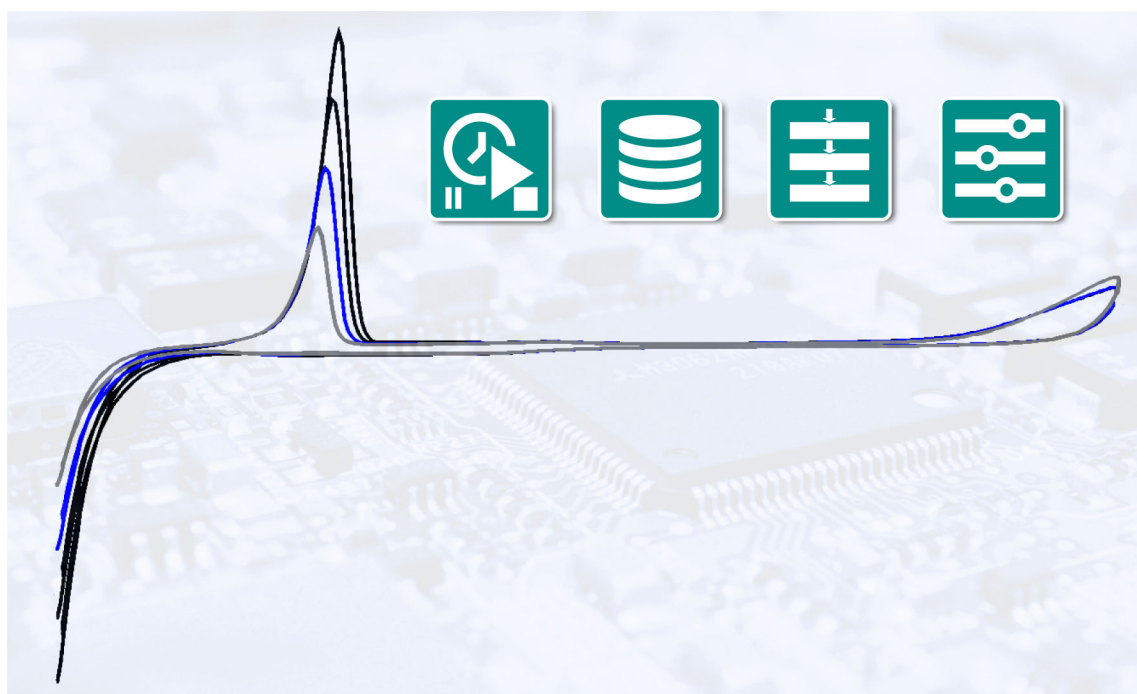




Tutorial CVS

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Tutorial CVS

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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 controls by way of a manual, a semiautomated and an automated determination of the suppressor and brightener concentration.

The devices, 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

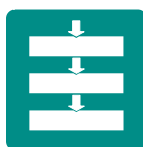
viva comprises the following program parts:

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
- Create 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 Perform the steps one after the other.
Method	Dialog text, parameter in the software
File ► New	Menu or menu item
[Continue]	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.
	WARNING Warning of optical radiation
	CAUTION This symbol draws attention to possible damage to instruments or instrument parts.



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/884 Professional VA
The use of the 894 Professional CVS is described in this tutorial. Similarly, the trials can also be carried out with the 884 Professional VA. In this case, use the **884_1** device instead of the **894_1** device.
- 858 Professional Sample Processor
- 807 Dosing Unit (3 with a 2 mL and 1 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: $c(\text{KCl}) = 3 \text{ mol/L}$
 - Electrolyte vessel filled with bridge electrolyte (e.g. 6.1245.010)
Bridge electrolyte: $c(\text{KNO}_3) = 1 \text{ mol/L}$
- Auxiliary electrode **AE** (6.0343.100)

Reagents

- **VMS** (Virgin Make-up Solution)
 $\beta(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 60 \text{ g/L}$
 $\sigma(5\text{H}_2\text{SO}_4) = 130 \text{ mL/L}$
 $\beta(\text{Cl}^-) = 50 \text{ mg/L}$
- **Suppressor concentrate**
 $\sigma(\text{suppressor}) = 1000 \text{ mL/L}$

- **Brightener concentrate**

$\sigma(\text{brightener}) = 1000 \text{ mL/L}$

Accessories

- Measuring vessel 10 - 90 mL (6.1415.210)
- Measuring vessel 10 - 150 mL (6.1415.250)
- Two 100 mL glass bottles
- 2 L glass bottle
- Bottle holder (6.2055.110)
- Three GL 45 on GL 45 thread adapters
- 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 2000 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: $\sigma(\text{suppressor}) = 10 \text{ mL/L}$.

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:

- Instruments
- 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 for the **Configuration** program part opens. Up to six subwindows can be displayed. Available are:

Shows the automatically detected devices.

Shows the automatically recognized dosing units.

Shows the data of the defined solutions.

Shows the data for all defined sensors and electrodes.

Shows the data of the automatically recognized Metrohm sample racks.

Shows the data of all common variables.



Devices

Dosing units

Solutions

Sensors/Electrodes

Rack data

Common 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 device

- Connect the 894 Professional CVS to the power grid by means of the power cord (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**.

The following message appears:

009-108 Save device – The new '894 Professional CVS' device with serial number 'serial number' has been detected. – Should it be saved to the device table?

2 Saving the device 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 the 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.

Sensors/Electrodes					
	Sensor name ▲	Sensor type	Device name	Set to work	Expiry date
▶ 1	Auxiliary electrode	Auxiliary electrode		2023-08-09	
2	MME	MME		2023-08-09	
3	RDE	RDE/SSE		2023-08-09	
4	Reference electr...	Reference electr...		2023-08-09	
5	scTRACE Gold	scTRACE Gold		2023-08-09	
6	Temperature sen...	Temperature sen...		2023-08-09	

Edit ▼

4.2 Methods for the manual determination

A method is a run instruction for processing a sample. It comprises all components necessary to record and evaluate measurement curves. 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 measurement curves
- 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.

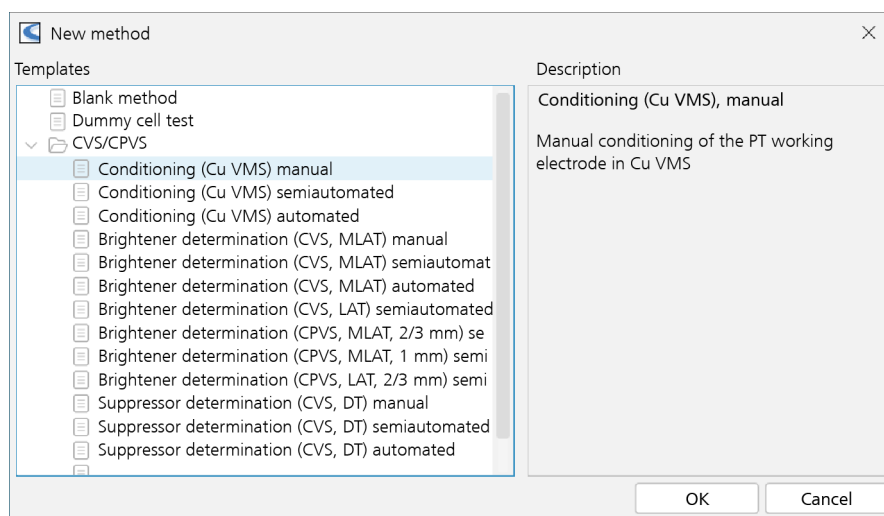
Metrohm recommends working with a method template or importing an example method. This ensures that all required commands are available and that the structure of the method is correct.

Loading a method template



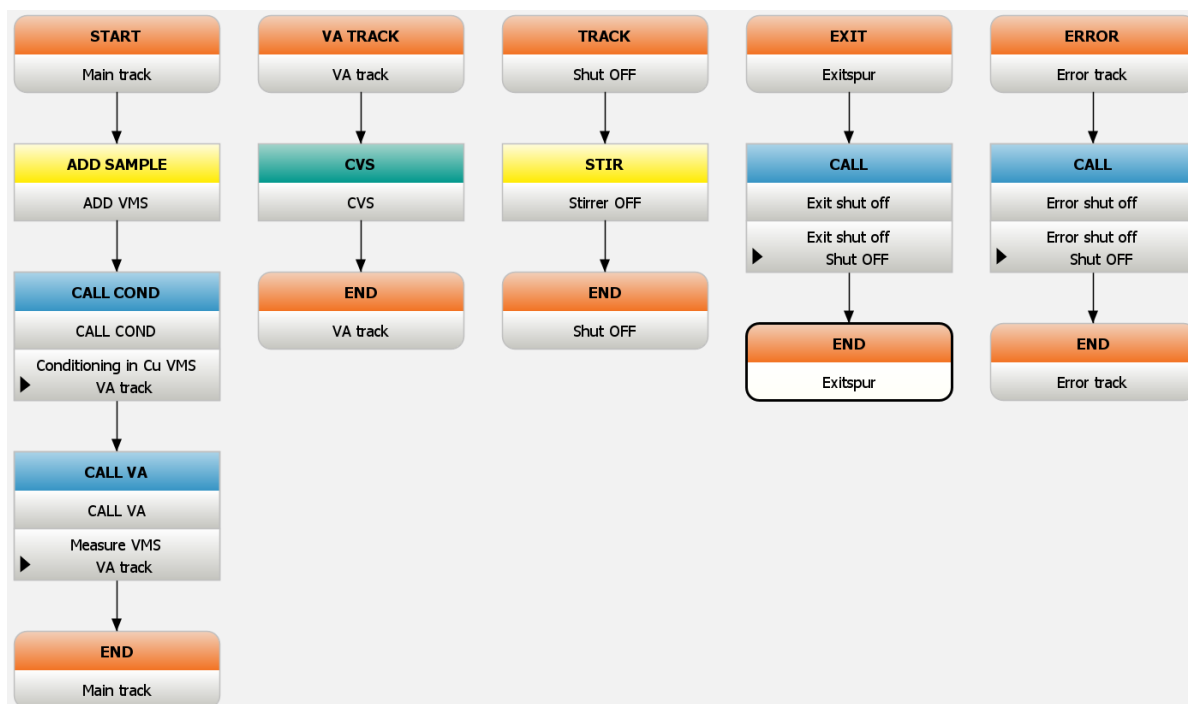
- 1 Click on the icon of the **Method** program part.

- 2** Open the **New method** dialog using the **File ► New...** menu.



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

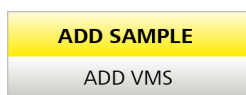
The method template opens.



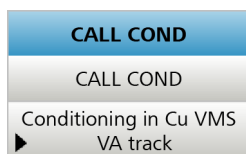
Meaning of the individual commands

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

Main track

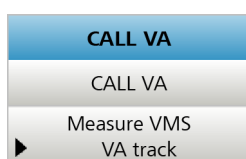


In this method, the VMS is added with the **ADD SAMPLE** command. This command is normally used to add a sample to the result calculation. In this example, the **ADD SAMPLE** command is used so that the measurement curve is displayed in blue (standard colour for measurement curves of samples). The volume used is the sample amount defined in the workplace or in the method under **Sample data variables** (see "Defining command parameters", page 12).



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. In this method, conditioning is carried out until the measurement curves are easily reproducible.

Measurement curves generated with the **CALL COND** command cannot be evaluated later.



The VA track is called again with the **CALL VA** command.

Measurement curves generated with the **CALL VA** command can be evaluated. These can be used to output the peak area or measurement signals at specific points, for example.

VA track

CVS
CVS

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

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.

Normal track Shut off

STIR
Stirrer OFF

The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track

CALL

Exit shut off

Exit shut off
Shut OFF

If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.

Error track

CALL

Error shut off

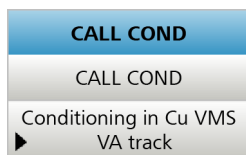
Error shut off
Shut OFF

If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and the determination is then ended.

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 **START** command.
The **START - Main track** dialog opens.
- 2 Navigate to the **Sample data variables** tab.
Double-click on the **Sample amount** entry in the table.
The **Sample data variable - Sample amount** dialog opens.
- 3 Next to the **Fixed value** check box, define the volume to be used for conditioning.
- 4 Close the dialog with **[OK]**.



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

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

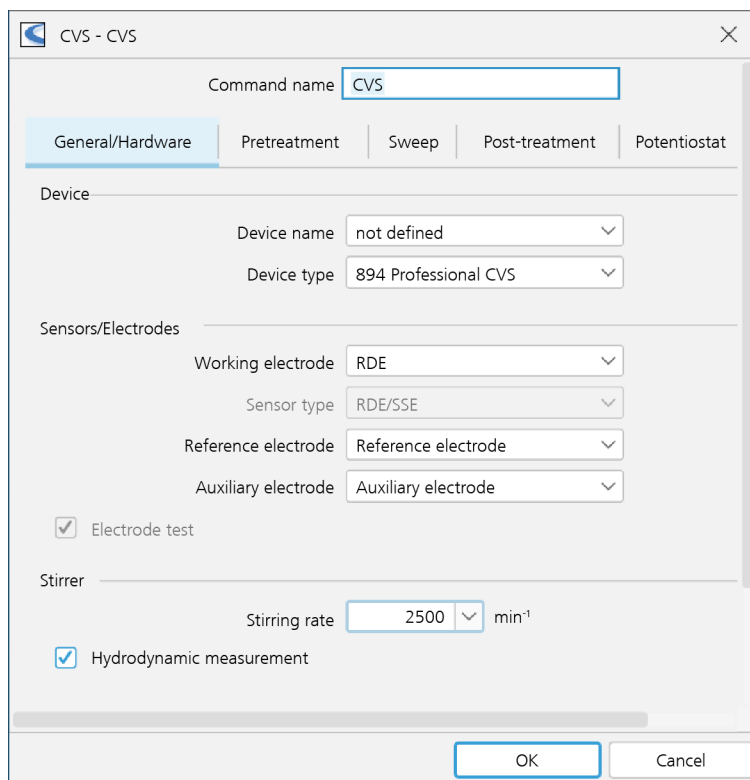
The application-specific stop criteria are defined for the VA track in this window. When a defined standard deviation of the measured peak area has been reached (or after a specified number of runs) the VA track is finished.

 A dialog window titled 'CALL COND - CALL COND'. It contains the following fields and options:

- Command name: CALL COND
- Call text: Conditioning in CU VMS
- Track name: VA track (dropdown)
- Stop criteria section:
 - ☒ Evaluation quantity:
 - VA measuring command: CVS (dropdown)
 - Substance: Cu (dropdown)
 - Standard deviation: 0.5 %
 - ☒ Number of runs:
 - Number of runs: 20
 - Action: Cancel command (dropdown)
 - ☐ Run time:
 - Run time: 0.0 min
 - Action: Cancel command (dropdown)
 - ☐ Condition:
 - Condition: (empty text box with a Σ icon)
 - Action: Cancel command (dropdown)
- Buttons: OK, Cancel



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



- 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).
- Select the **Sweep** tab.

DP - ASV

Command name: ASV

General/Hardware | Pretreatment | **Sweep** | Post-treatment | Potentiostat

Start potential: 1.625 V

1st vertex potential: -0.250 V

2nd vertex potential: 1.625 V

Potential step: 0.006 V

Potential step time: 0.060 s

Sweep rate: 0.100 V/s

Preparation cycles: 1

Measuring cycles: 2

Sweep duration: 113.76 s

OK Cancel

- 9 Enter the application-specific parameters from the application documentation.
- 10 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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Conditioning (Cu VMS), manual**.
- 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 Select the previously created method in the **Method** field.

► **Start**

4 Press **[Start]**.

The prompt for adding VMS appears:

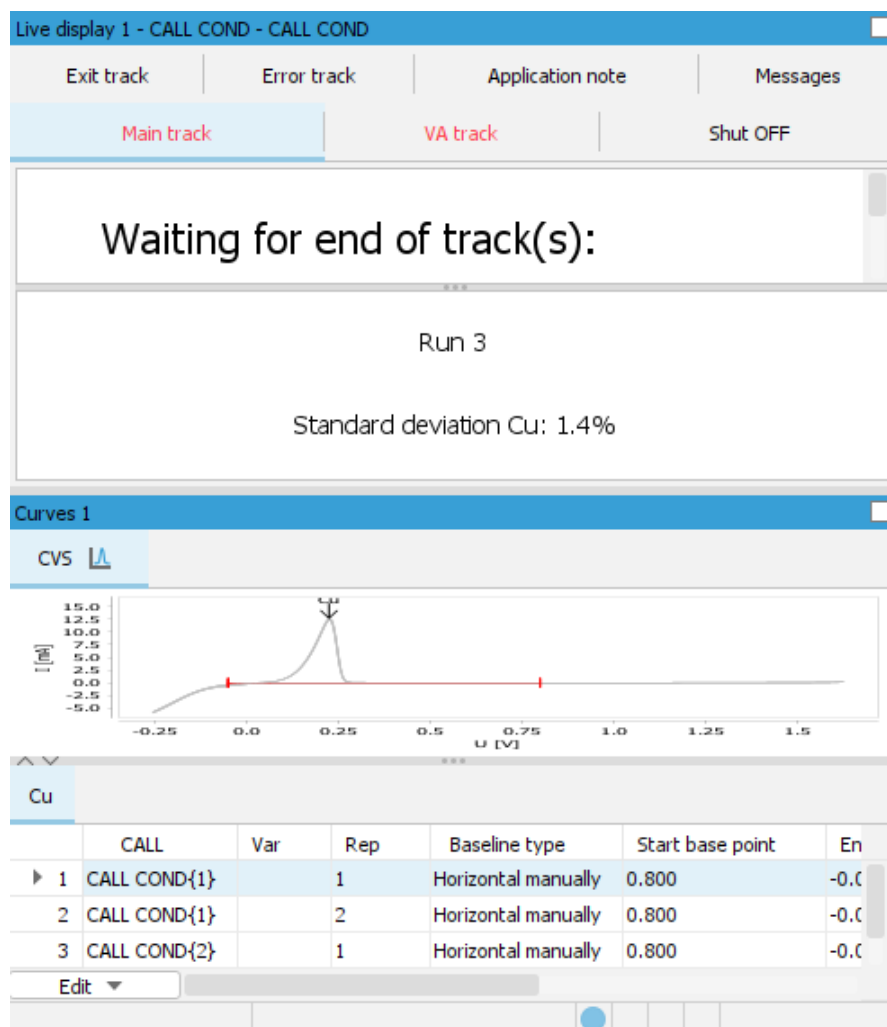
045-128 Add sample – Add 30.000 mL sample to the measuring vessel and click on **[Next]** to continue the track.

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

6 Click on **[Next]**.

Conditioning starts.

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 measured curves and the associated tables.



Conditioning is finished when a stop criterion has been reached. Then the VA track is called again with the **CALL VA** command and the VMS is measured again. The signal measured in the VMS (the conditioned area $\times [C]$) 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 12).

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

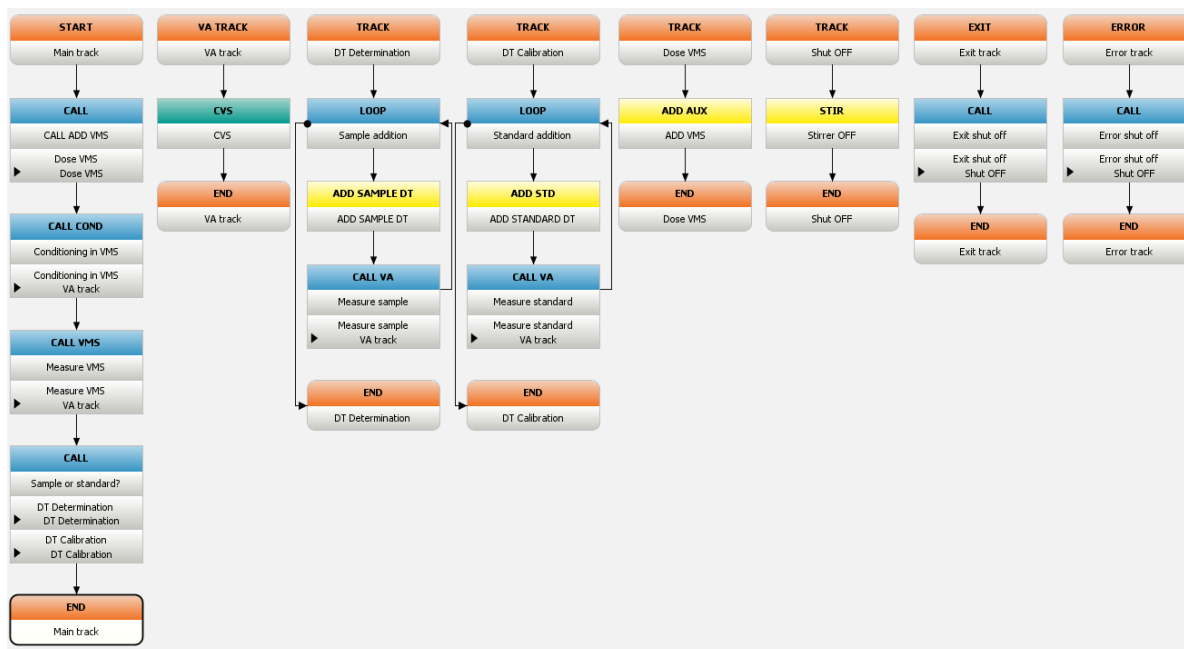
4.2.2.1 Creating a method

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

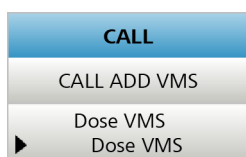
The method template opens.



Meaning of the individual commands

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

Main track

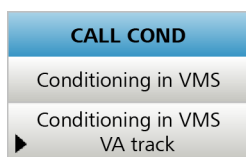


Calls the **VMS** track.

VMS normal track



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

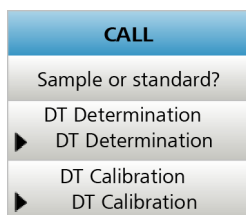


Calls the VA track. It is carried out until one of the defined stop criteria has been met. This command is used for conditioning the working electrodes in the VMS.



Calls the VA track again.

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 DT (Dilution Titration) calibration method.



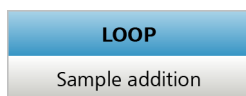
Depending on the sample type selected in the workplace (**Sample** or **Standard**), the **DT determination** or **DT calibration** track is called.

VA track



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

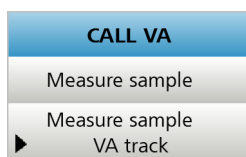
Normal track DT determination



After the **DT determination** track has been called by the **CALL - Sample or standard?** command, the **Add sample** prompt appears after each measuring cycle until the stop criteria defined in the command have been fulfilled.

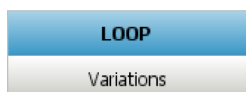


The addition of sample is defined in this command (number and size of the volume increment).

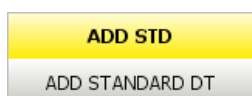


Calls the VA track in which the CVS measurements are carried out after the manual addition of sample.

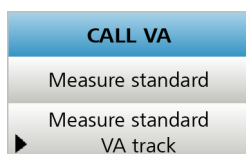
Normal track DT calibration



After the **DT calibration** track has been called by the **CALL - Sample or standard?** command, the **Add standard** prompt appears after each measuring cycle until the stop criteria defined in the command have been fulfilled.

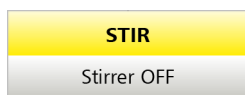


The addition of standard solution is defined in this command (number and size of the volume increment).



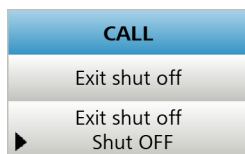
Calls the VA track in which the CVS measurements are carried out after the manual addition of suppressor standard solution.

Normal track Shut off



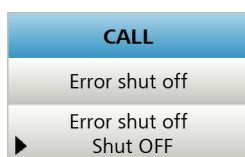
The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track



If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.

Error track



If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.

4.2.2.2 Defining the evaluation

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

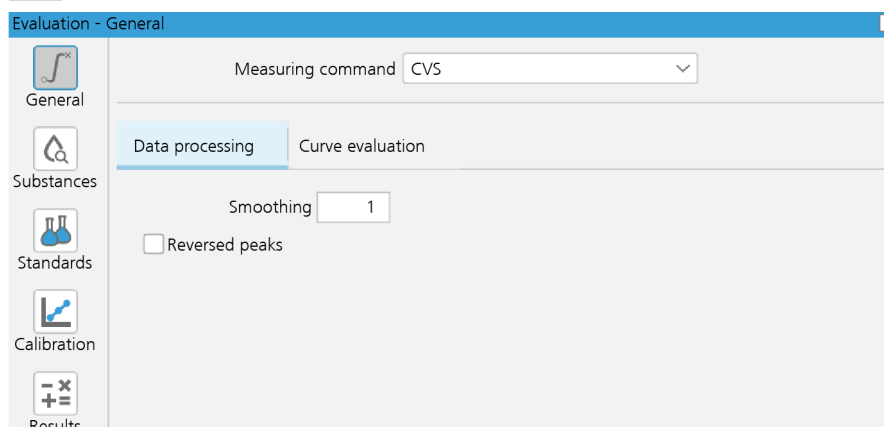
All relevant evaluation parameters are predefined in the method templates. The evaluation parameters can be defined individually, and the modified method template can then be saved again.

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 base point and the end base point are defined on the **Baselines** tab.



- 1 Click on the **Substances** button.

Substance	Active	Characteristi	Toleranc	Min. width	Max. width	Min. measu	Sweep direc
1 Suppressor	☒	0.2	0.2	0.01	1	200 pA	anodic
*							

Standards

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

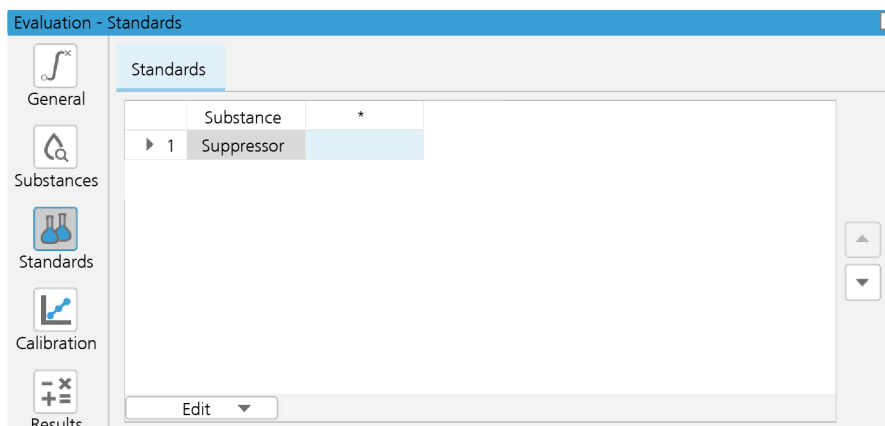


NOTE

The procedure described only works if no standard solution has been defined or if the name of the standard solution has been changed in the **ADD STANDARD DT** command.

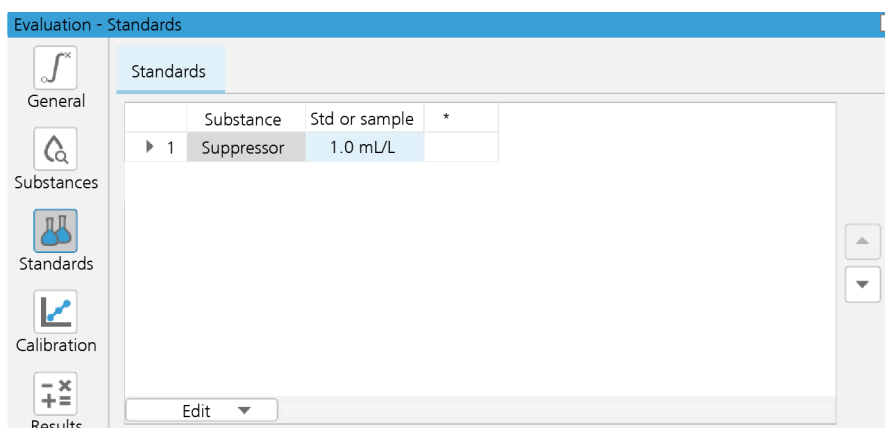


- 1 Click on the **Standards** button.



- 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.

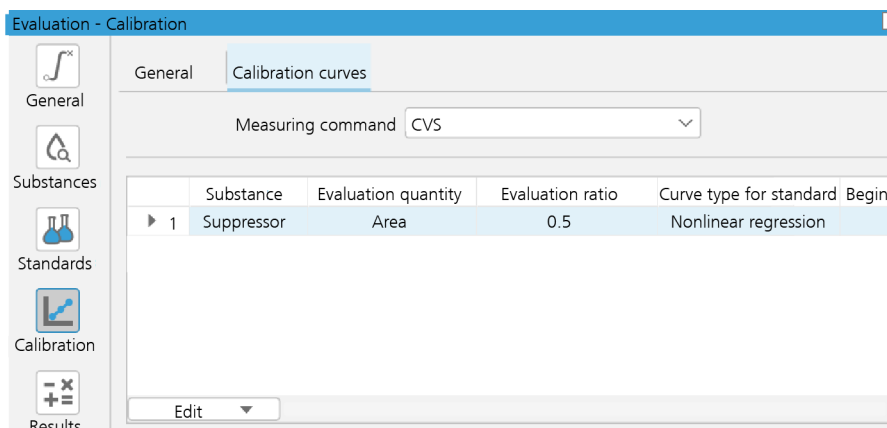
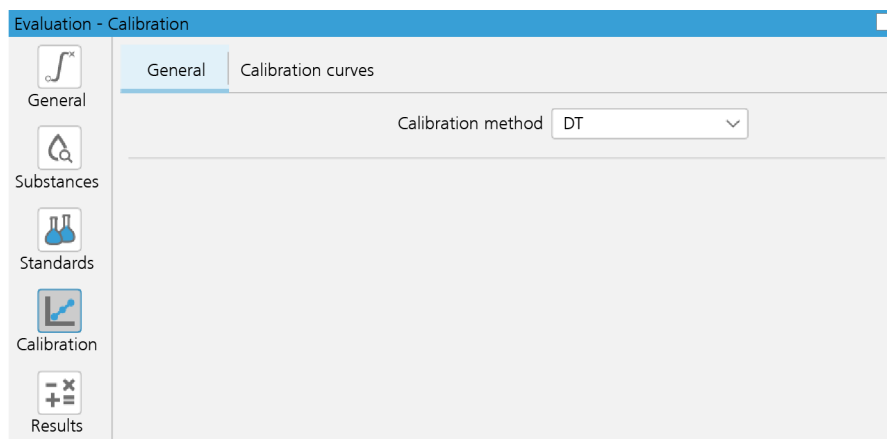


Calibration

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.



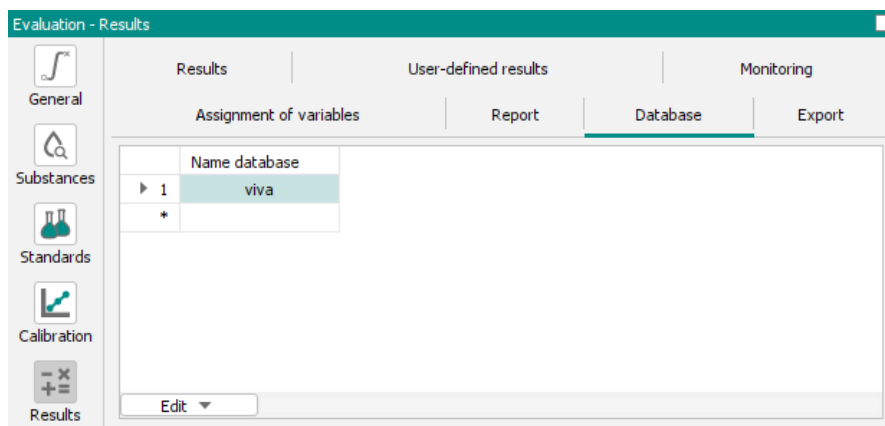
Results

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 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 a report (optional)

- Select the **Report** tab.
- Open the **Output** dialog 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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Suppressor determination (CVS, DT), manual**.
- 3 Click on **[Save]**.

4.2.2.3 Carrying out a determination

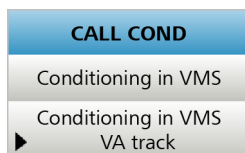
These steps are performed in the **Workplace** program part.



▶ *Start*

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 Select the previously created method in the **Method** field.
- 4 Select the **Standard** entry in the **Sample type** list box.
- 5 Press **[Start]**.
 - The prompt for adding VMS appears:
045-126 Add solution – Add 100.000 mL of the 'VMS' solution to the measuring vessel and click on [Next] to continue the track.
- 6 Pipette the volume of VMS displayed in the message 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 must be thoroughly rinsed with deionized water.

- 8 The VMS signal is now measured.

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

045-126 Add solution – Add 0.010 mL of the 'Standard or sample' solution to the measuring vessel and click on [Next] to continue the track.

- 10



NOTE

After conditioning, add all solutions to the measuring vessel via the pipetting opening so as to prevent the electrodes from being exposed to atmospheric oxygen during the measurement.

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 one of the stop criteria has been fulfilled. The stop criteria are 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 well with deionized water.

- 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.

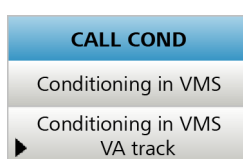
- 3** Select the previously created method in the **Method** field.

▶ *Start*

- 5** Press **[Start]**.

045-126 Add solution – Add 100.000 mL of the 'VMS' solution to the measuring vessel and click on [Next] to continue the track.

- 7** The following command is carried out after the addition:



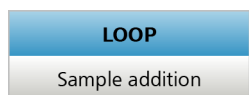
NOTE

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 must be thoroughly rinsed with deionized water.

- 9** The prompt for adding the sample appears:

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 one of the stop criteria has been fulfilled. The stop criteria are defined in the following command:



- 12** The determination is stored in the database as soon as the measurement is finished.
- 13** Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel well with deionized water.
- 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 peak area (charge Q_0) is calculated and stored as the intercept value. The intercept 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 cyclic voltammogram of the intercept solution (charge Q_0 of intercept solution. Q_0 = intercept value)
- the recording of the cyclic voltammogram of the intercept solution + sample (charge Q of sample)
- the recording of the cyclic voltammogram of the intercept solution + sample + standard addition 1 (charge Q of standard 1)
- the recording of the cyclic voltammogram 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

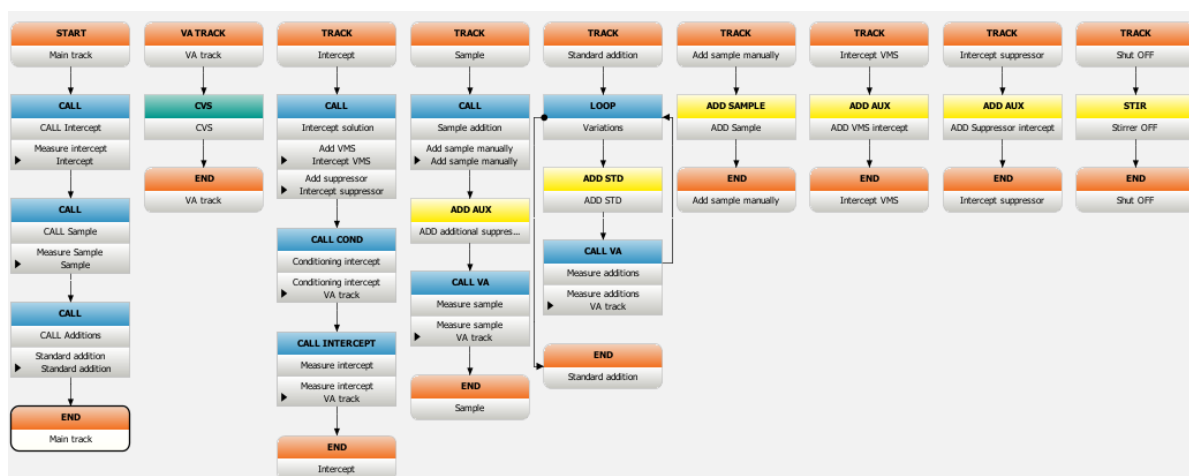


- 1 Click on the icon of the **Method** program part.

- 2 Open the **New method** dialog window using the **File ► New...** menu.
- 3 Under **Templates ► CVS/CPVS**, select **Brightener determination (CVS, MLAT), manual** in the left-hand part of the window and confirm with **[OK]**.

The method template opens.

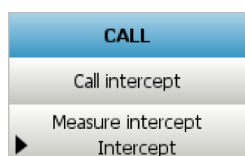
In addition to the tracks shown in the image, the method contains an exit track and an error track.



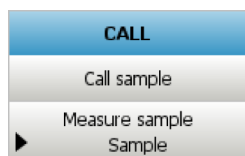
Meaning of the individual commands

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

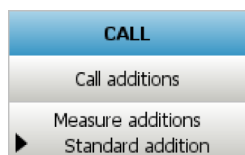
Main track



Calls the **Intercept** track.



Calls the **Sample** track.



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

VA track

CVS
CVS

(see "VA track", page 12).

Normal track intercept

CALL	
	Intercept solution
	Add VMS
▶	Intercept VMS
	Add suppressor
▶	Intercept suppressor

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

CALL COND

Conditioning intercept

Conditioning intercept
▶ VA track

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.

CALL INTERCEPT

CALL Intercept

Measure intercept

Intercept

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

Normal track Sample

CALL

Sample addition

Add sample manually

► Add sample manually

Calls the **Add sample manually** track.

ADD AUX

ADD additional suppress...

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.

CALL VA

Measure sample

Measure sample
▶ VA track

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

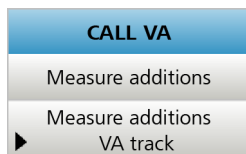
Normal track
Standard addition

LOOP

After the **Standard addition** track has been called by the **CALL additions** 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.

Normal track Add sample manually



Command for dosing the sample manually.

Normal track Intercept VMS



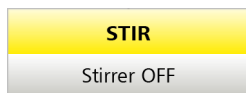
Command for dosing VMS of the intercept solution manually.

Normal track Intercept Suppressor



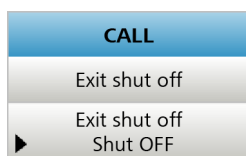
Command for dosing suppressor concentrate of the intercept solution manually.

Normal track Shut off



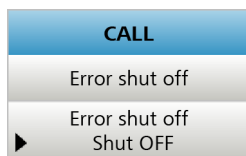
The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track



If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.

Error track



If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.

4.2.3.2 Defining the evaluation

Apart from the predefined parameters, the specific parameters for the evaluation of the measurement curves 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 **Substances - Recognition** dialog using the **Edit ► Properties...** menu.
- 3 Enter the application-specific value in the **Characteristic potential** field.

Substances - Recognition

Measuring command CVS

Substance Brightener

☒ Active

Characteristic postential 0.1 V

Tolerance 0.2 V

Min. width 0.01 V

Max. width 1 V

Min. measured quantity 200 pA

Sweep direction anodic

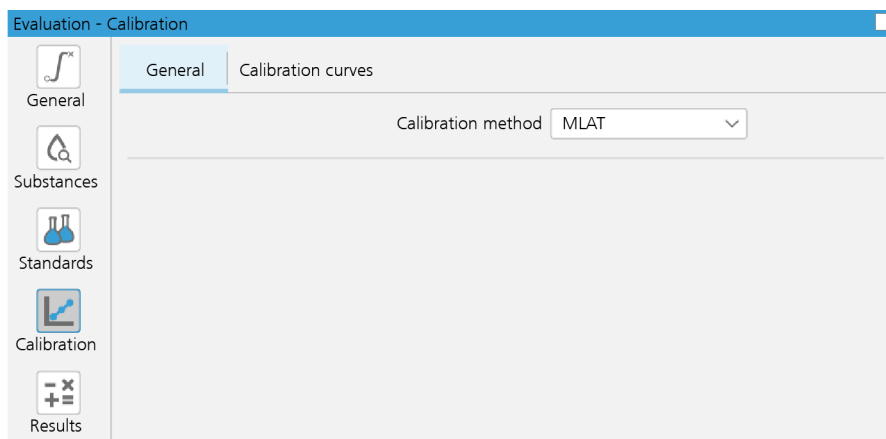
<< < 1 > >> *> of 1 OK Cancel

Calibration

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



- 1 Click on the **Calibration** button.



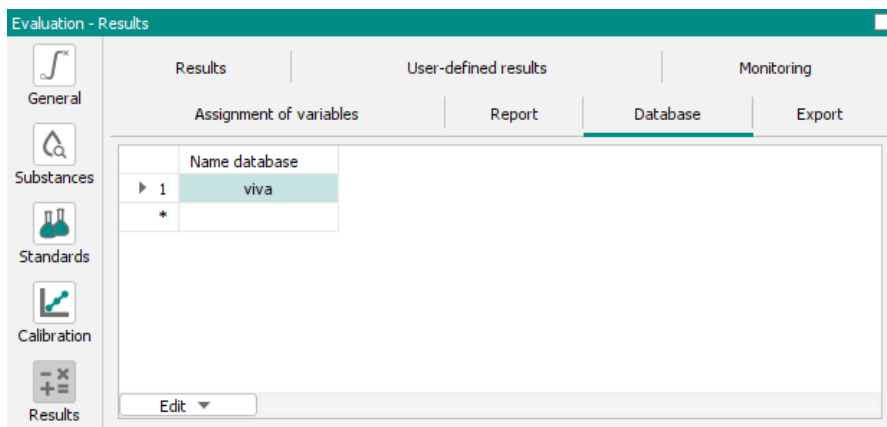
Results

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 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 a report (optional)

- Select the **Report** tab.
- Open the **Output** dialog 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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Brightener determination (CVS, MLAT), manual**.
- 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 Select the previously created method in the **Method** field.
- 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:



045-126 Add solution – Add 30.000 mL of the 'VMS' solution to the measuring vessel and click on [Next] to continue the track.

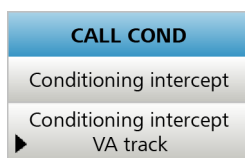
- 7** Pipette the volume of VMS displayed in the message into the measuring vessel and click on **[Next]**.

The prompt for adding suppressor concentrate appears:

045-126 Add solution – Add 1.200 mL of the 'Suppressor concentrate solution' to the measuring vessel and click on [Next] to continue the track.

- 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.

Once the measurement of the intercept value has been completed, the prompt for adding the sample appears:

045-128 Add sample – Add 10.000 mL sample to the measuring vessel and click on [Next] to continue the track.

11



NOTE

After conditioning, add all solutions to the measuring vessel via the pipetting opening so as to prevent the electrodes from being exposed to atmospheric oxygen during the measurement.

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:

045-126 Add solution – Add 0.200 mL of the 'Suppressor concentrate' solution to the measuring vessel and click on [Next] to continue the track.

- 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:

045-126 Add solution – Add 0.015 mL of the 'Brightener concentrate' solution to the measuring vessel and click on [Next] to continue the track.

- 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** The determination is stored in the database as soon as the measurement is finished.

- 16** Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel well with deionized water.

- 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 or standard



5.1 Configuration

5.1.1 Configuring the instrument

894 Professional CVS

(see chapter 4.1.1, page 8).

5.1.2 Configuring electrodes

(see chapter 4.1.2, page 9).

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 the 807 Dosing Unit and the 50 mL cylinder to the MSB connector 1 of the 894 Professional CVS.

The following message is displayed:

009-009 Other devices on the MSB – Peripheral devices were connected or removed from the MSB1 of device '894_1'. – Select the device in the device table in the 'Configuration' program part and initialize it using the context-sensitive 'Initialize' menu item.

- 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, then the following message will be displayed:

010-116 New dosing unit – A new dosing unit was recognized.
– You must first configure the dosing unit under 'Configuration - Dosing units' before using it.

Or:

If you have connected a dosing unit that has been previously configured, then the following message will be displayed:

010-130 New dosing unit – A new dosing unit was recognized. – Should the dosing unit be saved in the table of dosing units?

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

The following dialog is displayed:

Dosing unit - 50 mL VMS

×

Dosing unit

GLP

Hardware

Name

50 mL VMS

Comment

Device name / dosing device

Order number

6.3032.250

Serial number

10860160

Cylinder volume

50

mL

Cylinder serial number

1170

Parameters for preparation

Dosing port Prep/Empty

Dosing port 1

▼

Dosing rate Dosing port 1

maximum

▼

mL/min

Dosing rate Dosing port 2

maximum

▼

mL/min

Dosing rate Fill port

maximum

▼

mL/min

Dosing rate Special port

maximum

▼

mL/min

Tubing parameters

	Port	Length	Diameter
Dosing port 1	Port 1 ▼	138.0 cm	2.0 mm
Dosing port 2	Port 3 ▼	0.0 cm	2.0 mm
Fill port	Port 2 ▼	25.0 cm	2.0 mm
Special port	Port 4 ▼	0.0 cm	2.0 mm

Valve disk

Rotating direction

automatic

▼

Not over

Port 4

▼

OK

Cancel

- 4 Enter the name **50 mL VMS** in the **Name** field.
- 5 Select the value **maximum** in the **Dosing rate Dosing port 1** field.
- 6 Enter the length and the diameter of the tubings and capillaries that are actually connected in the **Tubing parameters** area (see *Manual 894 Professional CVS*).
- 7 Click on **OK**.

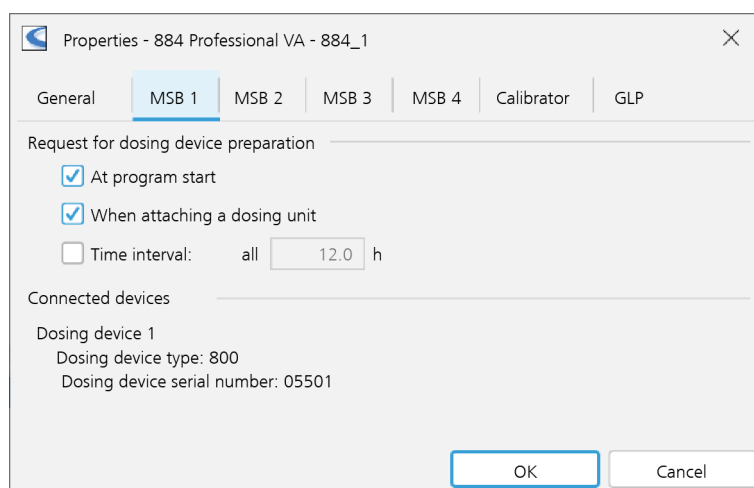
The dosing unit will be automatically displayed in the **Dosing units** subwindow of the **Configuration** program part.
- 8 Connect and name the other dosing units with a 2 mL cylinder as follows:

Name of dosing unit	Dosing rate Dosing port 1
2 mL Brightener	2.0 mL/min
2 mL Suppressor	2.0 mL/min
2 mL Standard or sample	2.0 mL/min

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 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 **50 mL VMS**.



Solution -



Solution

GLP

Solution name

VM5

Solution type

Auxiliary solution

Dosing unit

50 mL VMS

Comment

Manufacturer

Production date

2023-08-15

☐ Monitor solution

Working life

999

days

Expiry date

2026-05-10

Message

☐ Message per e-mail

E-mail...

☐ Acoustic signal

Action

☐ Record message

☒ Display message

☐ Cancel determination

OK

Cancel

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

3 Add the other three solutions in the same way:

Solution name	Dosing unit	Solution type
Brightener concentrate	2 mL Brightener	Standard solution
Suppressor concentrate	2 mL Suppressor	Auxiliary solution
Standard or sample	2 mL Standard 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.
 - Enable 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.

5.2 Methods for the semiautomated determination

A method is a run instruction for processing a sample. It comprises all components necessary to record and evaluate measurement curves. 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 measurement curves
- 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 must be saved.

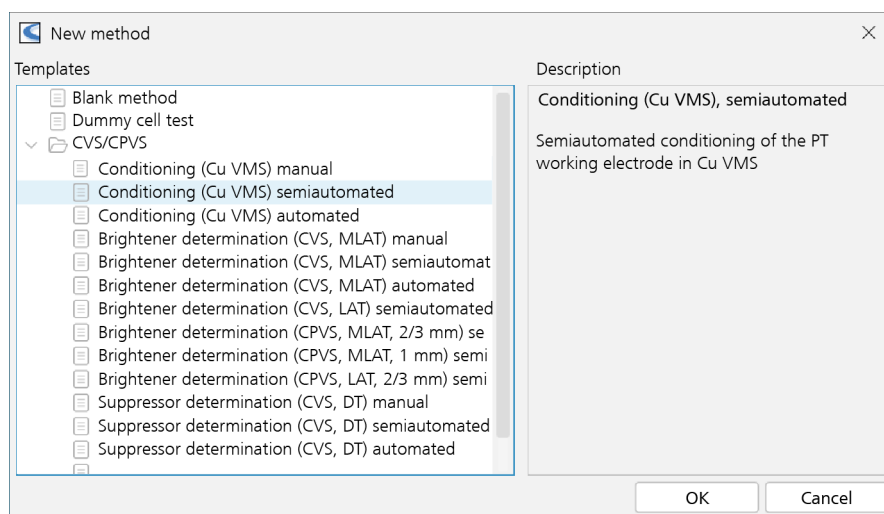
Metrohm recommends working with a method template or importing an example method. This ensures that all required commands are available and that the structure of the method is correct.

Loading a method template



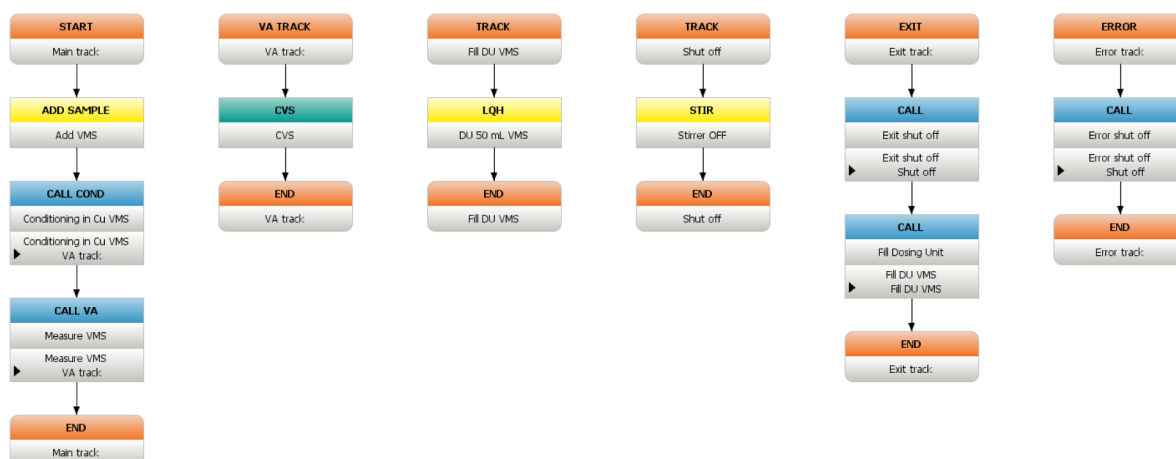
- 1 Click on the icon of the **Method** program part.

2 Open the **New method** dialog 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.

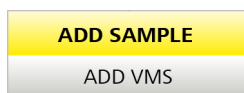


The method consists of a main track, a VA track and an exit track. The **CVS** command is transposed to a separate VA track in order to ensure that the same voltammetric parameters are used every time the command is called.

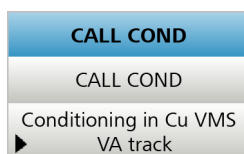
Meaning of the single commands

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

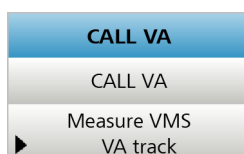
Main track



In this method, the VMS is added with the **ADD SAMPLE** command with the dosing unit **50 mL VMS**. This command is normally used to add a sample to the result calculation. In this example, the **ADD SAMPLE** command is used so that the measurement curve is displayed in blue (standard colour for measurement curves of samples). The volume used is the sample amount defined in the workplace or in the method under **Sample data variables** (see "Defining command parameters", page 12).



(see page 11).



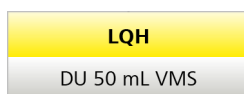
(see page 11).

VA track



(see page 12).

Normal track Fill DU
VMS



The **LQH** command fills the dosing unit when the determination is finished.

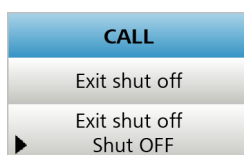
Normal track Shut off



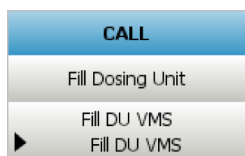
The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track

If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.



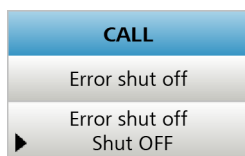
Calls the **Shut off** track.



Calls the **Fill DU VMS** track.

Error track

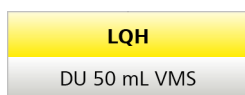
If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.



Calls the **Shut off** track.

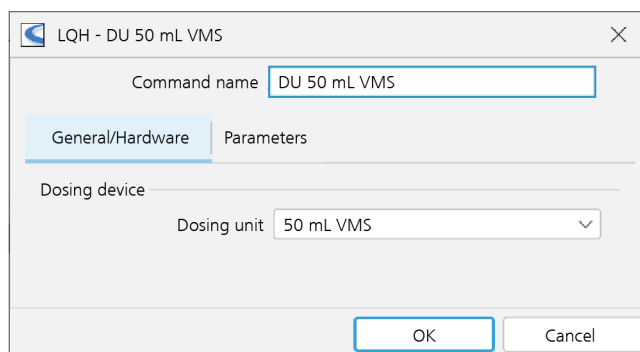
Defining command parameters

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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Conditioning (Cu VMS), semiautomated**.
- 3 Click on **[Save]**.

5.2.1.2 Carrying out the conditioning

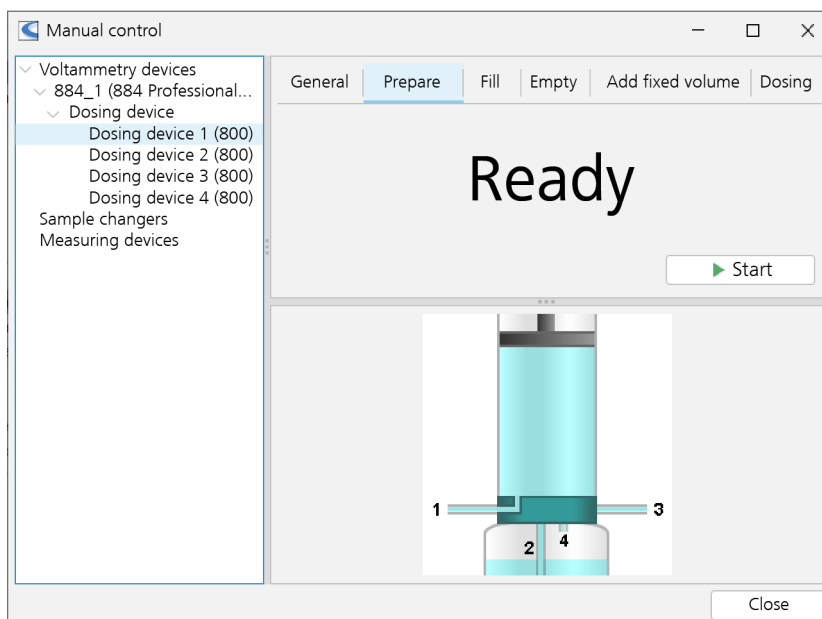
Preparing the dosing unit

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:

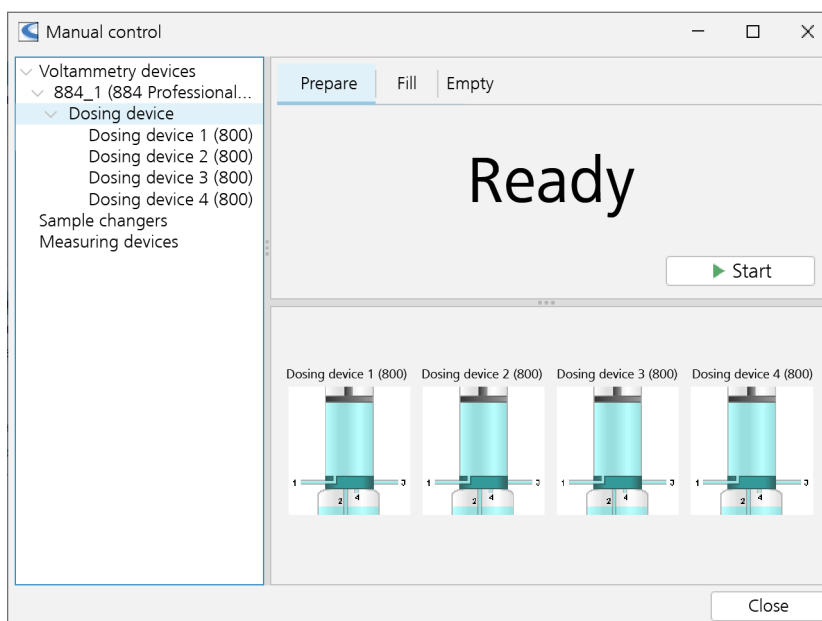


- 1 Click on the icon of the **Manual control** program part.
The **Manual control** dialog opens.
The connected devices are listed with their peripheral devices in the left-hand part of the window. In the right-hand part of the window, the functions of the selected device are displayed. In the following example, they are shown for Dosing device 1 (800), which corresponds to the **50 mL VMS** dosing unit.
- 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



► *Start*

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

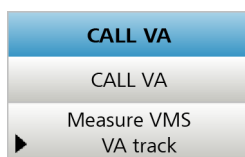
- 2 Select the **Single determination** tab in the **Run** subwindow.

- 3 Select the previously created method in the **Method** field.

- 4 Press **[Start]**.

The VMS volume defined in the **Add VMS** command is dosed by the **50 mL VMS** dosing unit into the measuring vessel. The Pt working electrode is then conditioned afterwards. 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 deionized water.

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

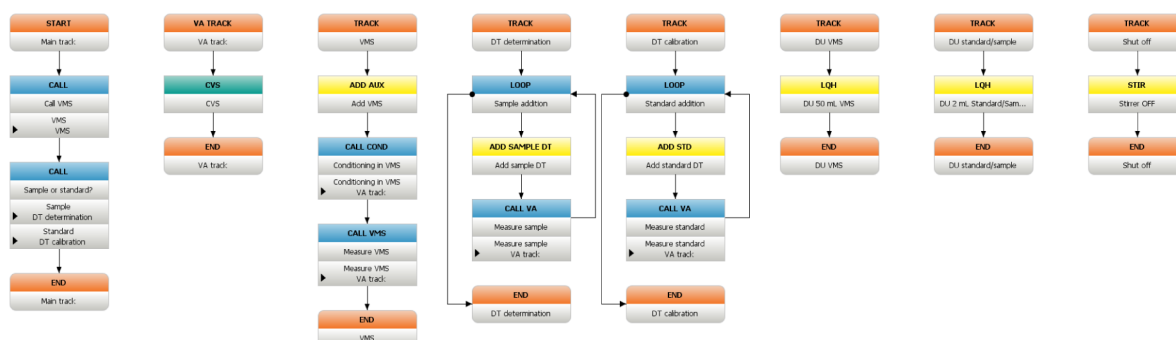
Loading a method template



- 1 Click on the icon of the **Method** program part.
- 2 Open the **New method** dialog 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.

In addition to the tracks shown in the image, the method contains an exit track and an error track.

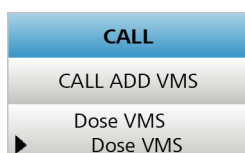


Meaning of the individual commands

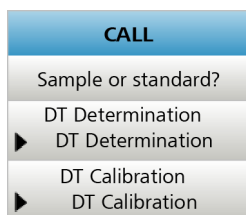
Apart from the **ADD** commands, the method run of the semiautomated determination of the suppressor concentration corresponds to the procedure used for the manual determination. The **Add with dosing device** option is selected for the parameter **Addition** in these commands.

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

Main track



(see page 18).

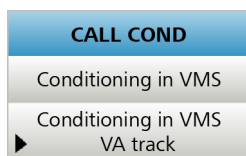


Depending on the sample type selected in the workplace (**Sample** or **Standard**), the **DT determination** or **DT calibration** track is called.

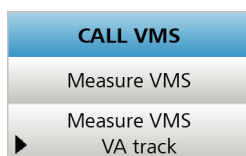
VMS normal track



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



(see page 11).



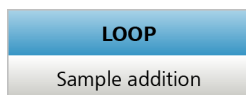
(see page 18).

VA track



(see page 12).

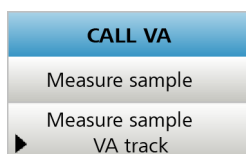
Normal track DT determination



(see page 19).



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



(see page 19).

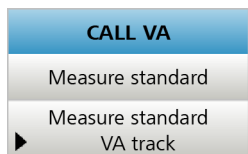
Normal track DT calibration



(see page 19).

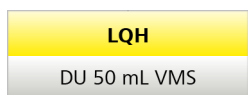


The automated addition of standard with a dosing device is defined in this command.



(see page 19).

Normal track Fill DU
VMS



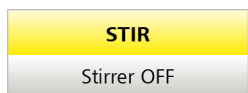
The **LQH** command fills the **50 mL VMS** dosing unit when the determination is finished.

Normal track Fill DU
standard/sample



The **LQH** command fills the **2 mL Standard or sample** dosing unit when the determination is finished.

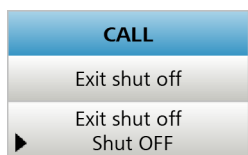
Normal track Shut off



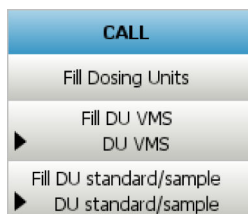
The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track

If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.



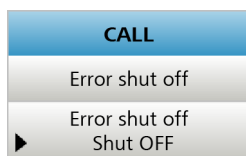
Calls the **Shut off** track.



Calls the **Fill DU VMS** and **Fill DU standard/sample** tracks.

Error track

If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.



Calls the **Shut off** track.

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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Suppressor determination (CVS, DT), semiautomated**.
- 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

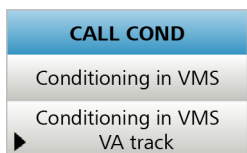
- 1 Prepare the **2 mL Standard or sample** dosing unit with suppressor standard solution and the **50mL VMS** dosing unit with VMS (see "Preparing the dosing unit", page 47).
- 2 Click on the icon of the **Workplace** program part.
- 3 Select the **Single determination** tab in the **Run** subwindow.
- 4 Select the previously created method in the **Method** field.
- 5 Select the **Standard** entry in the **Sample type** list box.
- 6 Press **[Start]**.



► **Start**

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

- 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

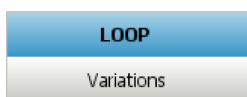
If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel must be thoroughly rinsed with deionized water.

- 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 **2 mL Standard or sample** dosing unit.

- 10** Step **9** is repeated until one of the stop criteria has been fulfilled. The stop criteria are defined in the following command:



- 11** All dosing units used are filled once the exit track is reached.

- 12** The determination is stored in the database as soon as the measurement is finished.

- 13** Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel well with deionized water.

- 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 **2 mL Standard or sample** dosing unit with sample and, if necessary, the **50 mL VMS** dosing unit with VMS (see "Preparing the dosing unit", page 47).

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



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

- 4 Select the previously created method in the **Method** field.

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

▶ Start

- 6 Press **[Start]**.

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

- 7 The following command is carried out after the addition:

CALL COND	
Conditioning in VMS	
Conditioning in VMS	
▶ VA track	

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 must be thoroughly rinsed with deionized 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 **2 mL Standard or sample** dosing unit.
- 10 Step 9 is repeated until one of the stop criteria has been fulfilled. The stop criteria are defined in the following command:

LOOP

Sample addition
- 11 All dosing units used are filled once the exit track is reached.
- 12 The determination is stored in the database as soon as the measurement is finished.
- 13 Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel well with deionized water.
- 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 28*). 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 using the **File ► New...** menu.

The method template opens.

The figure displays nine flowcharts, each representing a different instruction in the RISC-V processor. Each flowchart begins with a 'TRACK' block (orange) and concludes with an 'END' block (orange). The instructions and their corresponding blocks are as follows:

- Standard addition:** TRACK → ADD STD → END
- Add sample:** TRACK → ADD SAMPLE → END
- Add sample interval:** TRACK → ADD INT → END
- Interact:** TRACK → INTERACT → END
- Interact:** TRACK → INTERACT → END
- Interact:** TRACK → INTERACT → END
- Interact:** TRACK → INTERACT → END
- Interact:** TRACK → INTERACT → END
- Interact:** TRACK → INTERACT → END

The flowcharts illustrate the sequence of operations and the state of the processor at each step. The 'END' block in each flowchart indicates the completion of the instruction.

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

CALL

Call intercept

Measure intercept

Intercept

CALL

Call sample

Measure sample

Sample

- CALL
- Call additions
- Measure additions
- Standard addition

VA track

CVS
CVS

Tutorial CVS

CALL	
	Intercept solution
	Add VMS
►	Intercept VMS
	Add suppressor
►	Intercept suppressor

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

CALL COND
Conditioning intercept
Conditioning intercept ▶ VA track

(see page 30).

CALL INTERCEPT

Measure intercept

Measure intercept
Intercept

(see page 30).

Normal track Sample

CALL

Sample addition

Add sample manually

► Add sample manually

(see page 30).

ADD AUX

ADD additional suppress...

(see page 30).

CALL VA

Measure sample

Measure sample
VA track

Calls the VA track in which the CVS measurements are carried out after the addition of sample (*see page 12*).

Normal track
Standard addition

LOOP

After the **standard addition** track has been called by the **CALL additions** command, brightener standard solution is dosed until the stop criterion defined in the command has been fulfilled after 1 measuring cycle.

ADD STD

(see page 31).

CALL VA

Measure additions

Measure additions
▶ VA track

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

Normal track Add sample manually



Command for dosing the sample manually.

Normal track Intercept VMS



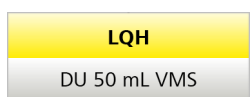
Command for the automated dosing of VMS of the intercept solution.

Normal track Intercept suppressor



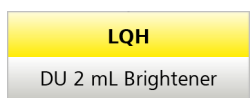
Command for the automated dosing of suppressor concentrate of the intercept solution.

Normal track Fill DU VMS



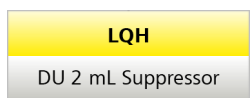
The **LQH** command fills the **50 mL VMS** dosing unit when the determination is finished.

Normal track Fill DU brightener



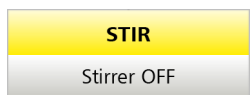
The **LQH** command fills the **50 mL Brightener** dosing unit when the determination is finished.

Normal track Fill DU suppressor



The **LQH** command fills the **2 mL Suppressor** dosing unit when the determination is finished.

Normal track Shut off



The stirrer can be switched on and off with the **STIR** command. In this method, the command is used to switch off the stirrer at the end of the method or in an error case.

Exit track

If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.

CALL

Exit shut off

Exit shut off
Shut OFF

Calls the **Shut off** track.

CALL	
	Fill Dosing Units
▶	Fill DU VMS Fill DU VMS
▶	Fill DU suppressor Fill DU suppressor
▶	Fill DU brightener Fill DU brightener

Calls the **Fill DU VMS**, **Fill DU brightener**, and **Fill DU suppressor** tracks.

Error track

If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.

CALL

Error shut off

Error shut off

Shut OFF

Calls the **Shut off** track.

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 previously created method in the **Method** field.
- 4 Prepare the following dosing units (*see "Preparing the dosing unit", page 47*):
 - **50 mL VMS** with VMS
 - **2 mL Brightener** with brightener concentrate
 - **2 mL Suppressor** with suppressor concentrate
- 5 Select the **Sample** entry in the **Sample type** list box.

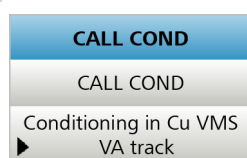
► *Start*

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

7 Press **[Start]**.

- The volume of VMS defined in the **Add VMS intercept** command is automatically dosed into the measuring vessel through the **50 mL VMS** dosing unit.
- The volume of suppressor concentrate defined in the **Add suppressor intercept** command is automatically dosed into the measuring vessel through the **2 mL Suppressor** dosing unit.

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 Once the measurement of the intercept value is completed, the prompt for adding the sample appears:

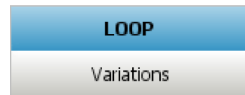
045-128 Add sample – Add 10.000 mL sample to the measuring vessel and click on **[Next]** to continue the track.

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 **2 mL Suppressor** dosing unit.

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 **2 mL 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** The determination is stored in the database as soon as the measurement is finished.
- 16** Empty the measuring vessel and thoroughly rinse the electrodes and the measuring vessel well with deionized water.
- 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 8).

858 Professional Sample Processor

1 Connecting the device

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

2 Switching on the device

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

The following message appears:

009-108 Save device – The new '858.0020' device with serial number 'serial number' has been detected. – Should it be saved to the device table?

3 Saving the device 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

- Select the **Tower** tab.

The screenshot shows the 'Properties - 858.0020 Professional Sample Processor' dialog box with the 'Tower' tab selected. The 'Starting position' is set to 'MSB 1'. The 'Tower parameters' section includes: 'Max. stroke path' (130 mm), 'Min. beaker radius' (aus mm), 'Lift rate' (25 mm/s), and 'Axial distance' (166.0 mm). The 'Swing Head' section includes: 'Serial number' (2342), 'Swing position' (0 mm), and 'Rinse position' (0 mm). A table shows 'External position' (1-4), 'Angle [°]' (60.0), and 'Work position [mm]' (0). Buttons for 'Edit', 'Configuration', 'OK', and 'Cancel' are visible.

External position	Angle [°]	Work position [mm]
1	60.0	0
2	60.0	0
3	60.0	0
4	60.0	0

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

6 Defining rack parameters

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

The screenshot shows the 'Properties - 858.0020 Professional Sample Processor' dialog box with the 'Rack' tab selected. The 'Starting position' is set to 'MSB 1'. The 'Rack' section includes: 'Rack name' (6.2041.450), 'Rack code' (000011), 'Number of positions' (112), and 'Shift rate' (20 %/s). Buttons for 'Rack data', 'Initialize rack', 'OK', and 'Cancel' are visible.

- Select the **Lift positions** tab.

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

 Rack data ✕

Rack name6.2041.450

Rack code000011

Number of positions112

Rack parameters

Lift positions

Special beaker

Tower 1

Work position125 mm

Rinse position0 mm

Shift position0 mm

Special position0 mm

Tower 2

Work position0 mm

Rinse position0 mm

Shift position0 mm

Special position0 mm

OK

Cancel

Close all dialogs 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:

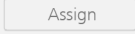
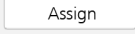
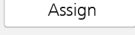
1 Setting the lift position

- 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** area. The rack position that is set is approached.

- Select the **Work position** position in the **Lift position** area in the **Target position** field.
- In the **Lift position** area, click on **[Start]**. The lift position that is set is approached.
- In the **Lift position** area, use the arrow key  to move the PEEK tubing slowly downwards until it is located no more than 0.5 mm above the bottom of the sample vial.

General	Move	Assign position	Pump
Rack position			
Current position		-----	
Target position		1 ▾	Shift rate 20 ▴ ▾ %/s  
Lift position			
Current position		0 mm	
Target position		Work position ▾ mm	Lift rate 25 ▴ ▾ mm/s  
Robotic arm position			
Current position		108.5 °	
Target position		0.0 ▾ °	Swing rate 55 ▴ ▾ %/s  
Ready			

- Once the PEEK tubing is correctly positioned, open the **Assign position** tab.
In the **Lift position** area, the new value is entered in the **Current position** field.
- Select the **Work position for** option in the **Lift position** area and select **Tower** in the selection list.
- In the **Lift position** area, click on **[Assign]**.

General	Move	Assign position	Pump
Rack position			
Current position		1	Special beaker 1 ▴ ▾ 
Lift position			
Current position		0 mm	☒ Work position for Tower ▾ ☐ Rinse position for Tower ▾ ☐ Shift position for Tower ▾ ☐ Special position for Tower ▾ ☐ Swing position External position ▾ 
Robotic arm position			
Current position		108.5 °	External position 1 ▴ ▾ 

Connecting an 800 Dosino with 807 Dosing Unit

(see "Connecting an 800 Dosino with dosing unit", page 38).

Initializing a dosing unit in 894 Professional CVS

(see "Initializing a dosing unit", page 39).

6.1.2 Configuring electrodes

(see chapter 4.1.2, page 9).

6.1.3 Configuring dosing units

(see chapter 5.1.3, page 38).

6.1.4 Defining solutions

(see chapter 5.1.4, page 41).

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

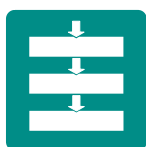
The suppressor concentration is determined with the calibration method

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

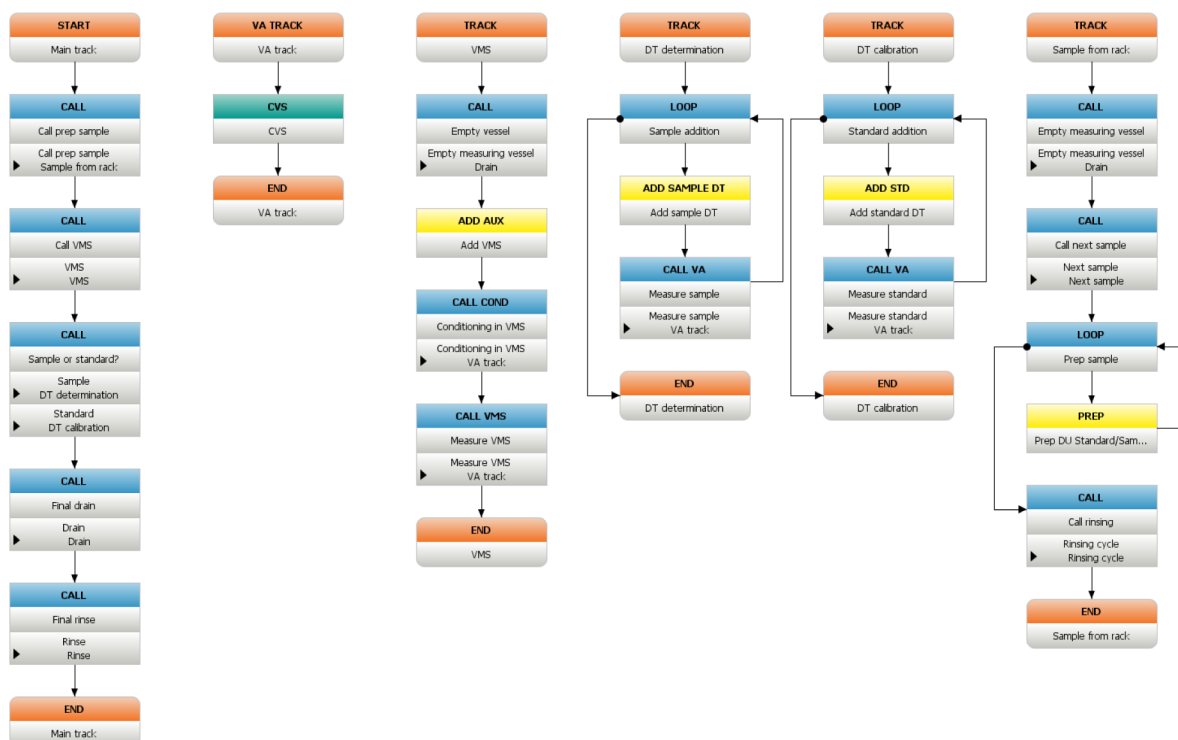
Loading a method template



- 1 Click on the icon of the **Method** program part.
- 2 Open the **New method** dialog 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].

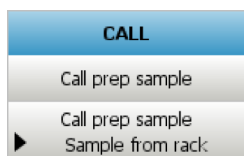
The method template opens. The following figure contains only a part of the complete method.



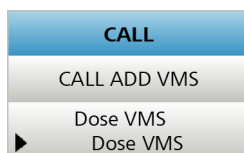
Meaning of the individual tracks and commands

The method run of the automated determination of the suppressor concentration largely corresponds to the procedure used for the semiautomated determination (*see page 50*). 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



Calls the track in which the dosing unit is rinsed with sample (**Sample from rack**).



Calls the track in which the VMS is automatically added with the dosing device (**VMS**).

Normal track Next sample

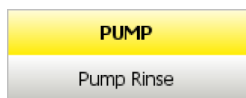
In this track, the PEEK tubing of the sample changer is lowered into the next sample.

Normal track Rinsing cycle

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

Normal track Rinse

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



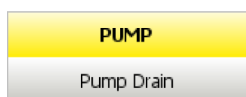
When doing so, adjust the application-specific pump time for rinsing to the measuring vessel volume in the **Duration** field.

 A configuration dialog box titled "PUMP - PUMP Rinse". It contains the following fields:

- Command name: Text box containing "PUMP Rinse".
- Device section:
 - Device name: Dropdown menu showing "858 Professional Sample Processor 1".
 - Device type: Dropdown menu showing "858.0020 Professional Sample Processor".
- Pumps section:
 - Tower: Dropdown menu showing "1".
 - Pump(s): Dropdown menu showing "2".
- Action section:
 - Switch on: Radio button (unselected).
 - Switch off: Radio button (unselected).
 - Duration: Radio button (selected), followed by a text box containing "18" and a dropdown menu showing "s".
- Buttons: "OK" and "Cancel" at the bottom right.

Normal track Drain

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



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





PUMP - PUMP Drain



Command name

PUMP Drain

Device

Device name

858 Professional Sample Processor 1

Device type

858.0020 Professional Sample Processor

Pumps

Tower

1

Pump(s)

2

Action

☐ Switch on

☐ Switch off

☒ Duration

50

s

OK

Cancel

Normal track Fill DU
VMS

LQH
DU 50 mL VMS

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

Normal track Fill DU
standard/sample

LQH

DU 2 mL Standard/Sam...

The **LQH** command fills the **2 mL Standard or sample** dosing unit when the determination is finished.

Normal track Shut off

In this track, the pumps and the stirrer are switched off and the PEEK tubing is lifted

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.

Series end track

In this track, the sample changer moves to the last sample position + 1, where a vessel with deionized water must be located. The dosing unit for the sample is then rinsed with deionized 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

If **[Stop]** is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run.

Calls the **Shut off**, **Fill DU VMS**, and **Fill DU standard/sample** tracks.

Error track

If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.

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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Suppressor determination (CVS, DT), automated**.
- 3 Click on **[Save]**.

6.2.1.2 Sample table

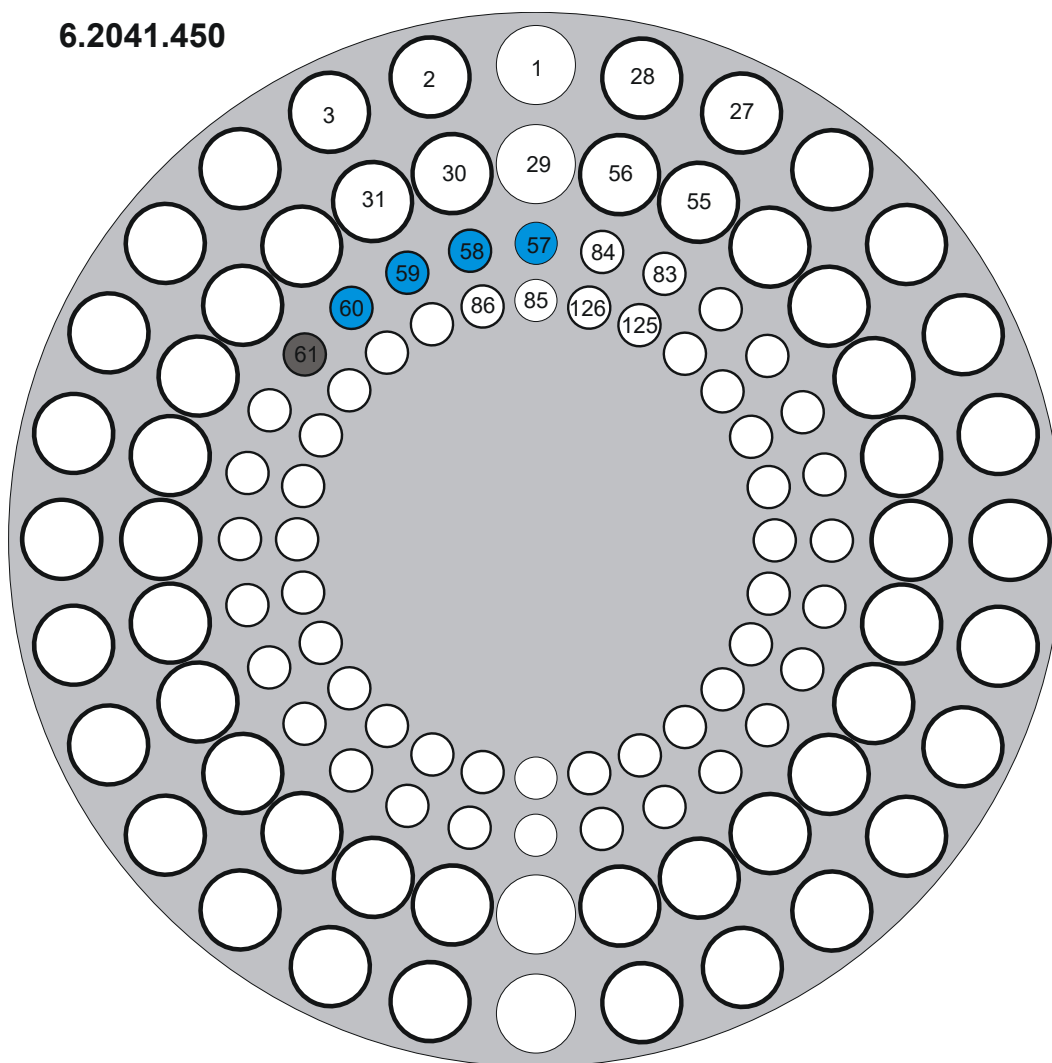
Filling the sample rack

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 deionized water must always be placed in the last sample position so that the dosing unit used can be rinsed with deionized water at the end of a sample series.

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

6.2041.450



- Standard or sample
- Rinsing solution (deionized 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 previously created method in the table and click on **[Open]**.

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

The method name is automatically entered in the **Method** field, e.g., **Suppressor determination (CVS, DT), automated**.

5 **Defining a 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 a 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:

Run

Single determination | **Determination series**

▶ Start ■ Stop ► Hold || Pause Status: READY

Determination parameters

User: _____ Sample number: 0

Remark: _____

Autostart: 0 of Sample table ▼

Sample data

	Method	ID 1	ID 2	ID 3	Sample type	Sample position	Sample amount	Sample amo
1	Suppressor d...	Std			Standard	1	1.0	mL
2	Suppressor d...	Sam...			Sample	2	1.0	mL
3	Suppressor d...	Sam...			Sample	3	1.0	mL
4	Suppressor d...	Sam...			Sample	4	1.0	mL
5	Suppressor d...	Sam...			Sample	5	1.0	mL
▶ *								

Edit ▼ Sample table ▼ Loaded

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 **50 mL VMS** dosing unit with VMS (see "Preparing the dosing unit", page 47).
- 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 Press **[Start]**.
- 6 The **Series start track** is carried out and the rack is initialized.
- 7 The **Sample from rack** track is called.

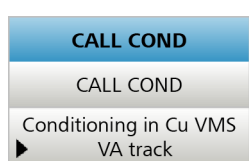


▶ Start

- The measuring vessel is emptied.
- The PEEK tubing is moved to the first sample position and lowered into the vial to the working position.
- The **2 mL Standard or sample** dosing unit 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 **50 mL VMS** dosing unit.

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

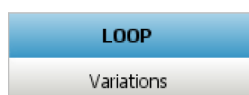
If the measuring cell is still contaminated with suppressor from previous determinations, then the defined relative standard deviation of 0.5% cannot be reached. In this case, the electrodes and the measuring vessel must be thoroughly rinsed with deionized water.

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 **2 mL Standard or sample** dosing unit.

12 Step **11** is repeated until one of the stop criteria has been fulfilled. The stop criteria are defined in the following command:



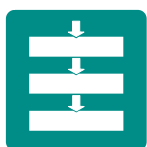
- 13** The measuring vessel is automatically rinsed twice with rinsing solution.
- 14** When the measurement is finished, the determination is stored in the database.
- 15** When the exit track is reached, all dosing units used are filled.
- 16** Steps **7** to **15** are repeated for each position defined in the sample table.
- 17** When the **Series end track** is reached (after the last sample in the sample table), the dosing unit **2 mL Std or sample** will be automatically prepared twice with deionized water and the PEEK tubing will be lifted to the shift position.
- 18** The **Error track** is run only 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.

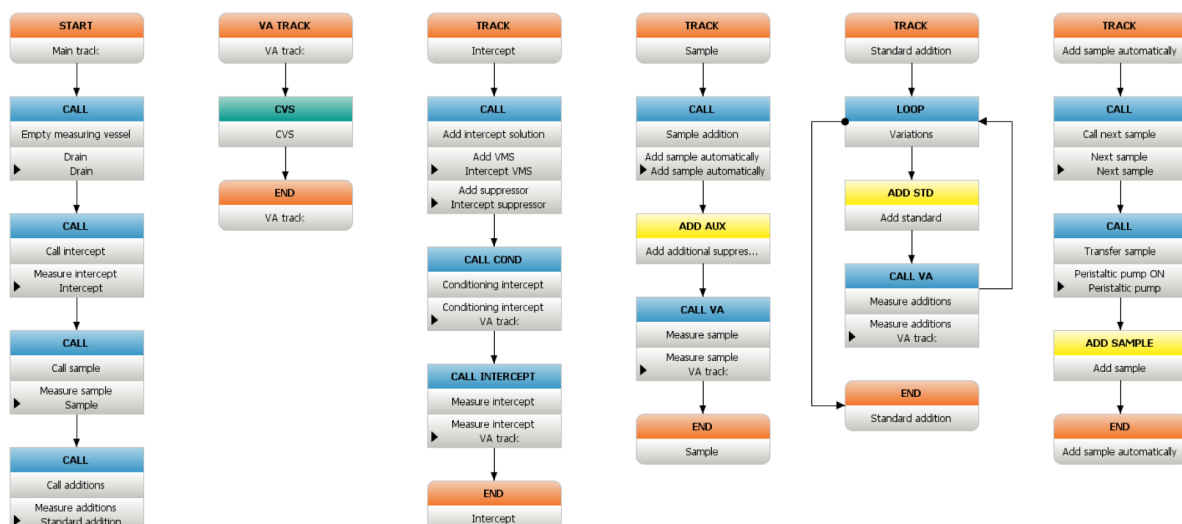
6.2.2.1 Creating a method

Loading a method template



- 1** Click on the icon of the **Method** program part.
- 2** Open the **New method** dialog 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. The following figure contains only a part of the complete method.

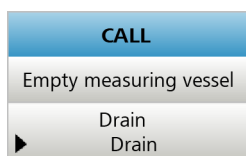


Meaning of the individual tracks and commands

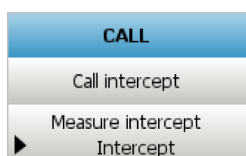
The method run of the automated determination of the brightener concentration largely corresponds to the procedure used for the semiautomated determination. However, additional automation and rinsing tracks are used for controlling the sample changer. The automatic rinsing of the measuring cell is achieved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

Main track

Compared to the semiautomated determination (*see page 50*), the method run contains the following additional commands:



Calls the track in which the measuring vessel is emptied (**Drain**).



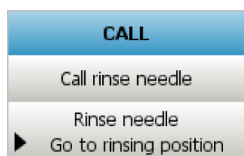
Calls the **Intercept** track.



Calls the **Sample** track.



Calls the **Standard addition** track.



Calls the track in which the PEEK tubing is rinsed (**Go to rinsing position**).



Calls the track in which the measuring vessel is rinsed (**Rinsing cycle**).

VA track

(see page 57).

Normal track

(see page 58).

Standard addition

Normal track Add sample automatically

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

Normal track Next sample

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

Normal track Go to rinsing position

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

Normal track Intercept VMS

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

Normal track Intercept suppressor

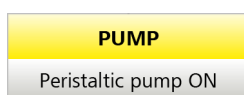
In this track, suppressor concentrate is added to the measuring vessel.

Normal track Rinsing cycle

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

Normal track Peristaltic pump

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



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

 PUMP - Peristaltic pump ON ✕

Command name

Device

Device name

Device type

Pumps

Tower

Pump(s)

Rate

Action

☐ Switch on

☐ Switch off

☒ Duration s

Normal track 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.

Normal track Drain

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

Normal track Fill DU
VMS

LQH
DU 50 mL VMS

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

Normal track Fill DU
suppressor

LQH

DU 2 mL Suppressor

The **LQH** command fills the **2 mL Suppressor** dosing unit when the determination is finished.

Normal track Fill DU
brightener

LQH
DU 2 mL Brightener

The **LQH** command fills the **50 mL Brightener** dosing unit when the determination is finished.

Normal track Shut off

In this track, the pumps and the stirrer are switched off and the PEEK tubing is lifted

<i>Series start track</i>	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.
<i>Exit track</i>	If [Stop] is pressed during an ongoing determination, then the exit track is run through and after that the determination is ended. The same happens in the normal method run. Calls the Shut off, Fill DU VMS, Fill DU suppressor, and Fill DU brightener tracks.
<i>Error track</i>	If an error that causes the determination to be interrupted occurs in an ongoing determination, then the error track is called and after that the determination is ended.

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 using the **File ► Save as...** menu.
- 2 Enter a method name in the **Method name** field, e.g. **Brightener determination (CVS, MLAT), automated**.
- 3 Click on **[Save]**.

6.2.2.2 Sample table

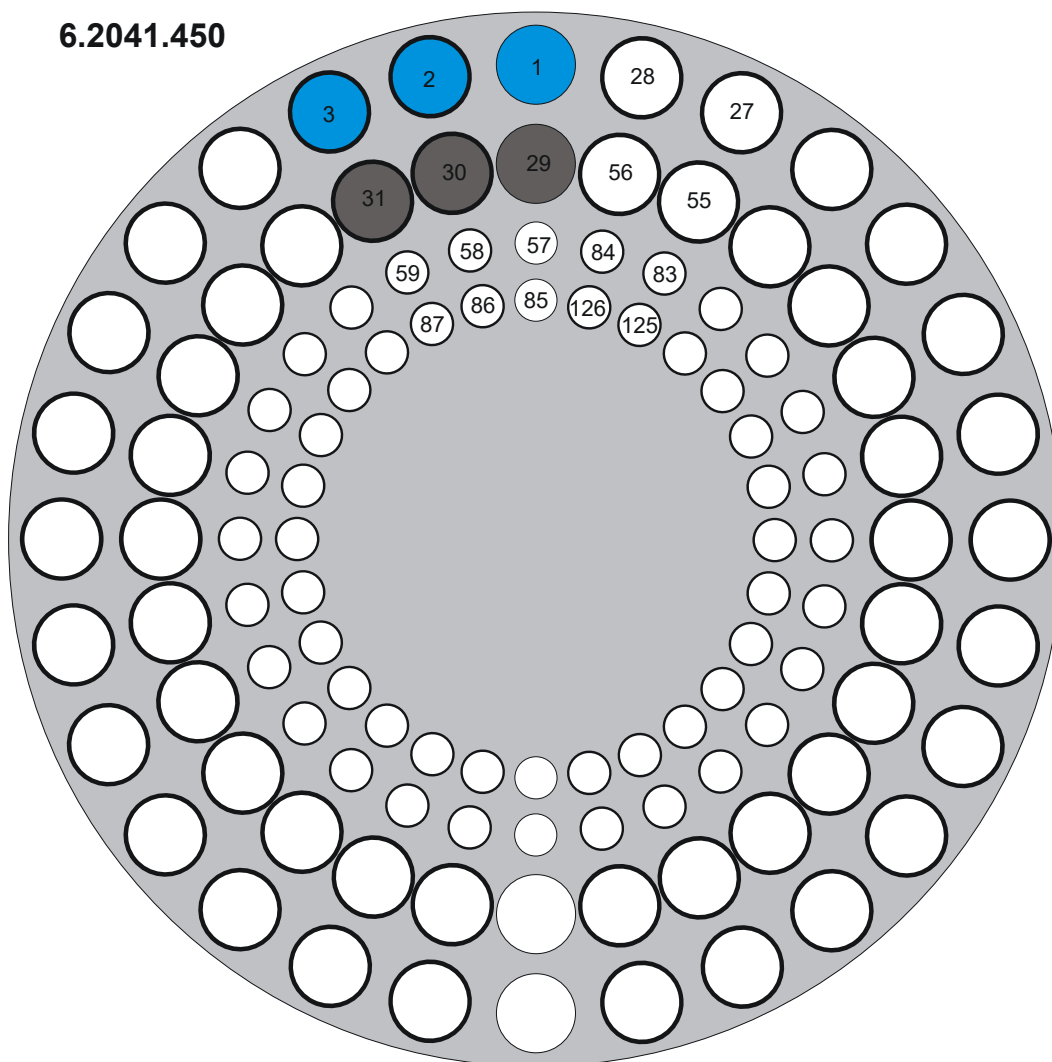
Filling the sample rack

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 (deionized water) in positions **29, 30 and 31**

6.2041.450



- Sample
- Rinsing solution (deionized 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 previously created method in the table and click on **[Open]**.

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

The method name is automatically entered in the **Method** field, e.g., **Brightener determination (CVS, MLAT), automated**.

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 a 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:

Run

Single determination

Determination series

▶ Start

■ Stop

▶ Hold

⏸ Pause

Status

READY

Determination parameters

User

Sample number

0

Remark

Autostart

0

of

Sample table

▼

Sample data

📄

PDF

↺

📄

⚙

↻

📄

	Method	ID 1	ID 2	ID 3	Sample type	Sample position	Sample amount	Sample amount
1	Brightener d...	Sam...			Sample	1	10	mL
2	Brightener d...	Sam...			Sample	2	10	mL
3	Brightener d...	Sam...			Sample	3	10	mL
*								

Edit

Sample table

Loaded

6.2.2.3 Carrying out a determination

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

Sequence of the determination series

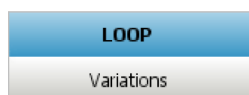


► Start

- 1 Prepare the dosing units: **50 mL VMS** with VMS, **2 mL Brightener** with brightener concentrate, and **2 mL Suppressor** with suppressor concentrate (see "Preparing the dosing unit", page 47).
- 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 Press **[Start]**.
- 6 The **Series start track** is carried out and the rack is initialized.
- 7 The **Pump Drain** 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 **50 mL VMS** dosing unit.
 - The volume of suppressor concentrate defined in the **Add suppressor intercept** command is automatically dosed into the measuring vessel through the **2 mL Suppressor** dosing unit.
- 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 **2 mL Suppressor** dosing unit.
- 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 **2 mL 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 tubing is moved to the rack position across from the current sample position (sample position + 28) and lowered to the work 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 **Rinsing cycle** track is called.
- 16** The determination is stored in the database as soon as the measurement is finished.
- 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 tubing is lifted to the shift position.

20

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 datasets 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 filter criterion 'New filter'** dialog using the **Edit ► Edit line** menu.

Edit filter criterion New filter

Link

AND

Field

More...

Condition

☐ Match case

☐ Use asterisk (*) as wildcard

OK

Cancel

- In the **Field** list box, highlight the **Method name** entry.
- Enter the method name **Suppressor determination (CVS, DT), semiautomated** in the **Comparative value** field and click on **[OK]**.
- 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 dataset in the overview table.
The associated measurement curve is displayed in the **Curves 1** subwindow.
- 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.

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 color 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 dataset 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 dataset 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 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.

The following message appears:

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

Changing the evaluation parameters



2 Opening a method

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

Substances - Recognition

Measuring command CVS

Substance Brightener

☒ Active

Characteristic postential 0.2 V

Tolerance 0.2 V

Min. width 0.01 V

Max. width 1 V

Min. measured quantity 200 pA

Sweep direction anodic

<< < 1 > >> *> of 1 OK Cancel

- 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.

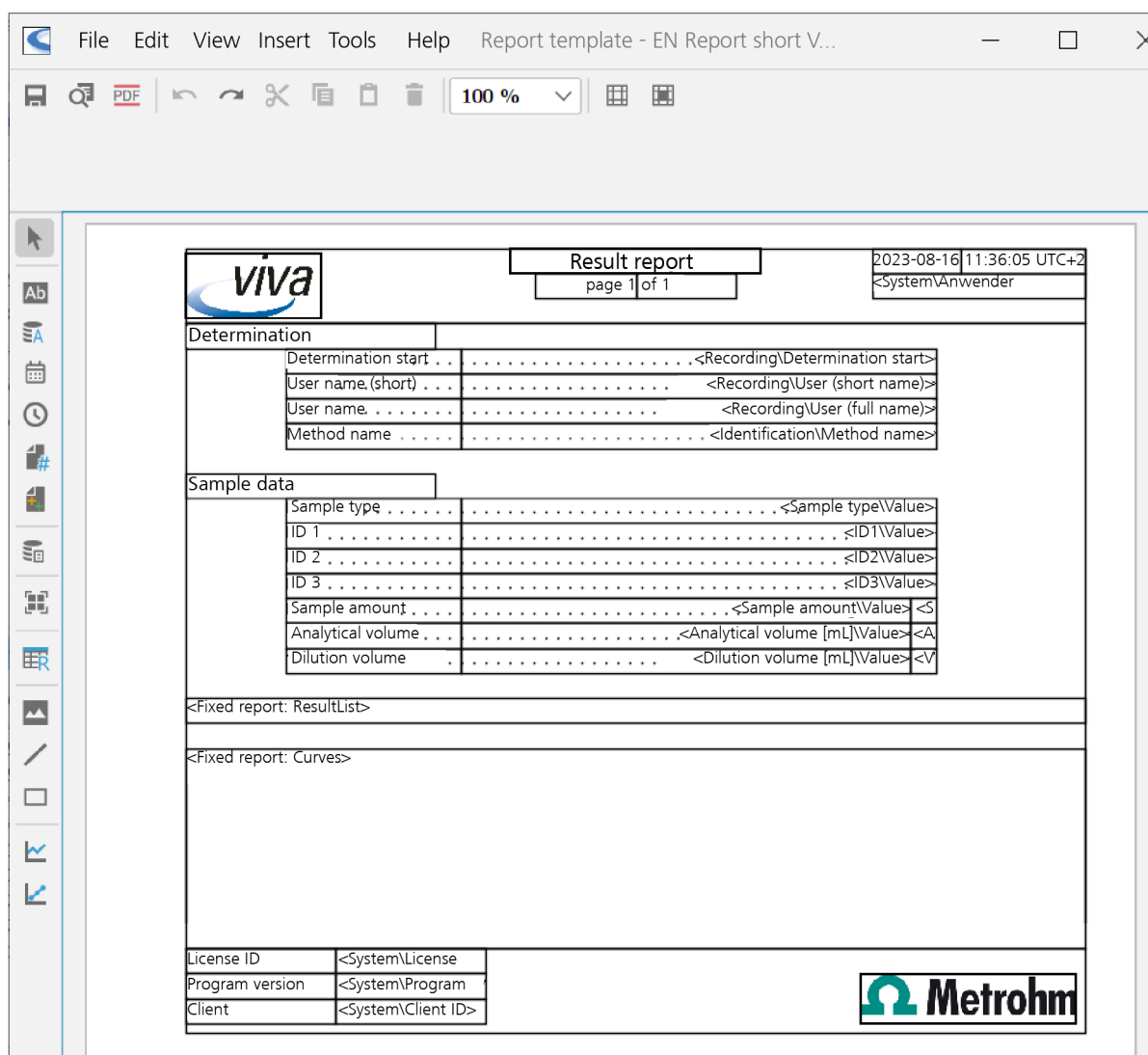
- 3 Select one or more determinations in the determination overview.
- 4 Click on the  icon or the **Tools ► Report templates ► Open...** menu item.

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.



Report template - EN Report short V...

100 %

viva **Result report** 2023-08-16 11:36:05 UTC+2
page 1 of 1 <System\Anwender>

Determination

Determination start	<Recording\Determination start>
User name (short)	<Recording\User (short name)>
User name	<Recording\User (full name)>
Method name	<Identification\Method name>

Sample data

Sample type	<Sample type\Value>
ID 1	<ID1\Value>
ID 2	<ID2\Value>
ID 3	<ID3\Value>
Sample amount	<Sample amount\Value>
Analytical volume	<Analytical volume [mL]\Value>
Dilution volume	<Dilution volume [mL]\Value>

<Fixed report: ResultList>

<Fixed report: Curves>

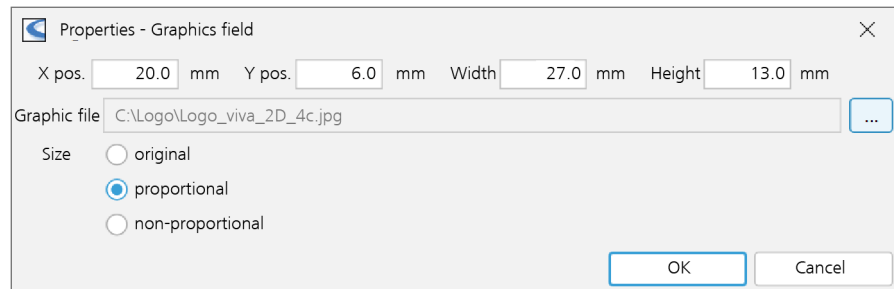
License ID	<System\License>
Program version	<System\Program>
Client	<System\Client ID>

Metrohm

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.

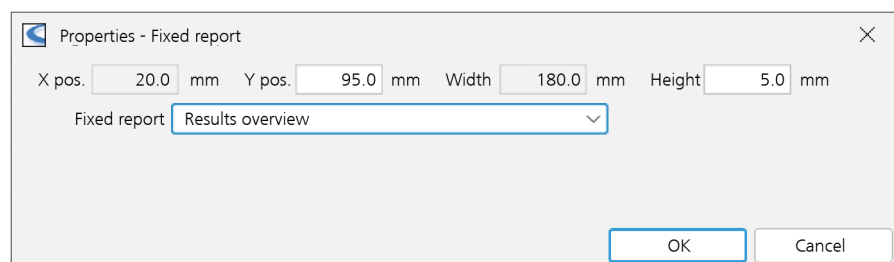


- 2 Open the dialog window for selecting the new graphics file by clicking on .
- 3 Select the desired new graphics file in JPG or PNG format and confirm with **[OK]**.
- 4 Adjust the position, width, height and size of the image.
- 5 Close the properties window with **[OK]**.

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]**.

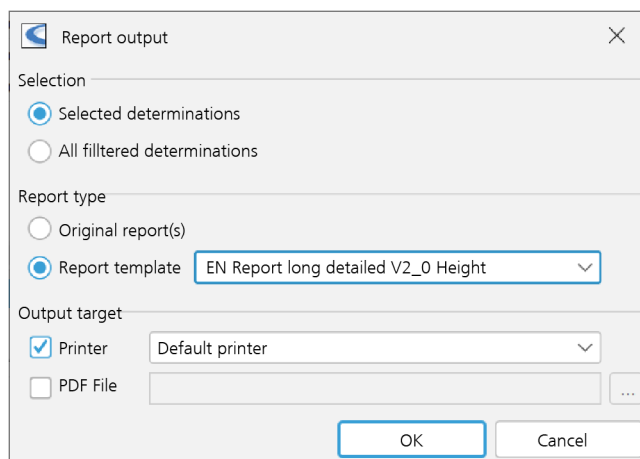
Saving the report template

- 1 Click on the **File ► Save as...** menu item.
The **Save report template** dialog 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 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 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.

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