinsing solution to the measuring vessel.

15 The measuring vessel is automatically rinsed twice with rinsing solution when the track **Rinsing cycles** is called.

16 When the measurement is finished, the determination is stored in the database.

17 When the exit track is reached, all dosing units used are filled.

18 Steps **7** to **17** are repeated for each position defined in the sample table.

19 When the **series end track** is reached (after the last sample in the sample table), the PEEK needle is lifted to the shift position.

20 The **error track** is only run if an error occurs. To prevent the measuring vessel from overflowing, the membrane pumps are switched off.

7 Editing determinations

7.1 Viewing determinations

You have multiple options for selecting and viewing your determinations:

- Sorting according to column
- Finding via a quick filter
- Finding with a special filter
- Via the **Search** menu

Sort

1 Click on the icon for the **Database** program part.

2 First click in the table with all the data sets on the column heading according to which the table is to be sorted.

The table is sorted according to the selected column in ascending order.

3 Click again on the same column title.

The table is sorted according to the selected column in descending order.

Quick filter

1 Click on the **Determinations** ▸ **Filter** ▸ **Quick filter** menu.

The cursor turns into a special filter symbol. When navigating within the table, the cells in which the cursor is located will have a yellow background.

2 Place the cursor in a cell serving as a filter criterion and double-click with the left mouse button.

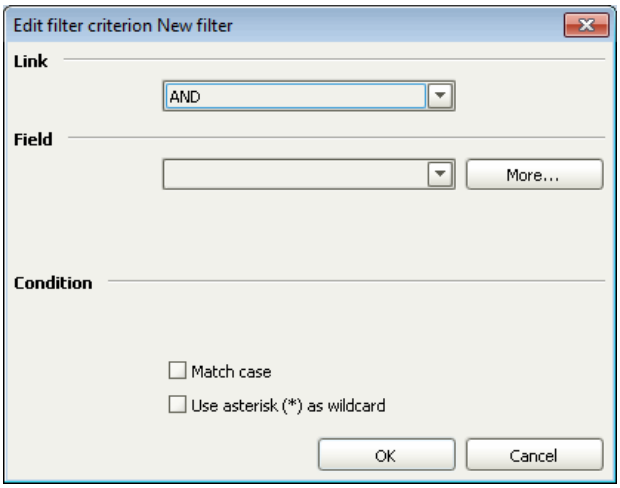
The data sets are filtered according to the content of the selected table field. The quick filter can be applied again within the filtered table.

Special filter

The special filter allows you to specify the filter conditions in detail.

1 Open the corresponding dialog window using the **Determinations ▸ Filter ▸ Special filter...** menu.

2 Open the **Edit 'New filter' filter criterion** dialog window using the **Edit ▸ Edit line** menu.



3 In the **Field** list box, highlight the **Method name** entry.

4 Enter the method name **Suppressor determination (CVS, DT), semiautomated** in the **Comparative value** field and click on **[OK]**.

5 In the **Special filter** dialog window, click on the **[Apply filter]** button and close the window.

The table containing all data sets of the method **Suppressor determination (CVS, DT), semiautomated** appears in the **Determination overview** subwindow.

The data of a highlighted data set appears in the other subwindows:

- The **Results** subwindow shows a table containing the substance concentrations in the samples and the user-defined results.
- The **Curves 1** subwindow shows the measurement curves and the calibration curves.
- The **Information** subwindow can be used to display information on the sample, the determination, the instruments, etc. above the individual tabs.

Searching

1. Open the **Search - Database 'Name'** dialog window using the **Determinations ▸ Search...** menu.
2. In the **Search in** list box, highlight the **User (short name)** entry.
3. Enter the required short name in the **Search word** field.
4. Click on **[Search next]**.

   The first line corresponding to the search term is highlighted.

7.2 Viewing results

Zooming with the mouse

Individual areas of a measurement or calibration curve can be displayed in magnified form by means of the zoom function.

1. Highlight a data set in the overview table.

   The associated measurement curve is displayed in the **Curves 1** sub-window.
2. With the left mouse button held down, drag a rectangle to the bottom right over the area that is to be magnified.

Resetting the zoom

1. Right-click on the measurement curve.
2. Click on the context-sensitive **Show all** menu command.

   The measurement curve is displayed at its original size again.

Changing the display of the measurement curve

You have the option to edit the properties of a measurement curve. You can change the display of the curve, the axis labeling or the scaling. Below you will learn how to change the labeling of the axes in the measurement curve and the line display. Proceed as follows:

1 Changing the axis label

- Right-click on the measurement curve.
- Select the **Properties curve 1…** menu item.
- Select the **x Axis** tab in the **Properties - Curve 1** dialog window.
- Click in the **Label** field and enter a new labeling for the x axis.
- Select the **y1 Axis** tab.
- Click in the **Label** field and enter a new labeling for the y1 axis.
- Click on **[OK]**.

2 Changing the line display

- Right-click on the measurement curve.
- Select the **Properties curve 1…** menu item.
- Select the **y1 Axis** tab.
- Select a new colour in the **Spiking/standard** list box.
- Enter the value **2** in the **Line thickness** list box.
- Click on **[OK]**.

Visualizing the calibration curve

1 Highlight a data set in the overview table.

2 Click on the icon in the **Curves 1** subwindow.

Calibration curve and calibration function are shown.

Displaying measurement curves

1 Highlight a data set in the overview table.

2 Click on the icon in the **Curves 1** subwindow.

The measurement curves are shown.

7.3 Reprocessing determinations

When a determination is reprocessed, variables and evaluations can be changed and the results recalculated. The reprocessed determination can then be saved in the database as a new version.

In this chapter, you will learn how to reprocess determinations on the basis of the following examples:

- recalculating a suppressor determination with a new calibration
- changing the characteristic potential for the brightener determination

Determinations of the type **Sample** can be recalculated with various calibrations (only for the calibration method DT). However, the determinations and the calibration must have been carried out with the same method. The method version may differ.

In order for determinations of the type **Sample** to be reprocessed with a new calibration, the selection of determinations may contain only **one** determination of the type **Standard**.

In order for the current calibration data to be used for the recalculation of the determination of the type **Sample**, the determination of the sample type **Standard** is recalculated by **viva** first. Afterwards, **viva** accesses the current calibration data to recalculate the samples.

Determination with new calibration

In order to recalculate a suppressor determination with a newly recorded calibration curve, proceed as follows:

1 Click on the icon for the **Database** program part.

2 Select the new standard and the required samples in the **Determination overview** subwindow.

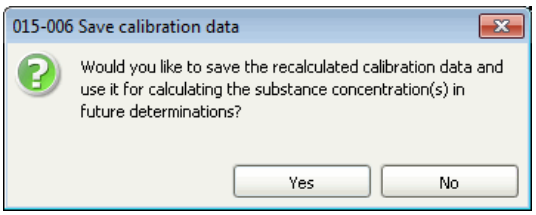
3 Open the **Reprocessing** dialog window using the **Determinations ▸ Reprocess...** menu or the icon.

4 Click on the **Recalculate** button.

The sample is recalculated with the new calibration curve. The newly calculated results are displayed in the **Result view** section.

5 Click on the **[OK]** button.

The following message appears:



6 Click on the **[Yes]** button.

Each determination that has been modified by reprocessing will be saved in the database as a new version with a version number increased by +1.

Changing the evaluation parameters

You will learn how to adjust the characteristic potential on the basis of this example.

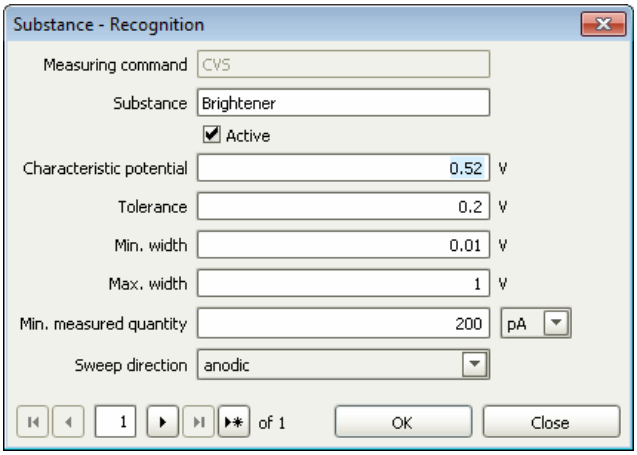
1 Click on the icon for the **Database** program part.

2 **Opening a method**

- Select a determination in the **Determination overview** sub-window.
- Open the **Reprocessing** dialog window using the **Determinations ▸ Reprocess...** menu or the icon.
- Click on the **Modify method** button in the **Evaluation** sub-window.
  The **Method editor** dialog window opens.
- Select the **Recognition** tab in the **Evaluation - Substances** subwindow.

3 Changing the characteristic potential

- Open the **Substances - Recognition** dialog window using the **Edit ▸ Properties...** menu.



- Enter a new value for the characteristic potential in the **Characteristic potential** field and close the dialog window with **[OK]**.
- Close the **Method editor** dialog window with **[OK]**.

4 Recalculating

- In the **Reprocessing** dialog window, click on the **Recalculate** button.
  The determination is recalculated with the new evaluation parameters and the result is shown in the **Result view** section on the **Results** tab.

7.4 Editing a report template

viva contains example report templates. These report templates can be adapted as needed. Modules can be added or removed and their properties can be modified. Only the **Fixed report** module cannot be edited. Below you will replace an image in the provided **EN Report short** report template and add a new fixed report.

Opening a report template

Proceed as follows to edit the **EN Report short** report template:

1 Select the **Database** program part.

2 Open the desired database.

3 Select one or more determinations in the determination overview.

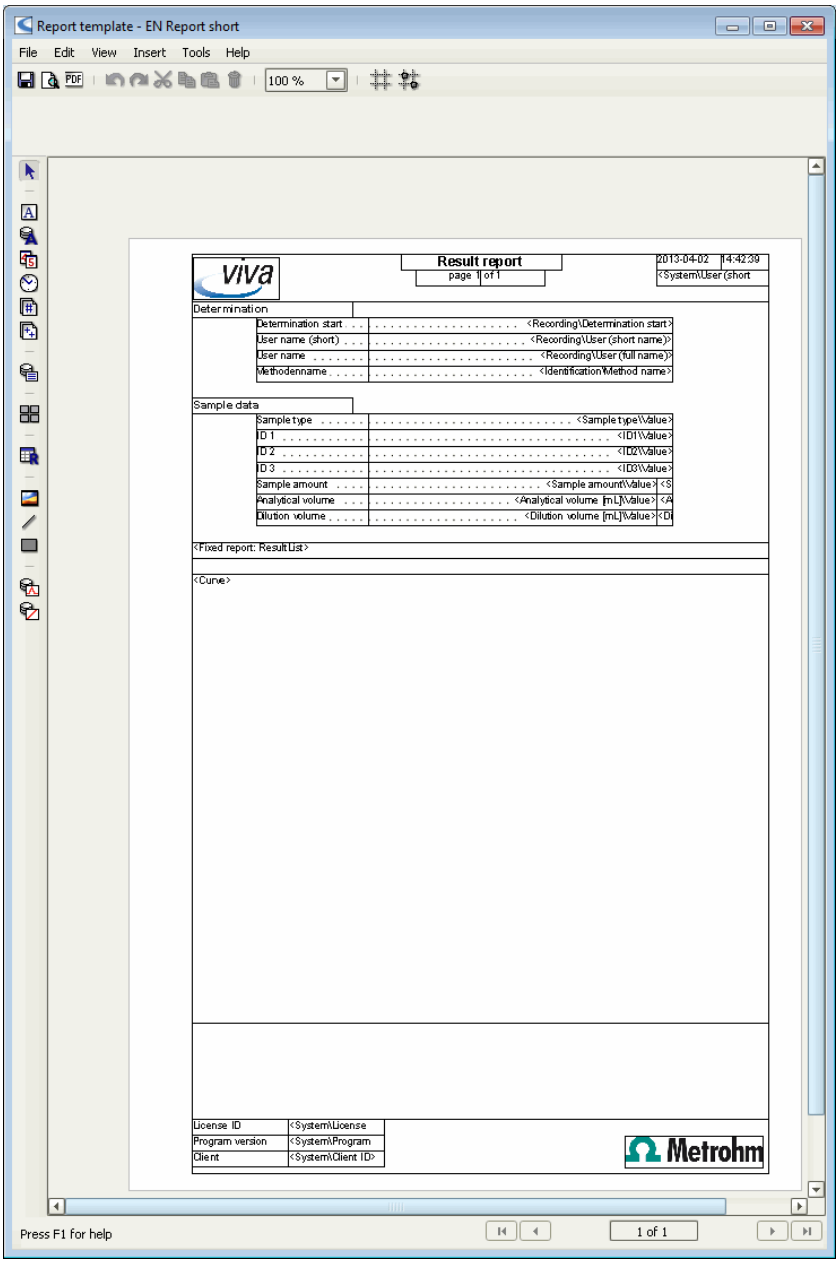
4 Click on the icon or the **Tools** ▸ **Report templates** ▸ **Open...** menu item.

The **Open report template** program window opens.

5 Select the **EN Report short** report template.

6 Click on **[Open]**.

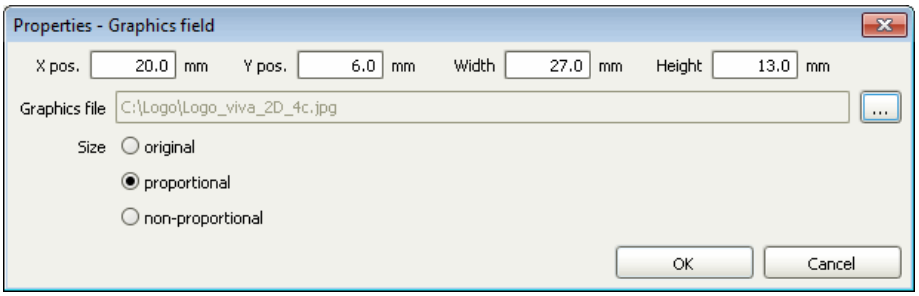
The program window with the selected report template opens.



Replacing an image

1 Select the icon on the module bar and double-click on the Metrohm logo in the bottom right corner of the report.

The properties window for the graphics field opens automatically.



2 Open the dialog window for selecting the new graphics file by clicking on ...

3 Select the desired new graphics file in JPG or PNG format and confirm with **[OK]**.

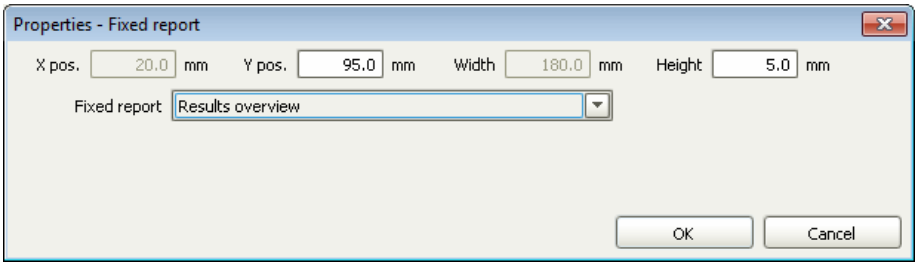
4 Adjust the position, width, height and size of the image.

5 Close the properties window with **[OK]**.

Inserting a new fixed report

1 Select the icon on the module bar and place it on the report template by creating a field with the left mouse button.

The properties window for the fixed report opens automatically.



2 Select the **Configuration used** option in the **Fixed report** field.

3 Close the properties window with **[OK]**.

Saving the report template

1 Click on the **File** ▸ **Save as...** menu item.

The **Save report template** dialog window opens.

2 Enter a name for the new report template and click on the **[Save]** button.

The report template is saved under the specified name.

7.5 Printing a determination report

Proceed as follows to print a determination report:

1 Select the **Database** program part.

2 Click on the icon or the **File** ▸ **Open...** menu item.

The **Open database** dialog window opens.

3 Select the desired database or enter the name in the **Database name** field.

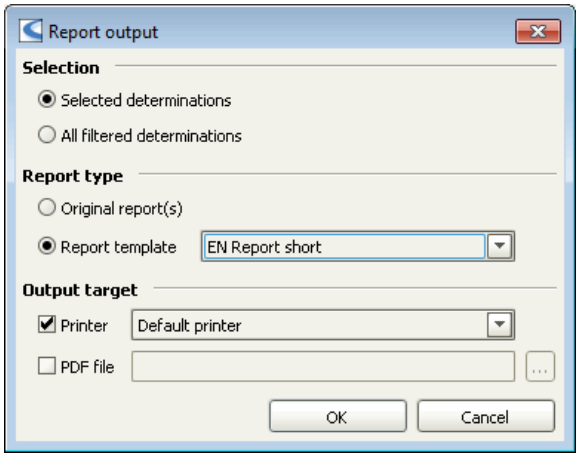
4 Click on **[Open]**.

The data sets of the selected database are displayed in the **Determination overview**. The database name is displayed in the title bar of the program; the number of currently opened databases is displayed in the left upper corner of the database icon.

5 Select the desired determinations.

6 Click on the **File** ▸ **Print** ▸ **Report...** menu item.

The **Report output** dialog window opens.



7 Select the **Report template** option and the desired report template under **Report type**.

8 Under **Output target**, select the **Printer** and/or **PDF file** check box.

NOTE

If several reports are output simultaneously as a PDF file, then an index will be automatically appended to the file name.

9 Click on **[OK]** in the **Report output** dialog window.

The reports of the selected determinations will be output.

Index

A

Automated determination
- Carry out a determination 75, 84
- Configuration 63
- Configure dosing units 67
- Configure electrodes 67
- Configure the instrument 63
- Define solutions 67
- Determine the brightener concentration 77
- Determine the suppressor concentration 67
- Method 67

C

Calibration curve
- Visualize 90
- Zoom 89

Configuration 5

D

Define rack parameters 65
Define tower parameters 64
Determination
- Edit 87
- Print report 97
- Quick filter 87
- Reprocess 91
- Search 89
- Sort 87
- Special filter 88
- View 87

E

Equipment
- Accessories 4
- Devices 3
- Electrodes 3
- Reagents 3

F

Fill the sample rack 71, 80
Filter
- Quick filter 87
- Special filter 88

I

Instrument
- Configure 7, 39, 63

Introduction 1

M

Manual determination 15
- Carry out a determination 25, 35
- Commands 11
- Configuration 7
- Configure electrodes 8
- Configure instrument 7
- Define command parameters 11
- Determine the brightener concentration 29
- Determine the suppressor concentration 18
- Method 9
- Method template 9

Measurement curve
- Change 90
- Change axis curve 90
- Change the line display 90
- Display 90

Measuring curve
- Zoom 89

P

Preparations 3
- Equipment 3
- Prepare solutions 4

Prepare solution
- Suppressor standard solution 4
- VMS 4

Program description 1

R

Readjust the work position 66
Report
- Edit a report template 93
- Print 97

Results
- View 89

S

Sample table 71, 80
Search 89
Semiautomated determination
- Carry out a determination 48, 53, 59
- Commands 46
- Configuration 39
- Configure dosing units 39
- Configure electrodes 39
- Configure instrument 39
- Define command parameters 46
- Define solutions 42
- Determine the brightener concentration 56
- Determine the suppressor concentration 50
- Method 44
- Method template 44

Start software 5
Suppressor standard solution
- Prepare solution 4

V

VMS
- Prepare solution 4

Z

Zoom 89