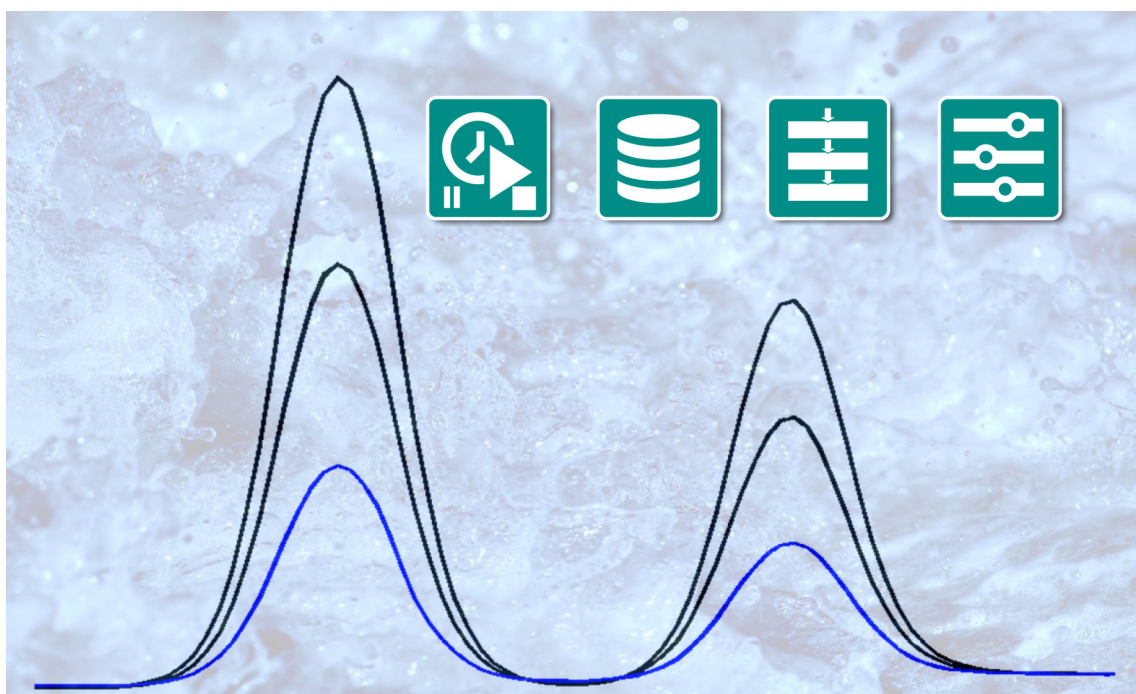




VA tutorial (trace analysis)

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VA tutorial (trace analysis)

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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 cadmium and lead with anodic stripping voltammetry.

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

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

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

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

1.2 Program description

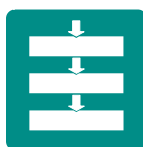
viva comprises the following program parts:

Configuration



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

Method



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

Workplace



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

Database



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

1.3 Symbols and conventions

The following symbols and formatting may appear in this documentation:

(5-12)	Cross-reference to figure legend The first number refers to the figure number, the second to the instrument part in the figure.
1	Instruction step 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

- 884 Professional VA
- 919 IC Autosampler plus
- 807 Dosing Unit (one with a 2 mL and one with a 5 mL glass cylinder)
- 800 Dosino
 - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing standard solution
 - 800 Dosino and 807 Dosing Unit with cylinder size 5 mL for dosing auxiliary solution (electrolyte)
- 843 Pump Station

Electrodes

- Working electrode **WE**
 - Multi-Mode Electrode pro (6.1246.120)
- Reference electrode **RE**
 - Reference electrode filled with reference electrolyte (e.g. 6.0728.120)
Reference electrolyte: $c(\text{KCl}) = 3 \text{ mol/L}$
 - Electrolyte vessel filled with bridge electrolyte (e.g. 6.1245.010)
Bridge electrolyte: $c(\text{KCl}) = 3 \text{ mol/L}$
- Auxiliary electrode **AE** (6.0343.100)

Reagents

- Caustic soda, Suprapur®, w(NaOH) = 30%
- Acetic acid, Suprapur®, w(CH₃COOH) = 100%
- KCl, Suprapur®
- Cd stock solution, β(Cd²⁺) = 1 g/L
- Pb stock solution, β(Pb²⁺) = 1 g/L

Accessories

- Measuring vessel 10 - 90 mL (6.1415.210)
- 100 mL glass bottle
- 250 mL glass bottle
- 2 L glass bottle
- Bottle holder (6.2055.110)
- Two thread adapters GL 45 on GL 45
- FEP tubing / M6 / 100 cm (6.1805.120)

- Six FEP tubings / M6 / 200 cm (6.1805.530)

2.2 Preparing the solutions

- KCl sodium acetate solution: $c(\text{KCl}) = 1.5 \text{ mol/L}$, $c(\text{CH}_3\text{COONa}) = 0.5 \text{ mol/L}$ 55.9 g KCl + 25 mL NaOH + 14.2 mL CH_3COOH filled up with ultrapure water to 500 mL.
- Standard solutions:
 - $\beta(\text{Cd}^{2+}) = 0.1 \text{ mg/L}$
 - $\beta(\text{Pb}^{2+}) = 0.5 \text{ mg/L}$



NOTE

Diluted solutions are prepared with $c(\text{HNO}_3) = 0.014 \text{ mol/L}$.



NOTE

Consult the Application Bulletin AB 231 for detailed information on how to prepare the solutions.

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



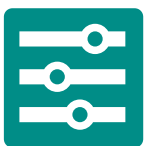
NOTE

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:



Devices

Dosing units

Solutions

Sensors/Electrodes

Rack data

Common variables

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.

Shows the data of all global variables.

Shows the saved calibration functions.

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 884 Professional VA).

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 Manual ASV determination with standard addition

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

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

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

- A method for the manual determination of cadmium and lead with anodic stripping voltammetry and the calibration method 'standard addition'.

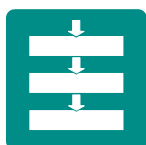
You will become acquainted with the basic functions and the structure of a method using these method templates.

4.2.1 Creating a method

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

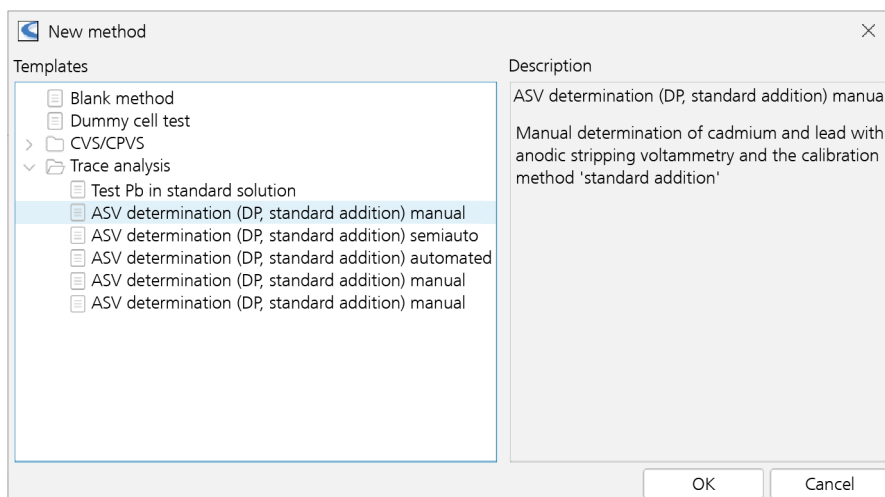
It is advisable to use a method template. You can, however, also create a new method from scratch. To do so, select the method template **Blank method**.

4.2.1.1 Loading a method template



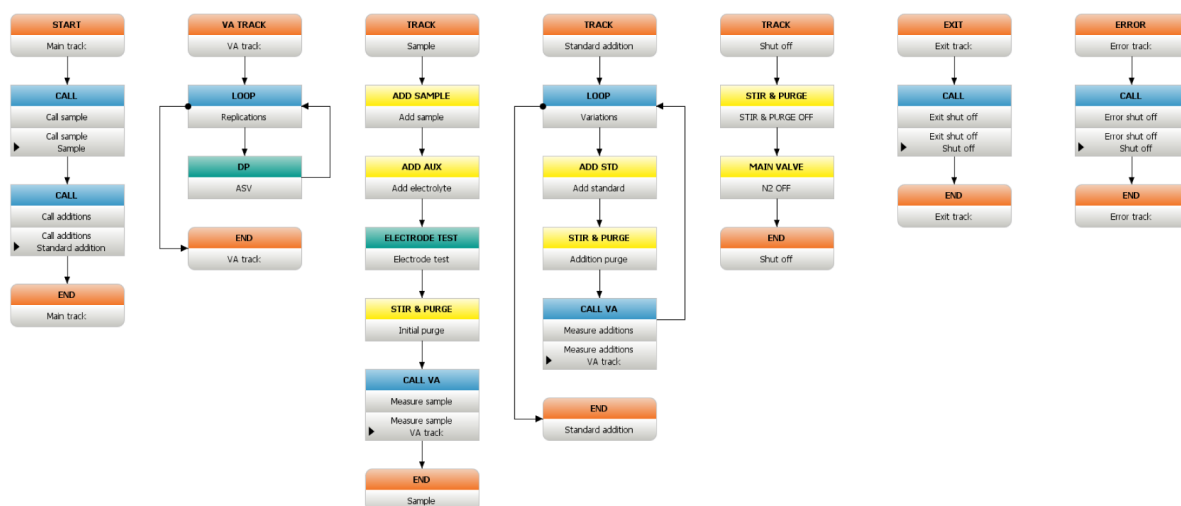
- 1** Click on the icon of the **Method** program part.

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



- 3** Under **Templates ► Trace analysis**, select **ASV determination (DP, standard addition)**, **manual** in the left-hand part of the window and click on **[OK]**.

The method template opens.



A method comprises the two subwindows **Method run** and **Evaluation**:

- The **Method run** subwindow contains all runs and parameters required for recording measurement curves.
- The **Evaluation** subwindow contains the settings for the automatic evaluation of measurement curves, the result calculation and the documentation.

The method run consists of different tracks. A track in turn consists of one or more commands with different functionalities. The color of the command indicates its functionality:

- Orange: start and end of a track
- Green: voltammetric commands that use the potentiostat/galvanostat of the 884 Professional VA
- Yellow: dosing, Liquid Handling and automation commands that are used for example for adding sample, electrolyte and standard solution
- Blue: call, communication and other commands

Call commands are used to change from one track to another. The commands are processed sequentially within a track. When a track finishes, the run returns to the call command that called the track.

The method run for the manual standard addition consists of the following tracks:

Track	Function
Main track	The Main track is the principal track of the method. Every analysis starts with the Main track . The commands in the Main track (CALL) call the corresponding tracks. When a called track has run through completely the next command in the Main track will automatically be executed.
VA track	The VA track contains the actual measurement. Voltammetry commands can only be inserted in a VA track (exception ELECTRODE TEST). This should ensure that the same voltammetric parameters are used for each measurement.
Sample	The Sample track is used to add and measure the sample.
Standard addition	The Standard addition track is used to add the standard solution and to measure the spiked sample.
Shut off	The Shut off track is used to stop the stirrer and to shut the main valve of the nitrogen supply.
Exit track	The Exit track is used to end the analysis. The Exit track is called automatically when the Main track has finished.
Error track	The Error track defines the procedure in case of an error. The Error track is called automatically when an error occurs.

The evaluation comprises the following sections:

General	General settings for the processing of the raw data.
Substances	The substances, the parameters for the peak detection and the baselines are defined here.
Standards	The concentrations of the standard solutions used are entered here.
Calibration	The calibration method, e.g. standard addition, is chosen here and various settings for creating a calibration curve can be made.
Results	Shows the automatically calculated results and possibility to create further user-defined results. The database where the carried out determinations are stored is also defined here.

4.2.1.2 Description of the method

In methods with standard addition, the sample is spiked several times with a known amount of analyte. This makes it possible to quantitatively determine the sample.

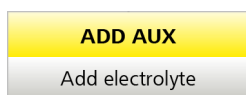
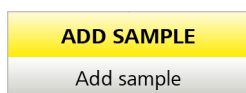
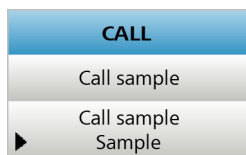
The method for the manual determination of cadmium and lead with standard addition consists of the following steps:

1. Add and purge sample manually
2. Measure the sample

3. Add and purge standard solution manually
4. Measure the single-spiked solution
5. Add and purge standard solution manually once again
6. Measure the double-spiked solution
7. Finish the measurement

Adding and purging sample (manually)

The analysis starts with the **CALL - Call Sample** command in the **Main track**. The command calls the **sample** track, which basically contains the steps for adding and purging the sample. The **Sample** track consists of the following commands that are executed in the specified sequence:

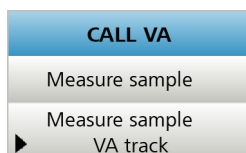


Prompts the operator to place the sample in the measuring vessel. The sample volume is defined in the **Workplace** program part (*see chapter 4.2.2, page 22*).

Prompts the operator to add the auxiliary solution (electrolyte). A double-click on the command opens a window in which the solution name and the volume can be specified.

Automatically starts an electrode test. It checks whether the electrodes are functioning correctly.

Regulates stirring and purging of the measuring solution. A double-click on the command opens a window in which the stirrer and the purging can be parameterized.



Measuring the sample

As soon as the sample has been added and purged, the measurement begins. The measurement of the sample (**VA track**) is called by the **CALL - Measure sample** command in the **Sample** track.

Starts the measurements in the differential pulse measuring mode. This command contains all the voltammetric measuring parameters. A double-click on the command opens a window with several tabs on which for example deposition potential, deposition time and the sweep parameters can be adjusted to the respective application.



NOTE

The correct parameters for your application can be found in the corresponding application documentation such as Application Bulletins or Application Notes (see <http://www.metrohm.com/en/applications/#>).



LOOP
Replications

The measurement is repeated until one of the stop criteria defined in the **LOOP - Replications** command has been met. In this example, the maximum number of runs is limited to two. The measurement is thus performed twice.

Adding and purging a standard solution

- CALL
- Call additions
- Call additions
- Standard addition

The sample is spiked with the standard solution after the sample measurement has been completed. For this, the **Standard addition** track is called by the **CALL - Call additions** command in the **Main track**. The **Standard addition** track in turn contains the following commands, which are executed in the specified sequence:

ADD STD
Add standard

Prompts the operator to add the standard solution. A double-click on the command opens a window in which the solution name and the volume can be specified.

STIR & PURGE

Addition purge

Controls stirring and purging of the solution spiked with the standard solution. A double-click on the command opens a window in which the stirrer and the purging can be parameterized.

CALL VA

Measure additions

Measure additions
▶ VA track

As soon as the standard solution has been added and purged, the measurement of the spiked sample begins. The measurement (**VA track**) is called by the **CALL VA - Measure additions** command in the **Standard addition** track. As a result of the **LOOP - Replications** command in the **VA track** the measurement is again carried out twice (see *"Measuring the sample", page 13*).

Measuring the double-spiked solution

LOOP

After the single-spiked solution has been measured twice, the solution is spiked and measured again as a result of the **LOOP - Variation** command in the **Standard addition** track. This means that the original sample is spiked twice in total (**LOOP - Variations**) and each solution is measured twice (**LOOP - Replications**).

Finishing the measurement

CALL

Exit shut off

Exit shut off
Shut OFF

After the double-spiked solution has been measured, the determination is canceled by the **Exit track**. The **CALL - Exit shut off** command calls the **Shut off** track. It specifies the sequence for shutting off the stirrer and the nitrogen supply.

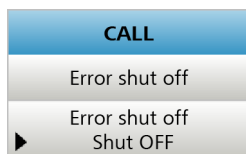
STIR & PURGE

STIR & PURGE OFF

Deactivates the stirrer and the purging of the measuring solution.



Closes the main valve of the 884 Professional VA for the nitrogen supply.



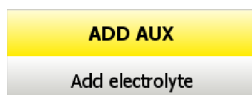
Error track

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

4.2.1.3 Defining command parameters

Prior to the analysis, 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 Specify the device used in the following commands. To do so, double-click on the command and select the correct device in the **Device name** field:
 - **DP - ASV**
 - **ELECTRODE TEST - Electrode test**
 - **STIR & PURGE - Initial purge**
 - **STIR & PURGE - Addition purge**
 - **STIR & PURGE - STIR & PURGE OFF**
 - **MAIN VALVE - N2 OFF**



- 2 Double-click on the **ADD AUX - Add electrolyte** command.
The **ADD AUX - Add electrolyte** dialog window opens.

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

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

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

ADD AUX - Add electrolyte

Command name

Auxiliary solution

Solution ▼

Volume mL

☒ Include volume in calculation

Addition

☒ Add manually

☐ Already added

☐ Add with dosing device

Message

☒ Display standard message

☐ Display message defined by the user

T

OK Cancel

- 4** Close the dialog window with **[OK]**.

ADD STD
Add standard

- 5** Repeat steps 2 - 4 for the standard solution (**ADD STD - Add standard** command).

DP
ASV

- 6** Double-click on the **DP - ASV** command. You can find the **Deposition potential** and the **Deposition time** (Potential # and Waiting time #) on the **Pretreatment** tab.

DP - ASV

Command name: ASV

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

Stirring time: 5.0 s

Cyclovoltammetric pretreatment

Start potential: -1.2 V

Vertex potential: -0.100 V

Sweep rate: 1 V/s

Cycles: off

Duration: - s

Potentiostatic pretreatment

Potential 1: -0.9 V Waiting time 1: 60.0 s

Potential 2: off V Waiting time 2: 0.0 s

Potential 3: off V Waiting time 3: 0.0 s

Potential 4: off V Waiting time 4: 0.0 s

Potential 5: off V Waiting time 5: 0.0 s

Equilibration time: 5.0 s

OK Cancel

The **Sweep** tab displays all parameters for the measurement of the voltammogram such as **Start potential** and **End potential**.

DP - ASV

Command name: ASV

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

Start potential: -0.8 V

End potential: -0.2 V

Potential step: 0.006 V

Potential step time: 0.1 s

Sweep rate: 0.060 V/s

Pulse amplitude: 0.05 V

Pulse time: 0.04 s

Measuring time: 0.02 s

Sweep duration: 10.00 s

OK Cancel

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

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

4.2.1.4 Defining the evaluation

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

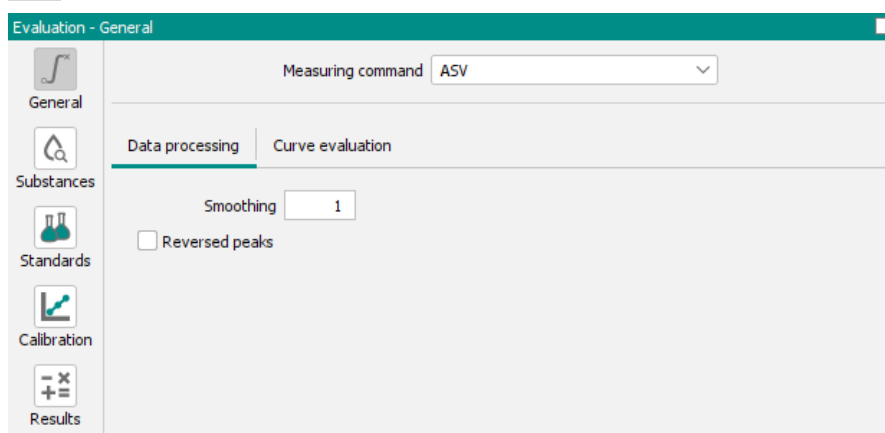
All evaluation parameters are predefined in the method templates. However, they need to be adapted to the respective application.

General

The parameters for processing the raw data and for curve evaluation, regardless of a substance evaluation are defined in the **General** section.

 $\int^x$

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



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

The entries on the **Data processing** tab are adopted. Fixed points can be defined on the **Curve evaluation** tab to read out single measuring points from one or more curves.

Substances

The substances that are to be searched for are 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 of the baseline are defined on the **Baselines** tab.

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

- 2 If you want to edit an entry, open the editing dialog by double-clicking on the line or highlight the cell and click on **Edit** to .

	Substance	Active	Characteristic potential	Tolerance	Min. width	Max. width	Min. measured quantity
1	Cd	☒	-0.58	0.05	0.01	0.5	200 pA
2	Pb	☒	-0.38	0.05	0.01	0.5	200 pA
*							

Standards

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



NOTE

The solution names entered here must be identical with the standard solutions in the method run (pay attention to upper/lower case) in order for the system to be able to match them.



- 1 Click on the **Standards** button.
- 2 Click on the **Edit ► Apply from ADD STD** menu.

The solution name entered in the **Solution** field in the **ADD STD** command is entered in the * column, if the solution is not already in the table. Adjust the values for the substance concentration in the standard according to the actual standard used.

	Substance	Standard	*
1	Cd	0.1 mg/L	
2	Pb	1.0 mg/L	

Calibration

The calibration method, in this case **Standard addition**, is selected in the **Calibration** section. The calibration curve type (only linear regression is possible for standard addition) and the evaluation quantity (peak area or peak height) are defined on the **Calibration curves** tab.



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

Evaluation - Calibration

General Calibration curves

Measuring command

	Substance	Evaluation quantity	Curve type	Weighting
▶ 1	Cd	Height	Linear regression	☒
2	Pb	Height	Linear regression	☒

Results

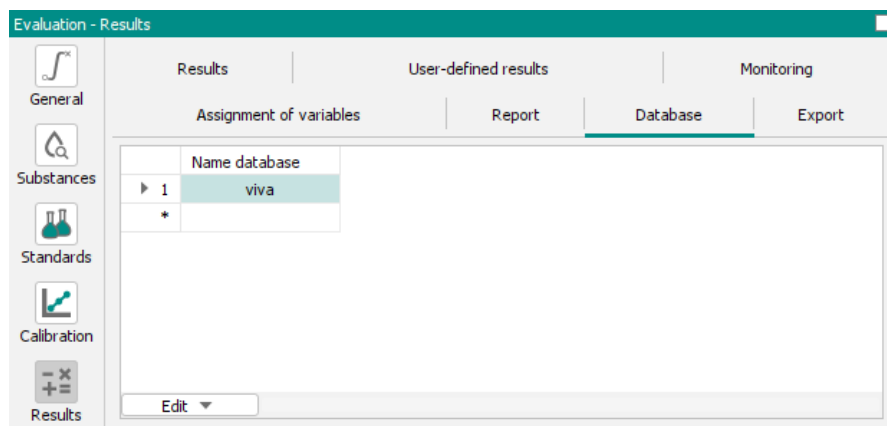
The database in which the determinations are to be stored is indicated in the **Results** section. The automatic printout, the export and additional results can be defined by the user.



1 Changing the database (optional)

The data is stored in the **viva** database by default. Proceed as follows if the data should be stored in another database:

- Click on the **Results** button.
- Select the **Database** tab.
- Open the **Select database** dialog using the **Edit ► Properties...** menu.
- Select another database in which the results are to be stored in the **Database** list box. If no other database is available, then a new database has to be created in the database manager first.
- 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]**.

4.2.1.5 Performing a method check

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

- 1 Click on the **File ► Method check** menu or the icon.
The method is checked. When the check has ended a message appears indicating any errors.
- 2 Confirm the message with **[OK]**.
- 3 Correct errors, if any.
- 4 Repeat the method check until the message **013-118 Method test ok** appears.

4.2.1.6 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 the name for the method in the **Method name** field (e.g. **Determination of Cd and Pb - manual**).

- 3** Click on **[Save]**.

4.2.2 Carrying out a determination

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



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

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

Run

Single determination | Determination series

Status: READY

Determination parameters

User: Sample number:

Remark:

Sample data

Method:

ID1:

ID2:

ID3:

Sample type:

Sample amount: Sample amount unit:

- 3** In the **Method** field, select the method created from the method template (e.g. **Determination of Cd and Pb - manual**).

- 4** Enter the sample IDs for identifying the sample in the fields **ID1 - ID3** if required.

- 5** Select the **Sample** option in the **Sample type** field.

- 6** Enter the sample volume (e.g. **10**) in the **Sample amount** field and select **mL** as **Sample amount unit**.



- 7** Press **[Start]** to start the analysis.
The analysis is started.

- 8 Follow the instructions of the application until the analysis has finished.

After the analysis has ended, a new entry is created in the predefined database and a report is printed out if this has been defined in the method.

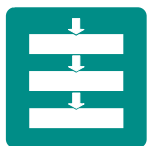
4.2.3 Adjusting a method

The method templates can be customized and saved as new methods if needed. The following chapters provide you with an overview of how to adjust an existing method and what you should pay attention to.

4.2.3.1 Adding standards with two different solutions

In the method template **ASV determination (DP, standard addition), manual**, the spiking for the standard addition is done with a mixed standard that contains both analytes. However, in certain cases it is easier to add the standards in separate solutions. This makes it easier to adjust the standard addition if the two analytes often have different ratios.

The following example shows you how to adjust an already defined standard solution and how to create an additional standard solution. The procedure is explained using the method template **ASV determination (DP, standard addition), manual**.



- 1
 - Click on the icon of the **Method** program part.
 - Load the **ASV determination (DP, standard addition), manual** method template if not already loaded (*see chapter 4.2.1.1, page 10*).
- 2 **Adjusting the existing standard solution in the method run**

Adjust the command for the standard solution already defined. Proceed as follows:

 - Double-click the **ADD STD - Add standard** command in the **Method sequence** subwindow.
 - Change the command name accordingly (e.g. **ADD Cd**).
 - Enter a new name in the **Solution** field (e.g. **Standard Cd**).
 - Adjust the addition volume if necessary.

- Confirm with **[OK]**.

ADD STD - Add standard

Command name

Standard

Solution

Addition increments

Number

Addition volume 1 mL

Addition

☒ Add manually

☐ Already added

☐ Add with dosing device

Message

☒ Display standard message

☐ Display message defined by the user

T

OK Cancel

3 Adding a new standard solution in the method run

In order to add a new standard solution, add a new command for the new standard solution in the method run. Proceed as follows:

- Move the cursor to the point in the method run where the new command should be inserted and right-click. In this case it is in the **Standard addition** track before the **STIR & PURGE - Addition purge** command.
- Select **New command...**
- In the command overview, select the **Dose ► ADD STD** command and confirm with **[OK]**.
- Open the parameterization of the new command by double-clicking on the command.
- Give the new command a name (e.g. **ADD Pb**).
- Enter a name in the **Solution** field (e.g. **Standard Pb**).
- Adjust the addition volume if necessary.

- Confirm with **[OK]**.

ADD STD - ADD STD 22

Command name: ADD Pb

Standard

Solution: Standard Pb

Addition increments

Number: 1

Addition volume 1: 0.100 mL

Addition

☒ Add manually

☐ Already added

☐ Add with dosing device

Message

☒ Display standard message

☐ Display message defined by the user

OK Cancel

4 Adjusting the standards in the evaluation parameters

Adjust the definitions of the standards in the evaluation parameters afterwards. Proceed as follows:

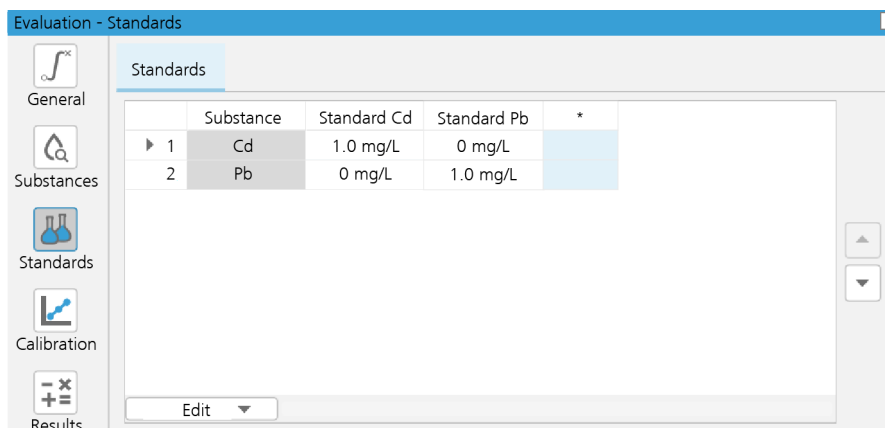
- Click on the **Standards** button in the **Evaluation** sub-window.
- Delete the existing standard. To do this, right-click on the column and select **Delete**.
- Right-click and select **Apply from ADD STD**.
- Double-click on the first column (**Standard Cd**). The **Standard** dialog field opens.
- Adjust the value for the Cd concentration according to the application documentation. Set the value for the not contained substance (in this case Pb) to **0**.
- Switch to the next column with the arrow button **[▶]** in the navigation bar.
- Enter the concentration for the second standard solution (**Standard Pb**) in the same way as before.
- Exit the dialog field with **[OK]**.



NOTE

In order for the software to be able to assign the correct standard solutions to the substances, the solution name of the standard solution in the **Evaluation** and the solution name in the **ADD STD** command in the **Method run** have to be identical (Note: pay attention to upper/lower case and spaces). This also applies to the solution name in the Configuration if solutions are to be added automatically. In case of automatic addition of solution it is advisable to prepare and select the solutions in the following order:

- **Configuration:** Define the solution in the **Solutions** sub-window (*see chapter 5.1.4, page 46*).
- **Method:** Select the solution name from the list in the **Method run** subwindow in the respective **ADD STD** command (*see chapter 5.2.1.3, page 50*).
- **Method:** Apply the solution names from the **Method run** using the **Apply from ADD STD** function according to the instructions in this chapter in the **Evaluation** subwindow.

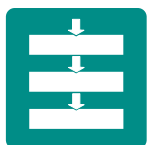


5 Saving a method

- Perform a method check (see chapter 4.2.1.5, page 21).
- Save the method if the method check was successful (see chapter 4.2.1.6, page 21).

4.2.3.2 Changing substances

In the **ASV determination (DP, standard addition), manual** method template, the sample is analyzed for Cd and Pb using standard addition. The following example shows you what needs to be changed if for example Zn and Cu are to be determined instead of Cd and Pb. Proceed as follows:



- 1
 - Click on the symbol of the **Method** program part.
 - If not already done, load the method template **ASV determination (DP, standard addition), manual** voltammetry command (see chapter 4.2.1.1, page 10).

- 2 **Adjusting the deposition and sweep parameters in the voltammetry command**
 - Double-click the **DP - ASV** voltammetry command in the **Method sequence** subwindow.
 - Adjust the potentials and times on the **Pretreatment** tab under **Potentiostatic pretreatment** according to the application documentation or the expected peak potentials. (In the example, the potential of -0.9 would have to be changed to -1.15 V due to the determination of Zn).
 - Adjust the start potential and the end potential on the **Sweep** tab according to the application documentation or the expected peak potentials. (In the example of the determination of Zn and Cu, the start potential would have to be changed to -1.15 V and the end potential to 0.05 V).

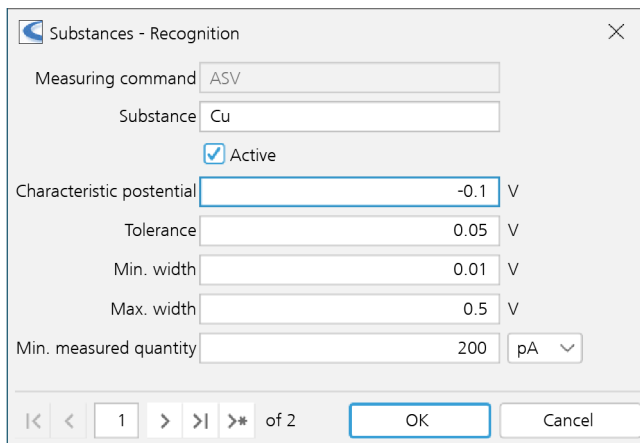
- 3 **Changing substances and standards in the evaluation parameters**
 - Click on the symbol of the **Method** program part.
 - Click on the **Substances**  button in the **Evaluation** subwindow.
 - Adjust the substances. To do this, double-click on the first substance (**Cd**). The **Substances - Recognition** dialog window opens.
 - Change the name of the substance (in this example **Zn**).
 - Enter the application-specific values for the **Characteristic potential** (in the case of Zn e.g. -1.0 V). The values for **Tolerance**, **Min. width/Max. width** and **Min. measured quantity** normally do not have to be adjusted.

2 Adjusting the deposition and sweep parameters in the voltammetry command

- Double-click the **DP - ASV** voltammetry command in the **Method sequence** subwindow.
- Adjust the potentials and times on the **Pretreatment** tab under **Potentiostatic pretreatment** according to the application documentation or the expected peak potentials. (Nothing needs to be changed if Cu should be added to the existing method in this example.)
- Adjust the start potential and the end potential on the **Sweep** tab according to the application documentation or the expected peak potentials. (The end potential has to be changed to 0.05 V if the existing method should be extended by Cu in the example. The start potential remains the same.)

3 Adding a new substance to the evaluation

- Click on the **Substances**  button in the **Evaluation** subwindow.
- Open the **Recognition** tab.
- Move the cursor to the empty row, right-click and select **New...**. The **Substances - Recognition** dialog window opens.
- Enter the new substance (in this example **Cu**).
- Enter the application-specific values for the **Characteristic potential** (in the example Cu -0.1 V). The values for **Tolerance**, **Min. width/Max. width** and **Min. measured quantity** normally do not have to be adjusted.
- Confirm with **[OK]**.



The image shows the 'Substances - Recognition' dialog box. It contains the following fields and values:

Field	Value	Unit
Measuring command	ASV	
Substance	Cu	
Active	☒	
Characteristic potential	-0.1	V
Tolerance	0.05	V
Min. width	0.01	V
Max. width	0.5	V
Min. measured quantity	200	pA

At the bottom, there are navigation buttons (back, forward, search, etc.), a page indicator '1 of 2', and 'OK' and 'Cancel' buttons.

4 Defining the concentration of the standard solution

- Click on the **Standards** button in the **Evaluation** subwindow.

- Adjust the concentration for the new substance if the standard is a mixed standard.
- Proceed as specified in *chapter 4.2.3.1 on page 23* if the standard addition should be carried out with a separate standard solution.

5 Saving a method

- Perform a method check (see chapter 4.2.1.5, page 21).
- Save the method if the method check was successful (see chapter 4.2.1.6, page 21).

4.2.3.4 Adding additional auxiliary solution

In certain cases an additional auxiliary solution needs to be added to the measuring vessel (e.g. water to dilute the sample or a complexing agent for AdSV measurements). Proceed as follows to add a new auxiliary solution:



- 1
 - Click on the icon of the **Method** program part.
 - Load the **ASV determination (DP, standard addition), manual** method template if not already loaded (*see chapter 4.2.1.1, page 10*).

2 Adding the auxiliary solution to the method run



NOTE

If the solution is added automatically, then the solution name in the **ADD AUX** command and in the **Configuration** have to be identical (Note: pay attention to upper/lower case and spaces). In this case it is therefore advisable to prepare and select the solutions in the following order:

- **Configuration:** Define the solution in the **Solutions** sub-window (see chapter 5.1.4, page 46).
- **Method:** Select the solution name from the list in the **Method run** subwindow in the respective **ADD AUX** command (see chapter 5.2.1.3, page 50).

- Move the cursor to the point in the method run where the command for adding the auxiliary solution should be inserted and right-click. In the case of adding water to dilute the sample this would be in the **Sample** track before the **ADD SAMPLE - Add sample** command.
- Select **New command**.
- In the command overview, select the **Dose ► ADD AUX** command and confirm with **[OK]**.

- Open the parameterization of the new command by double-clicking on the command.
- Give the new command a name (e.g. **ADD H2O**).
- Enter a name for the solution in the **Solution** field (e.g. **H2O**).
- Enter the volume of the solution to be added in the **Volume** field (e.g. **10**).
- Confirm with **[OK]**.

3 Saving a method

- Perform a method check (*see chapter 4.2.1.5, page 21*).
- Save the method if the method check was successful (*see chapter 4.2.1.6, page 21*).

4.2.3.5 Using solid or prediluted samples

Solid samples or liquid samples that are too concentrated can be dissolved or diluted prior to the determination. The procedure is described in the online help of **viva**.

In order for **viva** to be able to automatically calculate the concentrations, two other variables need to be defined in addition to **Sample amount** and **Sample amount unit**. One of them has to be assigned to **Sample data variables Analytical volume**, the other one to **Sample data variables Dilution volume**. The names are freely selectable. To make it easier, the following names are used here:

- **Sample amount:** (sample amount prior to dilution)

START - Main track

Command name: Main track

General | Application note | **Sample data variables**

	Name	Type	Assignment	Fixed value	Comment	Monitoring
1	ID1	Text	ID1		Sample identification 1	☐
2	ID2	Text	ID2		Sample identification 2	☐
3	ID3	Text	ID3		Sample identification 3	☐
4	Sample type	Text	Sample type		Sample type	☐
5	Sample amount	Number	Sample amount		Sample amount	☐
6	Sample amount unit	Text	Sample amount unit		Sample amount unit	☐
7	Analytical volume	Number	Analytical volume		Analytical volume	☐
8	Dilution volume	Number	Dilution volume		Dilution volume	☐

New Properties Delete

OK Cancel

Carrying out a determination

Proceed as follows to start the determination of the solid or prediluted sample:



- 1 Click on the icon of the **Workplace** program part.
- 2 In the **Method** field, select the method created from the method template.
- 3 Enter the amounts and volumes used for the dilution in the fields of the corresponding **Sample data variables** (as an example 0.5 g of a solid sample are diluted and filled up to 100 mL; 10 mL of this are used for the determination):
 - **Sample amount:** Sample amount prior to dissolving or dilution, in the example **0.5**
 - **Sample amount unit:** Unit of the sample amount prior to dissolving or dilution, in the example **g**
 - **Analytical volume:** Volume of the diluted sample, which will be used for the analysis. The value must be in mL, in the example **10** mL.
 - **Dilution volume:** Total volume to which the sample was diluted to prior to analysis. The value must be in mL, in the example **100** mL.

- 4** Carry out the determination (see chapter 4.2.2, page 22). The automatically calculated result has the unit #g/g (the correct prefix is automatically assigned) and corresponds to the 0.5 g of solid sample.



NOTE

For methods without predilution (**Sample data variables Analytical volume** and **Dilution volume** are not visible on the workplace), the volume (or mass or piece) specified under **Sample amount** in the **ADD SAMPLE** command is added to the measuring vessel.

For methods with predilution (**Sample data variables Analytical volume** and **Dilution volume** are visible below the **Sample amount** on the workplace), the volume specified under **Analytical volume** has to be added to the measuring vessel.

Run

Single determination | Determination series

Status: **READY**

Determination parameters

User: Sample number:

Remark:

Sample data

Method: Determination of Cd and Pb - manual

ID1:

ID2:

ID3:

Sample type:

Sample amount: Sample amount unit:

Analytical volume: mL

Dilution volume: mL

4.3 Manual ASV determination with external calibration

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

- A method for the manual determination of cadmium and lead with anodic stripping voltammetry and the calibration method 'external calibration'.

4.3.1 Creating a method

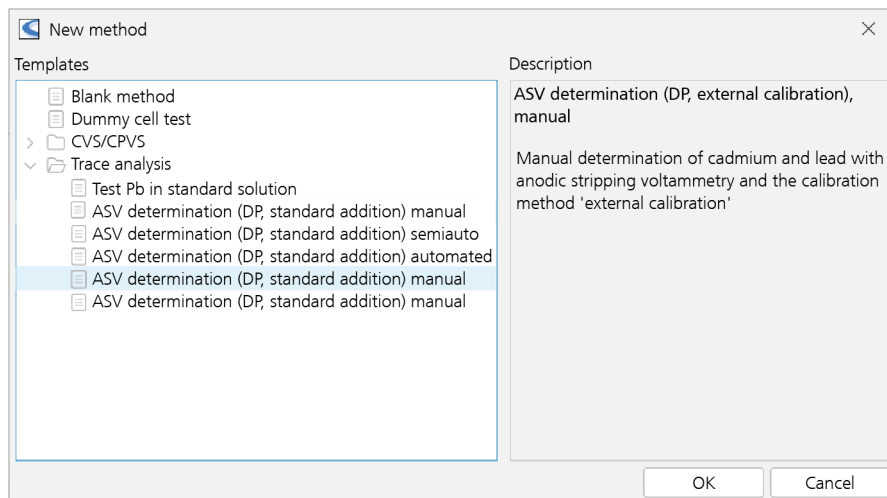
viva comprises method templates that contain all commands required to perform a determination. These method templates can be customized. You can, for instance, change parameters, select a different database to store determinations or add further commands.

4.3.1.1 Loading a method template



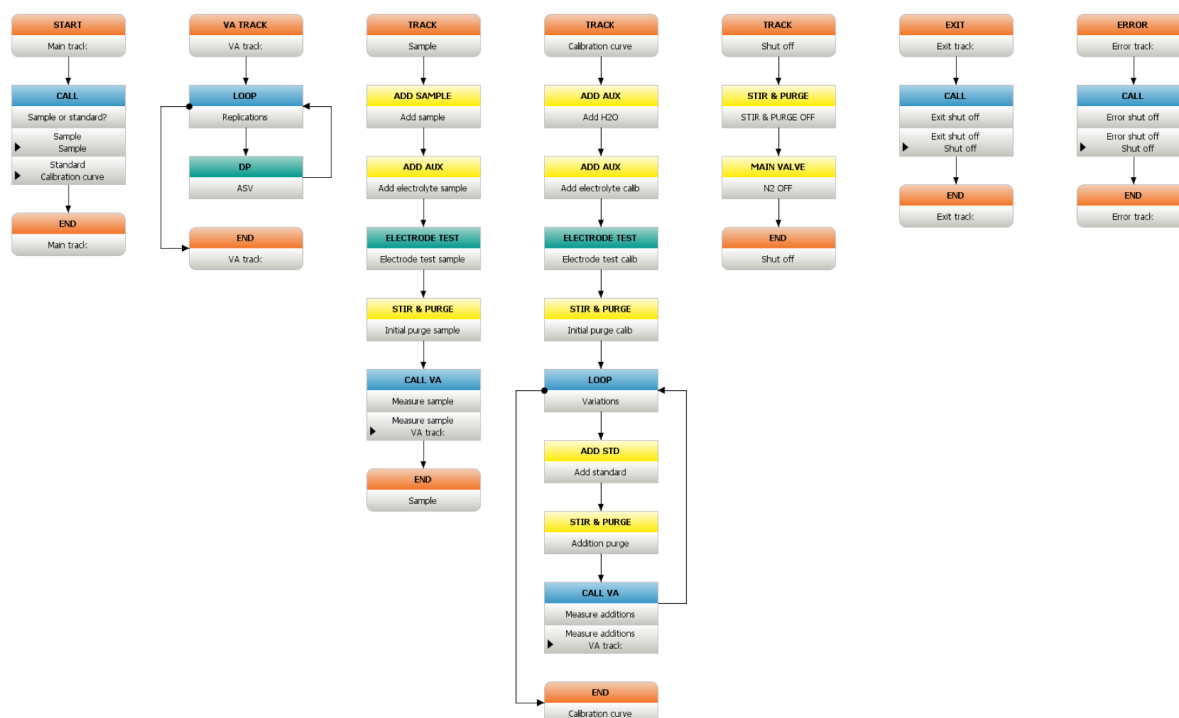
- 1 Click on the icon of the **Method** program part.

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



- 3 Under **Templates ► Trace analysis**, select **ASV determination (DP, external calibration), manual** in the left-hand part of the window and click on **[OK]**.

The method template opens.

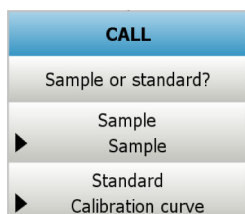


The method for manual ASV determination with external calibration basically has a similar structure as the method for manual ASV determination with standard addition (*see chapter 4.2.1.1, page 10*). The main difference between the methods is the **Calibration curve** track instead of the **Standard addition** track and the conditional call of the **Sample** or **Calibration curve** tracks from the main track.

Track	Function
Main track	For external calibration, the CALL command has a condition which makes the method run dependant on the sample type selected in the workplace.
Calibration curve	The Calibration curve track contains the necessary commands for recording the calibration curve. In contrast to the Sample track, ultra-pure water is added instead of sample. The number of calibration points can be specified in the LOOP - Variations command.

Recording a calibration curve or measuring the sample

The method starts with the conditional call **CALL - Calibration or sample**. If the sample type **Standard** is selected in the workplace, then the **Calibration curve** track is called. However, if the sample type is **Sample**, then only the **Sample** track is run through.



LOOP

Variations

4.3.1.2 Description of the method

The method for the manual determination of cadmium and lead with external calibration consists of the following steps:

1. Add and purge water and electrolyte manually.
2. Manually adding a known amount of cadmium and lead.
3. Measuring the solution.
4. Manually adding cadmium and lead again and measuring the solution again.
5. Repeat addition and measurement until the number of calibration points specified in the method has been reached.
6. Measurement has ended. The software saves the calibration curve.

1. Add and purge sample and electrolyte manually.
2. Measure the sample.
3. Measurement has ended. The software compares the sample signal to the calibration curve and calculates the result.



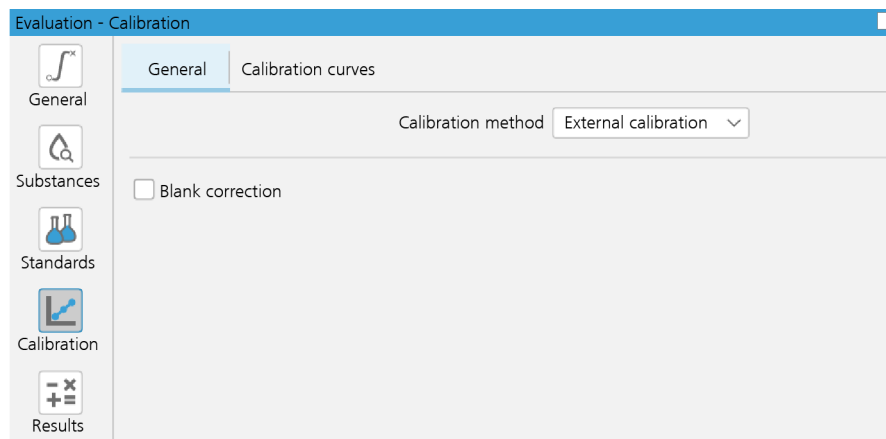
The method name is used to assign the correct calibration curve to the sample. To be sure that this assignment is correct, the method name must not be changed between recording the calibration curve and measuring the sample.

(see chapter 4.2.1.3, page 15)

4.3.1.4 Defining the evaluation

(see chapter 4.2.1.4, page 18)

Ensure that **Calibration method External calibration** is selected under **Calibration ► General**.



4.3.1.5 Performing a method check

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

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

The method is checked. When the check has ended a message appears indicating any errors.
- 2 Confirm the message with **[OK]**.
- 3 Correct errors, if any.
- 4 Repeat the method check until the message **013-118 Method test ok** appears.

4.3.1.6 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 the name for the method in the **Method name** field (e.g. **ASV determination with external calibration**).
- 3 Click on **[Save]**.

4.3.2 Carrying out a determination

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

4.3.2.1 Recording a calibration curve



- 1 Click on the icon of the **Workplace** program part.
- 2 Select the **Single determination** tab in the **Run** subwindow.
- 3 In the **Method** field, select the method created from the method template (e.g. **ASV determination with external calibration**).
- 4 Enter the sample IDs for identifying the sample in the fields **ID1 - ID3** if required.
- 5 Select **Standard** in the **Sample type** field.
- 6 Press **[Start]**.
- 7 Pipette the volume of water displayed in the message into the measuring vessel. Confirm the addition by clicking on **[Next]**.
The prompt for adding the auxiliary solution appears.
- 8 Pipette the volume of auxiliary solution displayed in the message into the measuring vessel.
- 9 Lower the measuring head arm with the electrodes.
- 10 Click on **[Next]**.

▶ *Start*



NOTE

All solutions that still need to be added, must be added to the measuring vessel via the pipetting opening so as to keep the back diffusion of atmospheric oxygen as low as possible.

- 11 Pipette the volume of standard solution displayed in the message into the measuring vessel.
- 12 Click on **[Next]**. The first standard solution is measured twice. Then the prompt for adding the standard solution appears again.
- 13 Pipette the volume of standard solution displayed in the message into the measuring vessel.
- 14 Click on **[Next]**. The next standard solution is measured twice. Then the prompt for adding the standard solution appears again.
- 15 Repeat steps 13 and 14 until the measurement has ended. After the calibration has ended, a new entry is created in the predefined database and in the calibration data pool (can be found in the **Configuration** under **Calibration data**).

4.3.2.2 Determining the concentration in the sample



- 1 Click on the icon of the **Workplace** program part.
- 2 Select the **Single determination** tab in the **Run** subwindow.
- 3 In the **Method** field, select the method created from the method template (e.g. **ASV determination with external calibration**).
- 4 Enter the sample IDs for identifying the sample in the fields **ID1 - ID3** if required.
- 5 Select the **Sample** option in the **Sample type** field.
- 6 Enter the sample volume (e.g. **10**) in the **Sample amount** field and select **mL** as **Sample amount unit**.
- 7 Press **[Start]** to start the analysis.
The prompt for adding the sample appears.
- 8 Pipette the sample volume displayed in the message into the measuring vessel.

► *Start*

- The sample is measured twice. After the determination has ended, a new entry is created in the predefined database.

5 Semiautomated determination

In a semiautomated determination, samples, standard and auxiliary solutions can be added either automatically via dosing units or manually via the pipetting opening.

The following equipment is required for a semiautomated determination:

- 884 Professional VA
- 807 Dosing Unit (one with a 2 mL and one with a 5 mL glass cylinder)
- 800 Dosino
 - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing standard solution
 - 800 Dosino and 807 Dosing Unit with cylinder size 5 mL for dosing auxiliary solution (electrolyte)



NOTE

The sample is still added manually in the following example.



5.1 Configuration

5.1.1 Configuring the instrument

(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 807 Dosing Units connected to the 884 Professional VA 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. Then the 884 Professional VA has to be initialized again.

Connecting an 800 Dosino with dosing unit

Proceed as follows to connect an 800 Dosino to an 884 Professional VA:

- 1 Connect the connection cable of the 800 Dosino with the 807 Dosing Unit and the 5 mL cylinder to one of the MSB connectors of the 884 Professional VA.

The following message is displayed:

009-009 Other devices on the MSB – Peripheral devices were connected or removed from the MSB1 of '884_1' device. – 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 884 Professional VA in the device table of the **Configuration** program part.

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

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


Dosing unit - 5 mL Electrolyte
✕

Dosing unit

GLP

Hardware

Name

50 mL Electrolyte

Comment

Device name / dosing device

Order number

6.3032.150

Serial number

10510126

Cylinder volume

5

mL

Cylinder serial number

3120

Parameters for preparation

Dosing port Prep/Empty

Dosing port 2

▼

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 ▼	135.0 cm	2.0 mm
Dosing port 2	Port 3 ▼	0.0 cm	2.0 mm
Fill port	Port 2 ▼	15.0 cm	2.0 mm
Special port	Port 4 ▼	0.0 cm	2.0 mm

Valve disk

Rotating direction

automatic

▼

Not over

Port 4

▼

OK

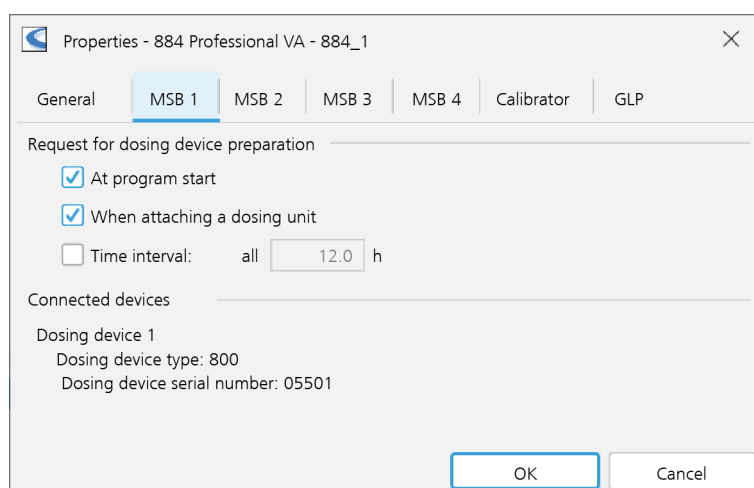
Cancel

- 4 Enter the name **5 mL Electrolyte** in the field **Name**.
- 5 Enter the length and the diameter of the tubings and capillaries that are actually connected in the section **Tubing parameters** (see *Manual 884 Professional VA* or the Application Bulletin (e.g. AB 425 or 426) with the installation instructions for the respective system).
- 6 Click on **[OK]**.
The dosing unit will be automatically displayed in the **Dosing units** subwindow of the **Configuration** program part.
- 7 Connect the other dosing unit with the 2 mL cylinder and name the **2 mL standard**. Also enter the respective lengths and diameters of the tubings for this dosing unit.

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 of the 884 Professional VA (e.g. **884_1**) and double-click on it.
The **Properties – 884 Professional VA - 'Device name'** dialog opens.
- 2 Apply the default settings in the **Request for dosing device preparation** section on the **MSB 1 to MSB 4** tabs.



- 4** Prepare the other solution in the same way:

5.2 Semiautomated ASV determination with standard addition

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

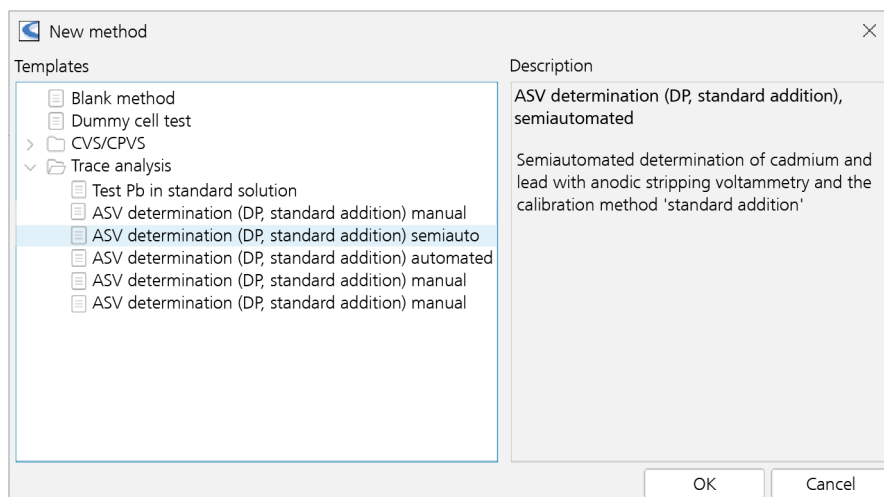
In this chapter, you will use a method template to create a method for the semiautomated determination of cadmium and lead with anodic stripping voltammetry and the calibration method 'standard addition'. You will become acquainted with the basic functions and the structure of a method using this method template.

5.2.1 Creating a method

5.2.1.1 Loading a method template

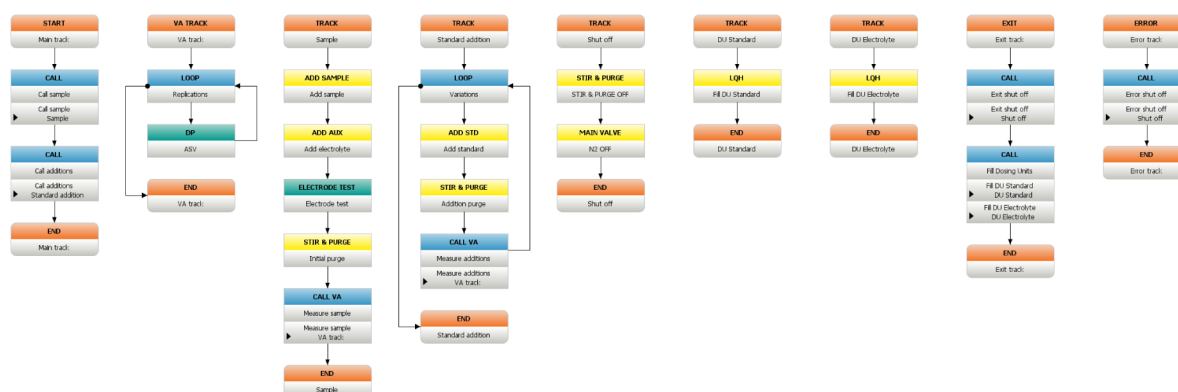


- 2 Open the **New method** dialog using the **File ► New...** menu.



- 3** Under **Templates ► Trace analysis**, select **ASV determination (DP, standard addition), semiautomated** in the left-hand part of the window and click on **[OK]**.

The method template opens.



The evaluation does not differ from that of a manual determination with standard addition. The method run of the semiautomated ASV determination largely corresponds to the procedure of the manual ASV determination (*see chapter 4.2.1.1, page 10*). In contrast to the manual ASV determination, the standard solution and the auxiliary solution are dosed automatically.

Compared with the manual determination, the method run contains the following additional tracks:

Table 1 Tracks

Track	Function
DU Standard	The DU Standard track is used to refill the dosing unit of the standard solution with standard solution after the determination has ended and to return the piston to the starting position.
DU Electrolyte	The DU Electrolyte track is used to refill the dosing unit of the auxiliary solution (electrolyte) with auxiliary solution after the determination has ended and to return the piston to the starting position.

5.2.1.2 Description of the method

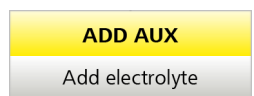
The method for semiautomated ASV determination basically has the same structure as the method for manual ASV determination (*see chapter 4.2.1.2, page 12*). The sample is still added manually. In contrast to the manual ASV determination, the standard solution and the electrolyte are automatically dosed into the measuring vessel with a Dosino. This has the following consequences for the method template:

Addition of standard solutions and auxiliary solutions

The **Add with dosing device** check box is enabled under **Addition** in the command for dosing the standard solution (**ADD STD - Add standard**).



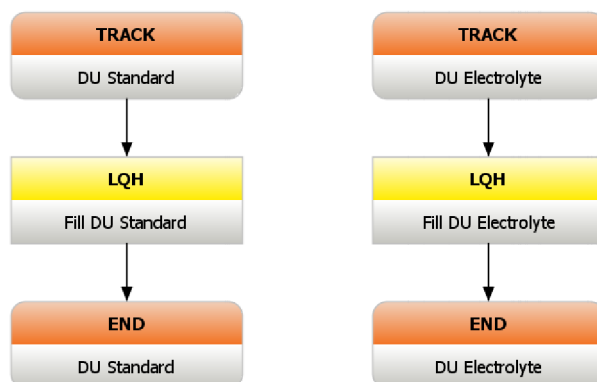
The **Add with dosing device** check box is enabled under **Addition** in the command for dosing the auxiliary solution (**ADD AUX - Add electrolyte**).



The **Dosing rate** and **Filling rate** can be defined under **Dosing device** for both commands.

Tracks DU Standard and DU Electrolyte

The two commands **LQH - Fill DU Standard** and **LQH - Fill DU Electrolyte** refill the two Dosinos with standard solution or electrolyte after the determination. Both tracks are called simultaneously by the **CALL - Fill Dosing Units** command in the **Exit Track**.



5.2.1.3 Defining command parameters



NOTE

For more information on command parameters, refer to *chapter 4.2.1.3 on page 15*.

In contrast to the manual determination, the standard solution and the auxiliary solution are dosed into the measuring vessel with a Dosino.



- 1 Double-click the **ADD STD - Add standard** command. The **ADD STD - Add standard** dialog window opens.
- 2 Select **Standard** under **Solution**

ADD STD - Add standard

Command name

Standard

Addition increments

Number

Addition volume 1 mL

Addition

☐ Add manually

☐ Already added

☒ Add with dosing device

Dosing device

Dosing rate mL/min

Filling rate mL/min

OK Cancel



NOTE

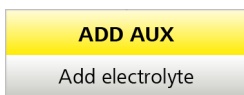
The dosing rate should not be greater than 2 mL/min for solutions that are added via a capillary (< 1 mm inner diameter, as for example 4-way micro dosing tip).

- 3 Adjust the volume if necessary and exit the dialog field with **[OK]**.



NOTE

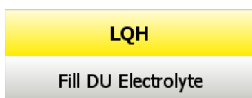
If the **Standard** solution is not in the list, then **Standard solution** was accidentally not selected as solution type in the configuration for this solution.



- 4 Double-click on the **ADD AUX - Add electrolyte** command. The **ADD AUX - Add electrolyte** dialog window opens.

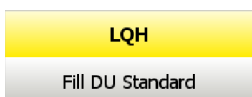
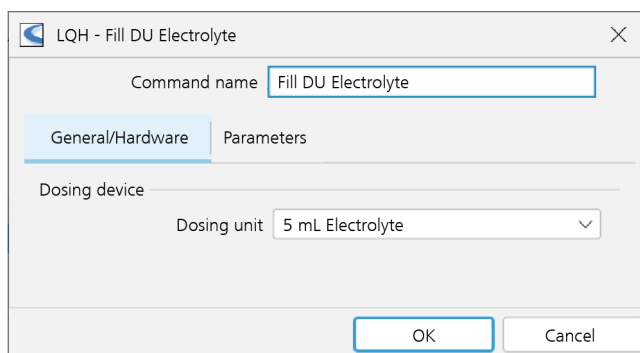
- 5 Select **Electrolyte** under **Solution**.

- 6 Adjust the volume if necessary and exit the dialog field with **[OK]**.



- 7 Double-click on the **Fill DU Electrolyte** command. The **LQH - Fill DU Electrolyte** dialog window opens.

- 8 Select the name of the dosing unit (in this case **5 mL Electrolyte**) on the **General/Hardware** tab.



- 9 Repeat the procedure for the dosing unit with the standard solution. Select the **2 mL Standard** dosing unit here.

5.2.1.4 Defining the evaluation

(see chapter 4.2.1.4, page 18)

5.2.1.5 Performing a method check

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

- 1 Click on the **File ► Method check** menu or the  icon.
The method is checked. When the check has ended a message appears indicating any errors.
- 2 Confirm the message with **[OK]**.
- 3 Correct errors, if any.
- 4 Repeat the method check until the message **013-118 Method test ok** appears.

5.2.1.6 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 the name for the method in the **Method name** field (e.g. **Determination of Cd and Pb - semiautomated**).
- 3 Click on **[Save]**.

5.2.2 Carrying out a determination

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.

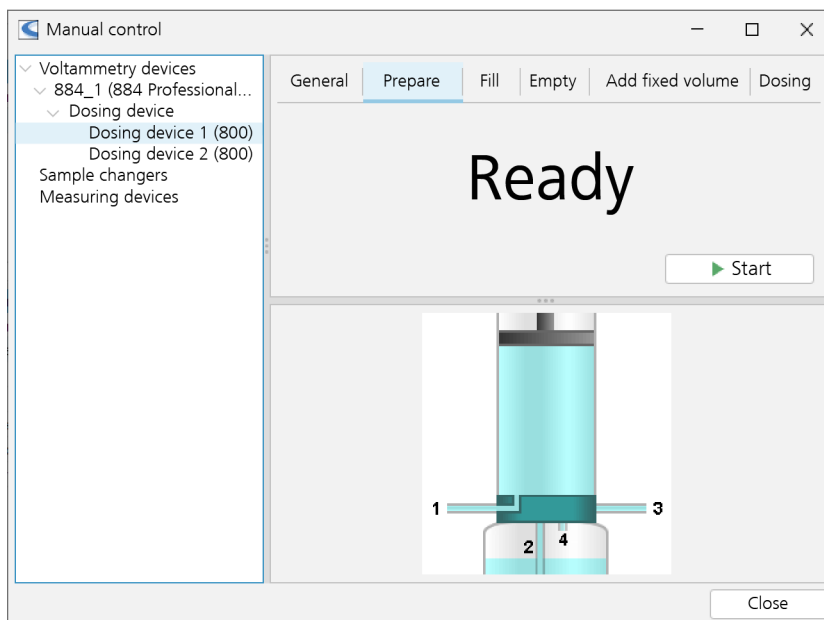
Proceed as follows:



- 1 Click on the icon of the **Manual control** program part.
The **Manual control** dialog opens.

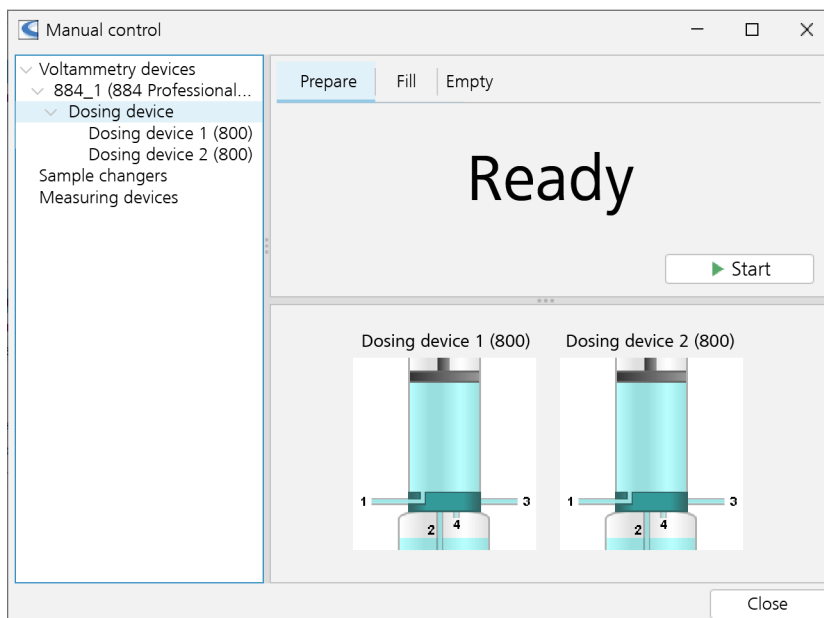
The connected devices are displayed with their peripheral devices in the left-hand part of the window. In the right-hand part of the window, the functions of the selected device are displayed. In the following example, they are shown for Dosing device 1 (800).

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



or

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





- 3** Remove the measuring vessel and place a waste beaker under the measuring head in the drip pan.
- 4** Select the **Prepare** tab and click on **[Start]**.
- 5** We recommend preparing the dosing units a second time to prevent dilution or contamination of the solution in the dosing cylinder. To do this, 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.

Carrying out a determination



- 1 Click on the icon of the **Workplace** program part.
- 2 Select the **Single determination** tab in the **Run** subwindow.
- 3 In the **Method** field, select the method created from the method template (e.g. **Determination of Cd and Pb - semiautomated**).
- 4 Enter the sample IDs for identifying the sample in the fields **ID1 - ID3** if required.
- 5 Select the **Sample** option in the **Sample type** field.
- 6 Enter the sample volume (e.g. **10**) in the **Sample amount** field and select **mL** as **Sample amount unit**.
- 7 Press **[Start]** to start the analysis.
The prompt for adding the sample appears.
- 8 Pipette the sample volume displayed in the message into the measuring vessel.
- 9 Click on **[Next]**.

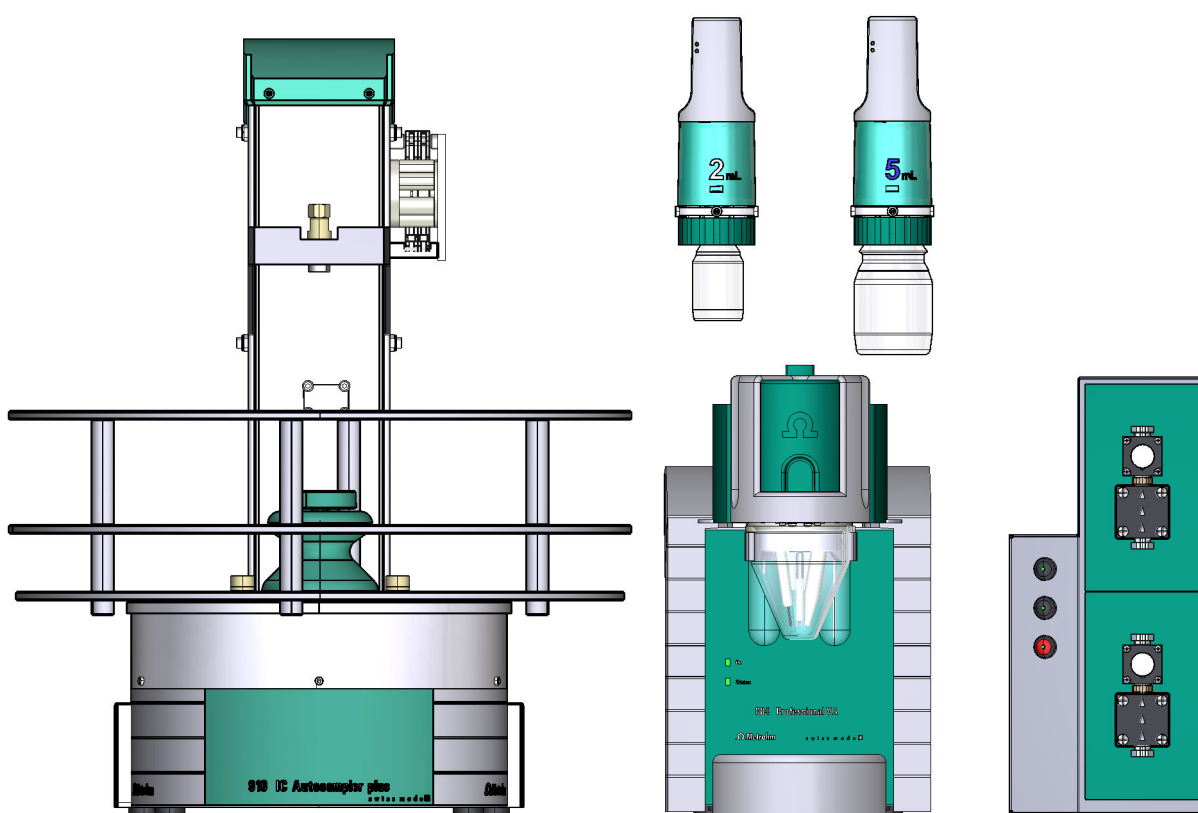


VA tutorial (trace analysis)

6 Automated determination

The following equipment is required for an automated determination:

- 884 Professional VA
- 919 IC Autosampler plus
- 843 Pump Station
- 807 Dosing Unit (one with a 2 mL and one with a 5 mL glass cylinder)
- 800 Dosino
 - 800 Dosino and 807 Dosing Unit with cylinder size 2 mL for dosing standard solution
 - 800 Dosino and 807 Dosing Unit with cylinder size 5 mL for dosing auxiliary solution (electrolyte)



6.1 Configuration

6.1.1 Configuring the instrument

884 Professional VA

(see chapter 4.1.1, page 8).

919 IC Autosampler plus

1 Connecting the device

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

2 Switching on the device

The parameters of the 919 IC Autosampler plus are detected automatically.

The following message appears:

009-108 Save device – The new '919.0020 IC Autosampler plus' device with serial number 'serial number' was detected. – Should it be saved to the device table?

3 Saving the device in the table

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

The **Properties - 919 IC Autosampler plus - 'Device name'** dialog window opens.

4 Changing the device name (optional)

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

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

5 Defining tower parameters

- In the device table in the **Devices** subwindow, select the newly entered instrument and double-click on it.
The **Properties - 919 IC Autosampler plus - 'Device name'** dialog window opens.



- Select the **Tower** tab.


Properties - 919.0020 IC Autosampler plus - 919 IC Autosampler plus
✕

Starting position
MSB 1
MSB 2
MSB 3
GLP

General
Tower
Rack

Tower parameters

Max. stroke path
 mm

Min. beaker radius
 mm

Lift rate
 mm/s

Axial distance
 mm

Swing Head

Serial number

Swing position
 mm

Rinse position
 mm

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 **135** in the **Max. stroke path** field.

6 Defining rack parameters

- Select the **Rack** tab.

The number of the rack currently on the sample changer is displayed in the **Rack name** field. For trace analysis this is usually 6.2041.510.

Properties - 919.0020 IC Autosampler plus - 919 IC Autosampler plus

Starting position | MSB 1 | MSB 2 | MSB 3 | GLP

General | Tower | **Rack**

Rack name: 6.2041.510

Rack code: 010110

Number of positions: 57

Shift rate: 20 %/s

Rack data

Initialize rack

OK Cancel

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

- Select the **Lift positions** tab.

- Enter **125** as a temporary value for **Tower 1** in the **Work position** field.



NOTE

Tower 2 is not available, therefore no values have to be entered under **Tower 2**.

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

Readjusting the work position

For the determination, the entire sample is transferred to the measuring vessel with the peristaltic pump built into 919 IC Autosampler plus. To ensure that this transfer is completed to 100%, the needle has to be correctly adjusted. Proceed as follows:



1 Setting the lift position

- Click on the **Manual** program part.
- Place an empty sample vial in the desired position (1 to 56) on the rack.
- Select **Sample Changers ► 'Device name' (919.0020 IC Autosampler plus) ► Tower 1** in the device selection window.

6.1.3 Configuring dosing units

(see chapter 5.1.3, page 43)

6.1.4 Defining solutions

(see chapter 5.1.4, page 46)

6.2 Automated ASV determination with standard addition

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

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

In this chapter, you will use a method template to create a method for the automated determination of cadmium and lead with anodic stripping voltammetry and the calibration method 'standard addition'. You will become acquainted with the basic functions and the structure of a method using this method template.

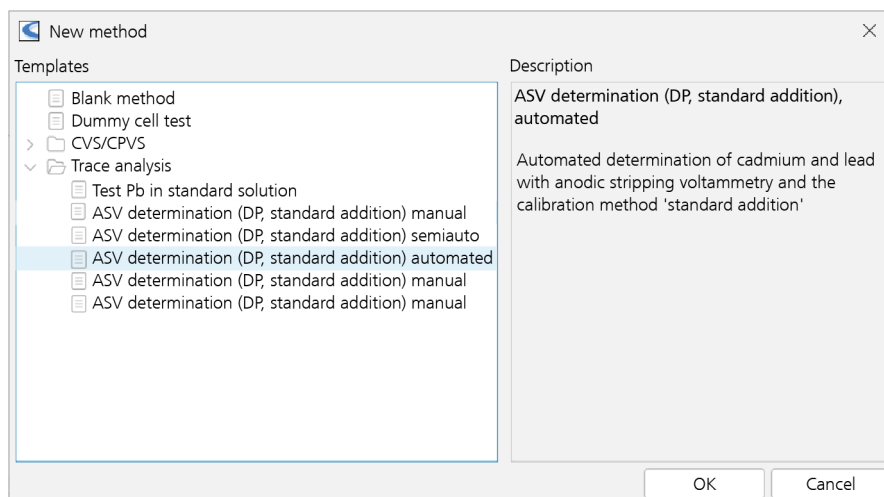
6.2.1 Creating a method

6.2.1.1 Loading a method template



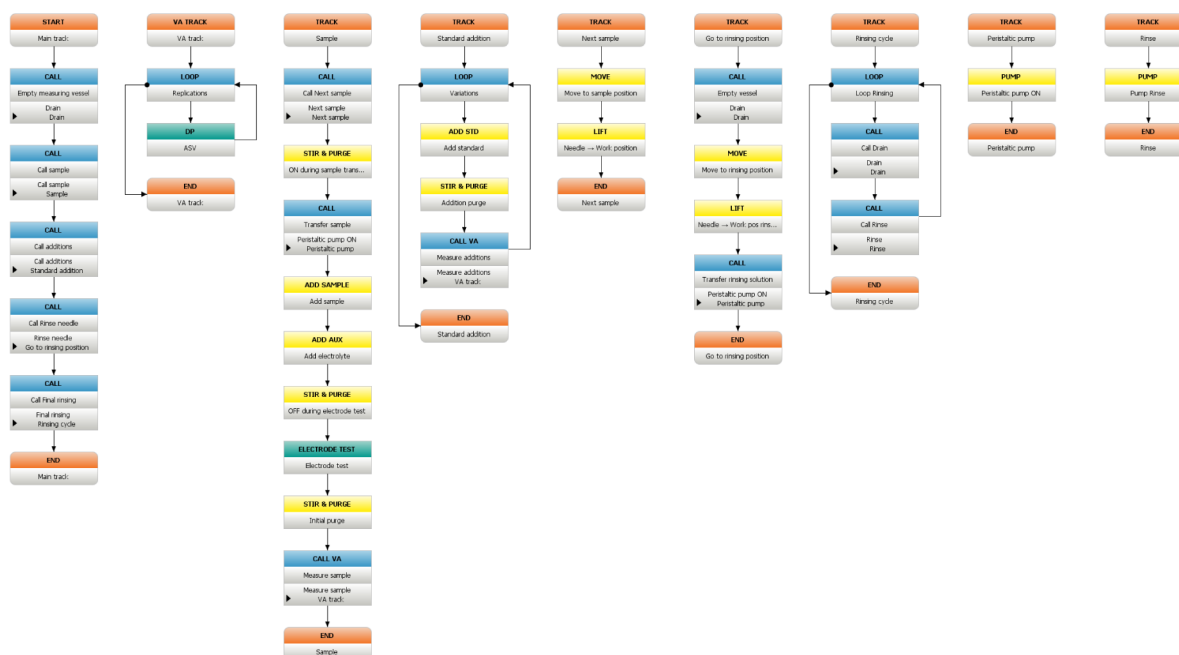
1 Click on the icon of the **Method** program part.

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



- 3** Under **Templates ► Trace analysis**, select **ASV determination (DP, standard addition), automated** in the left-hand part of the window and click on **[OK]**.

The method template opens.



The evaluation does not differ from that of a manual or semiautomated determination with standard addition.

The method run of the automated ASV determination largely corresponds to the procedure of the manual ASV determination (see chapter 4.2.1.1, page 10) and the semiautomated ASV determination (see chapter 5.2.1.1, page 47). Additional tracks and commands

are needed to control the sample changer and to automatically empty and rinse the measuring vessel.

Compared with the semiautomated determination, the method run contains the following additional tracks:

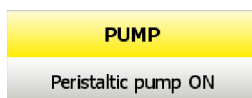
Table 2 Tracks

Track	Function
Next sample	The Next sample track is used to move to the next sample position on the rack of the sample changer and to lower the needle into the sample.
Go to rinsing position	The Go to rinsing position track is used to rinse the transfer tubing between sample changer and measuring vessel to prevent carry-over between samples.
Rinsing cycle	The Rinsing cycle track is used to empty and rinse the measuring vessel after the measurement has ended. The procedure is repeated for as many times as defined in the LOOP - LOOP Rinsing command.
Peristaltic pump	The Peristaltic pump track is used to transfer the sample into the measuring vessel using the peristaltic pump built into the sample changer.
Rinse	The Rinse track is used to switch on the external pump for rinsing the measuring vessel.
Drain	The Drain track is used to switch on the external pump for emptying the measuring vessel.
Shut off	The Shut off track is used to stop the stirrer and the nitrogen supply. In addition, all pumps are deactivated and the needle of the sample changer is moved to the home position.
Series start track	The Series start track is used to initialize the sample rack. This means that the rack and the lift are reset, the rack code is read out and the respective rack data is transferred to the sample changer.

6.2.1.2 Description of the method

The method for the automated determination of cadmium and lead with standard addition consists of the following steps:

1. Empty the measuring vessel
2. Add and purge sample and electrolyte with automation
3. Measure the sample
4. Add and purge standard solution with automation
5. Measure the single-spiked solution
6. Add and purge standard solution once again with automation
7. Measure the double-spiked solution



Switches on the peristaltic pump of the sample changer for a predefined time. This causes the sample to be pumped from the sample changer into the measuring vessel via the transfer tubing.

**NOTE**

The application-specific operation time of the peristaltic pump has to be adjusted to the sample volume to be transferred in the **Duration** field. The time must be chosen in such a way that 100% of the sample volume can be safely transferred.

The addition of the auxiliary solution (electrolyte) via the Dosino, along with the electrode test and the purging of the measuring solution, are done in the same way as in semiautomated (see chapter 5.2.1.2, page 49) or manual determination, respectively (see chapter 4.2.1.2, page 12).

Switches the stirrer and the purging off.

**Measuring the sample**

The sample is measured in the same way as in the manual ASV determination (see "Measuring the sample", page 13).

Adding and purging a standard solution automatically

The automatic addition of the standard solution via a Dosino is done in the same way as in the semiautomated determination (see chapter 5.2.1.2, page 49).

Measuring the single-spiked solution

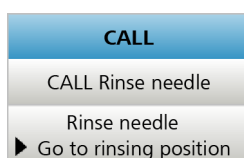
The single-spiked sample is measured in the same way as in the manual ASV determination (see "Measuring the single-spiked solution", page 14).

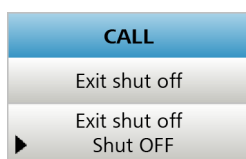
Measuring the double-spiked solution

The double-spiked sample is measured in the same way as in the manual ASV determination (see "Measuring the double-spiked solution", page 14).

Rinsing the transfer tubing

Calls the **Go to rinsing position** track.





Finishing the measurement

Calls the **Shut off** track.



Deactivates the two external pumps for emptying and rinsing of the measuring vessel.



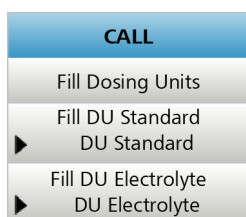
The arm of the sample changer with the needle moves to the home position.



Deactivates the stirrer and the purging of the measuring solution.



Closes the main valve of the 884 Professional VA for the nitrogen supply.



Calls the tracks for filling the Dosinos (*see chapter 5.2.1.2, page 49*).

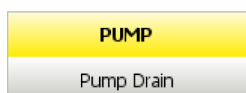
6.2.1.3 Defining command parameters



NOTE

For more information on command parameters, observe *chapter 4.2.1.3 on page 15* and *chapter 5.2.1.3 on page 50*.

In addition to the command parameters already described in the chapters on the manual and semiautomated determination, the pump times of the peristaltic pump and the external pumps also need to be defined. Proceed as follows:



- 1 Double-click on the **PUMP - PUMP Drain** command.

The **PUMP - PUMP Drain** dialog window opens.

- 2 Enter the desired pump time in the **Duration** field. The table below is a guideline for the pump time.

6.2.1.4 Defining the evaluation

(see chapter 4.2.1.4, page 18)

6.2.1.5 Performing a method check

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

- 1 Click on the **File ► Method check** menu or the  icon.
The method is checked. When the check has ended a message appears indicating any errors.
- 2 Confirm the message with **[OK]**.
- 3 Correct errors, if any.
- 4 Repeat the method check until the message **013-118 Method test ok** appears.

6.2.1.6 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 the name for the method in the **Method name** field (e.g. **Determination of Cd and Pb - automated**).
- 3 Click on **[Save]**.

6.2.2 Creating a sample table

Filling the sample rack

The 6.2041.510 sample rack used comprises 56+1 positions. The positions 1–28 are provided for the samples and the positions 29–56 for the rinsing solutions.

The method template has been devised for the 6.2041.510 rack. Generally, any sample position may be used. The important thing is that for each sample there is a rinsing solution available in the corresponding position. This must be positioned 28 positions after the sample. Example:

- The rinsing solution for sample 1 must be on position 29 (1+28).
- The rinsing solution for sample 3 must be on position 31 (3+28).



Creating a sample table

- 1 Switch to the **Workplace** program part.
- 2 Select the **Determination series** tab in the **Run** subwindow.

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	ID2	ID3	Sample type	Sample position	Sample
▶ *							

Edit Sample table Loaded

- 3 Open the **Edit line - Working sample table - Workplace 'Name'** dialog window using the **[Edit] ▶ Edit line** button.
- 4 In the **Method** field, select the method created from the method template (e.g. **Determination of Cd and Pb - automated**).

Edit line - Working sample table - Workplace

Method: Determination of Cd and Pb - automated

ID1: Sample

ID2: _____

ID3: _____

Sample type: Sample

Sample position: 1

Sample amount: 10

Analytical volume: _____

Dilution volume: _____

Sample amount unit: mL

Line: 1 of 1

Apply Close

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	Determinati...	Sam...			Sample	1	10	mL
2	Determinati...	Sam...			Sample	2	10	mL
3	Determinati...	Sam...			Sample	3	10	mL
4	Determinati...	Sam...			Sample	4	10	mL
5	Determinati...	Sam...			Sample	5	10	mL
▶ *								

Edit ▼ | Sample table ▼ | Loaded | ASV determination (modified)

6.2.3 Carrying out a determination

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



- 1 Click on the icon of the **Workplace** program part.
- 2 Select the **Determination series** tab in the **Run** subwindow.
- 3 Load the previously saved sample table **ASV determination** using the **Sample table ► Load...** button.
- 4 Fill the sample rack with sample and rinsing solution according to the sample table.
- 5 Ensure that the dosing units to be used are filled with the corresponding solutions (electrolyte, standard).
- 6 Press **[Start]** to start the analysis.

▶ Start

The analysis is started. The sample is automatically transferred to the measuring vessel. Auxiliary solution and standard are automatically dosed at the specified point in the run. At the end of the determination, the measuring vessel is emptied and rinsed. After the analysis

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.

- 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 curves

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.

- Enter the value **2** in the **Line thickness** list box.
- Click on **[OK]**.

3 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]**.

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:

- Adjusting peak detection
- Adjusting baselines and base points
- Adjusting concentration and volume of standards
- Adjusting the volume of auxiliary solutions

3 Recalculating

- Close the **Method editor** dialog window with **[OK]**.
- 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** sub-window on the **Results overview** tab.

4 Applying the changes to the database

Exit the **Reprocessing** dialog window with **[OK]** in order for the changes to be applied to the database.

7.3.3 Changing baselines and base points in the method

1 Opening reprocessing

- Open reprocessing (*see chapter 7.3.1, page 80*).
- Click on the **Modify method** button on the **Method** tab in the **Modifications** subwindow.
The **Method editor** dialog opens.
- Select the **Baselines** tab in the **Evaluation - Substances** sub-window.

2 Adjusting baselines and base points

- Select the substance in the table. Open the **Substances - Base-line** dialog using the **Edit ► Properties...** menu. Alternatively, double-click on the line of the substance.

- Adjust the parameterization as needed.
- Close the dialog window with **[OK]**.

- Confirm with **[OK]**.

4 Recalculating

- Close the **Method editor** dialog window with **[OK]**.
- 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** sub-window on the **Results overview** tab.

5 Applying the changes to the database

Exit the **Reprocessing** dialog window with **[OK]** in order for the changes to be applied to the database.

7.3.6 Adjusting a sample amount and volume of auxiliary solutions



NOTE

The volume of an auxiliary solution can be changed only in manual determinations. If the auxiliary solution was dosed automatically, then no changes can be made afterwards.

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

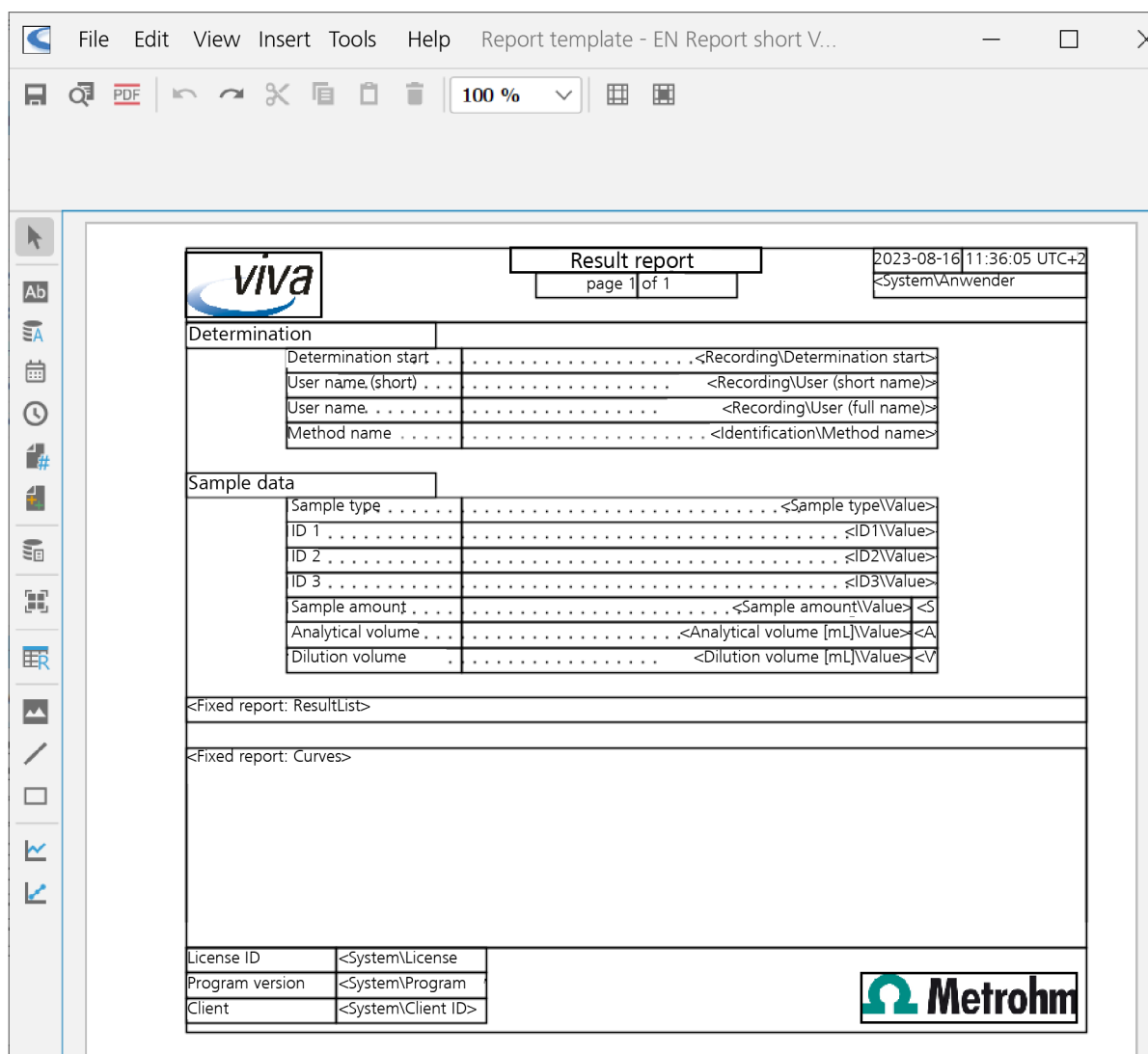
Proceed as follows to edit the **EN Report short** report template:

- 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 V3_0** report template.
- 6 Click on **[Open]**.

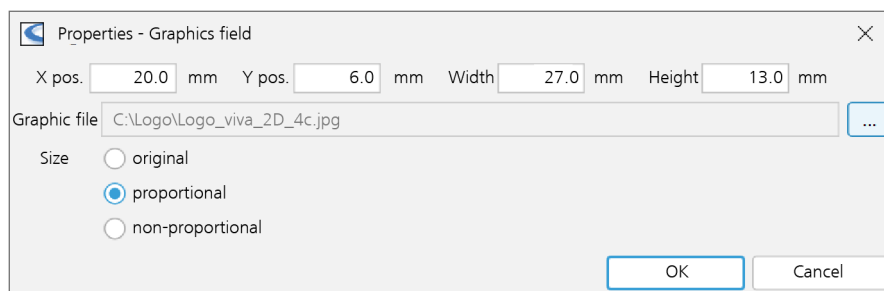
The program window with the selected report template opens.



Replacing an image

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

The properties window for the graphics field opens automatically.

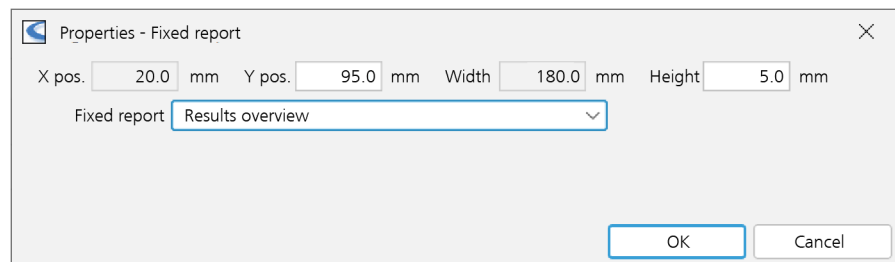


- 2 Open the dialog window for selecting the new graphics file by clicking on .
- 3 Select the desired new graphics file in JPG or PNG format and confirm with **[OK]**.
- 4 Adjust the position, width, height and size of the image.
- 5 Close the properties window with **[OK]**.

Inserting a new fixed report

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

The properties window for the fixed report opens automatically.



- 2 Select the **Configuration used** option in the **Fixed report** field.
- 3 Close the properties window with **[OK]**.

Saving the report template

- 1 Click on the **File ► Save as...** menu item.
The **Save report template** dialog opens.
- 2 Enter a name, e.g. Short report, for the new report template and click on the **[Save]** button.
The report template is saved under the specified name.

