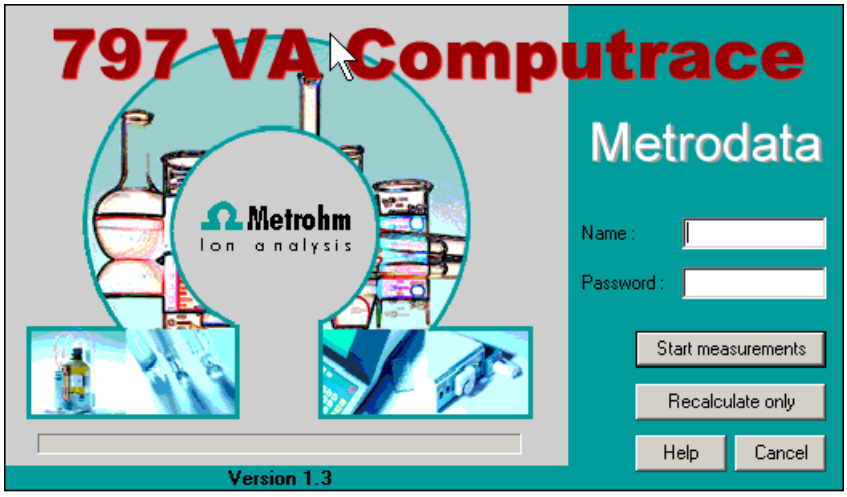
# 797 VA Computrace




Software Version 1.3.x

Manual
8.797.8002EN

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## Software Version 1.3.x

## Manual

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

Documentation in additional languages can be found on *http://products.metrohm.com* under **Literature/Technical documentation**.

# Table of contents

# 1 Introduction

## 1.1 Purpose of program

«797 VA Computrace Software 1.3.x» is the name of the control software for the PC-controlled 797 VA Computrace System for voltammetric analysis. This system consists of the following parts:

1.797.0010 **VA Computrace Stand** with accessories

6.2151.020 **USB Cable**

6.6053.030 **797 VA Computrace Software 1.3.x**

For a detailed description of the hardware components of the 797 VA Computrace System, see the **797 Hardware Manual**.

This **797 Software Manual** describes the features and operation procedures of the 797 VA Computrace Software 1.3.x, which comprises the clearly arranged user interface with a task bar that can be clicked for control of the instrument, method development and the recording and evaluation of the voltammograms.

Depending on the objective, the 797 VA Computrace Software 1.3.x can be used in **two different operating modes**:

- The **exploratory mode** for **qualitative analysis** is suitable for practice-oriented voltammetry training at universities, technical colleges and in plants. It allows the user to apply ten different VA measurement techniques and to compare their results.
- The **determination mode** is used for **quantitative analysis** of inorganic or organic substances. Calibration can be done via standard addition or calibration curves. Additionally, a multitude of electroplating bath calibration techniques are available. Signal evaluation and concentration calculation are automatic. On completion of the measurement, a report can be compiled to suit individual requirements and printed out. The most important methods for the determination of metals or other substances can be called up directly. All curves appearing on the screen, i.e. voltammograms and calibration curves plus the results can be transferred to other Windows applications via the Windows Clipboard. Data export in ASCII format is also possible.

## 1.2 General information

### Hardware requirements for the PC

| | |
|---|---|
| Computer | Pentium III with 1 GHz or higher |
| Operating system | Windows™ 2000, Windows™ XP Professional, Windows™ Vista Professional |
| Free space on hard disk | 40 MB for program files |
| Working memory RAM | 256 MB |
| Graphics resolution | 1024×768 or more |
| Interface | 1 free USB connection |
| Printer | Any printer supported by operating system |

**Note**: Set the screen saver to "None" and deactivate any energy saving features. Additionally, do not use several other programs together with VA Computrace.

### Demo version

If the 797 VA Computrace Software 1.3.x (6.6053.030) is installed on a PC without installation of VA Computrace stand, this software can be used as a demo version, which is restricted to the recalculation of determination or signal files.

### Registration

Please send us your **8.797.8027 Registration card** as soon as possible. Only registered users will get updated program versions at a special price.

## 1.3 Installation

### Installation of the hardware

1. Switch on PC and start operating system (Windows™ 2000, Windows™ XP Professional, Windows™ Vista Professional) without connection of the VA Computrace via USB cable.
2. Insert installation CD into CD drive.
3. If the autorun option for the CD drive is disabled, select **<Start>** and **Run**. Browse for the **Setup.exe** file on the installation CD and click on **<OK>**.
4. Click on "**797**" and follow the instructions given in the setup program.
5. The software package will be installed in the desired directory (the default directory is **Program Files/Metrohm/797 VA Computrace**). In addition to the program files, the following folders are installed:

**Data**

Folder for storage of new signal (***.sig**) and determination files (***.dth**). In Windows Vista, this folder is stored in **ProgramData/Metrohm/797 VA Computrace**.

**Demo data**

Folder containing signal and determination file examples. The subfolder CVS contains examples for the electroplating bath analysis, the subfolder **Practical Voltammetry** all examples of the **8.757.5003 Metrohm Monograph "Practical Voltammetry"**, which is available from Metrohm on request. In Windows Vista, this folder is stored in **ProgramData/Metrohm/797 VA Computrace.**

**Note:** The signal and determination file examples are installed as **read-only**.

**Firmware**

Folder for storage of new files (*.exe) for a firmware update.

**Hardware**

Folder for storage of firmware files (*.x).

**Method**

Folder for storage of method files (***.mth**). You find some basic examples in the **Method** folder and more examples in the subfolders **Application Bulletin**, **Application Notes** and **CVS**. In Windows Vista, this folder is stored in **ProgramData/Metrohm/797 VA Computrace.**

**XML**

Folder for storage of files which are needed for viewing XML files in a browser.

6. Connect VA Computrace to the PC using the **6.2151.020 USB cable**. The PC detects a new USB device and starts the setup wizard. Insert installation CD into CD drive and follow the wizard instructions always selecting the recommended default options.
7. Start the 797 VA Computrace software.
8. In the login-window click **Start measurements** without entering anything for Name and Password.

## Installation of Dosing Devices

Up to seven Dosing Devices (possible: **700/800 Dosino**, **685/805 Dosimat**) can be connected to the MSB ports of the 797 VA Computrace stand or (in case you installed one) the 846 Dosing Interface.

Connection of Dosing Devices:

1. Switch off the 797 VA Computrace stand.

2. If required, connect the 846 Dosing Interface to one of the USB ports of the 797 VA Computrace or the PC. Connect the 846 Dosing Interface to the mains supply.
3. Connect the Dosing Device via MSB connection to the 797 VA Computrace stand or the 846 Dosing Interface.
4. Switch on the 797 VA Computrace stand.
5. Open 797 VA Computrace Software 1.3.x and log in.
6. Open the **GENERAL SETTINGS** window in **MAIN WINDOW / Settings**, activate the **Dosinos** (or **Dosing Interface**) tab and click the 

button.
7. Choose for menu item **Prep/Empty via port** the port which is used for the functions "Prep" and "Empty". Recommended is **Port 3** (doesn't lead to the measuring cell but to a waste container). Using **Port 3** you can reduce contamination of the measuring cell and the electrode. Moreover the dosing unit can be rinsed and emptied faster.

   **Note:** If you choose **Port 3** for menu item **Prep/Empty via port**, you must install an **FEP Tubing Connection 6.1805.530** from **Port 3** to a waste container.

8. Choose the number for **No. of Prep cycles**. It defines the number of "Prep-Cycles" conducted before starting the measurement or before starting the sample table.

### Installation of 863 Compact VA Autosampler

For automated voltammetric trace analysis it is possible to connect an **863 Compact VA Autosampler**, a **843 Pump Station** and up to three **Dosing Devices** (four more with a 846 Dosing Interface) to the 797 VA Computrace stand. Proceed as follows:

1. Switch on the PC
2. Connect the **797 VA Computrace stand** and the **843 Pump Station** (Remote 1) using the cable 6.2141.280 (see *797 Hardware Manual*).
3. Connect **863 Compact VA Autosampler** and the **843 Pump Station** (Remote 2) using cable 6.2141.230.
4. Install the accessories on the **863 Compact VA Autosampler** (see *797 Hardware Manual*).
5. Connect the Dosing Devices to the 797 VA Computrace or the 846 Dosing Interface (via MSB).
6. Connect the **797 VA Computrace stand** to the PC (via USB).
7. Switch on the **797 VA Computrace stand**, the **863 Compact VA Autosampler** and the **843 Pump Station**.
8. Set **Method 2** at the **863 Compact VA Autosampler** (see *863 Instructions for Use*).

9. Start the 797 VA Computrace Software 1.3.x.
10. Set hardware settings for the **863 Compact VA Autosampler**.
11. Check the checkbox for **Relay box / Pump Station** on the **Automation** tab of the **GENERAL SETTINGS** window, and define the default settings for the pumps.
12. Set hardware settings for **Dosing Devices**.
13. Define the addition or predose solution in the **DOSINOS** window.

### Installation of 838 Advanced Sample Processor

To automate Electroplating bath analysis with CVS it is possible to connect an **838 Advanced Sample Processor**, a **843 Pump Station** and up to three **Dosing Devices** (four more with a 846 Dosing Interface) to the 797 VA Computrace stand. Additionally, up to three Dosing Devices can be connected to the **838 Advanced Sample Processor** via MSB (but they can't be controlled by the 797 Software in that case). Proceed as follows

1. Switch on the PC.
2. Connect the **797 VA Computrace stand** and the **843 Pump Station** (Remote 1) using cable 6.2141.290 (see 797 Hardware Manual).
3. Connect the **838 Advanced Sample Processor** and the **843 Pump Station** (Remote 2) using cable 6.2141.290.
4. Install the accessories on the **838 Advanced Sample Processor** (see *797 Hardware Manual*).
5. Connect the Dosing Devices to the 797 VA Computrace or to the 846 Dosing Interface (or the 838 Advanced Sample Processor) (via MSB).
6. Connect the **797 VA Computrace stand** to the PC (via USB).
7. Switch on the **797 VA Computrace stand**, the **838 Advanced Sample Processor** and the **843 Pump Station**.
8. Specify a suitable method at the 838 Advanced Sample Processor and adjust it if necessary (see *838 Manual*).
9. Start the 797 VA Computrace Software 1.3.x.
10. Choose the **838 Advanced Sample Processor** for menu item **Sample Processor** on the **Automation** tab of the **GENERAL SETTINGS** window, and check the field **Relay box / Pump Station** on the **Automation** tab of the **GENERAL SETTINGS** window.
11. Make hardware settings for the **838 Advanced Sample Processor**, and define the default settings for the **843 Pump Station**.

12. Make hardware settings for **Dosing Devices**.
13. Define the addition or predose solution in the **DOSINOS** window.

### Deinstallation

1. Select **<Start>** / **Settings / Control panel.**
2. Double-click the **Software** icon.
3. Select **797 VA Computrace** in the list and click on **<Add/remove>**. Select the **Remove** option and click on **<Next>**. All program files and icons should be removed.

## 1.4 Overview of program windows

797 VA Computrace consists of different windows whose functionality is linked together. The different windows are:

| | |
|---|---|
| **MAIN WINDOW** | File administration, printing, mode selection, opening of other program windows, utilities, login and user rights, settings, window handling |
| **EXPLORATORY SPECIFICATIONS** | Method definition for exploratory mode |
| **EXPLORATORY CURVES** | Display of exploratory mode curves and curve evaluation |
| **WORKING METHOD SPECIFICATIONS** | Definition of the working method for determination mode |
| **MONITOR** | Start of determinations, live display |
| **DETERMINATION CURVES** | Display of determination and calibration curves, modification and recalculation of determinations |
| **RESULTS** | Display of determination reports |
| **SAMPLE TABLE** | Display of sample table (only available if "863 Compact VA Autosampler", or "838 advanced Sample Processor" and **Use sample table** is selected for **Working method source** on the **Automation** tab of the **GENERAL SETTINGS** window) |
| **COMPUTRACE CONTROL** | Manual control of 797 VA Computrace stand |
| **DOSINO CONTROL** | Manual control of Dosing Devices (Possible: 700/800 Dosino, 685/805 Dosimat) |

| | |
|---|---|
| **PUMP CONTROL** | Manual control of siphoning and rinsing pump |
| **FILM DEPOSITION** | Program for Hg film deposition on solid state electrodes |
| **CLEANING PROCEDURE** | Program for cleaning procedures for solid state electrodes |

## 1.5 Overview of file types

The following file types are produced by the 797 VA Computrace Software 1.3.x:

***.csv** **Text file in .csv-format** (ASCII file) for data export
Results can be stored as .csv-file. CSV stands for comma separated values, i.e. the entries of a file are separated by a comma.
Text files in .csv-format suit perfectly for the import in spreadsheets like Microsoft Excel.
The .csv-files are also used for data import into a LIMS (Labor Information Management System).

***.dth** **Determination file** (binary file)
Contains determination data and method.
The ***.dth** file is stored automatically in the **Data** folder if the autosave option is enabled in the **GENERAL SETTINGS** window.

***.mth** **Method file** (binary file)
Contains the method.

***.sig** **Signal file** (binary file)
Contains exploratory data and exploratory method. The ***.sig** file is stored automatically in the **Data** folder if the autosave option is enabled in the **GENERAL SETTINGS** window.

***.spt** **Sample table file** (binary file)
Contains sample table data.

***.txt** **Text file** (ASCII file) for data export
A ***.txt** file is produced if methods, results, measurement points of determination files or measurement points of signal files are exported.
In the case of **methods**, this data file contains a block of working method and sample data followed by the voltammetric parameters block and a peak evaluation block. On the bottom, it has a block substance evaluation, a block baseline, a block solutions and a block export options.
In the case of **results**, this data file contains a block of determination data followed by a method and a sample data block. On the bottom are a substance evaluation, a solutions and a final re-

sults block.
In the case of **determination point export**, this data file contains a block of the used method parameters followed by the sweep blocks of X and Y values each preceded by VR number and number of measurement points.
In the case of **extended determination point export**, this data file contains a block of the used method parameters followed by the voltammetric parameters, a block peak evaluation, a block baseline, a block solutions, a block export options and the sweep blocks of X and Y values each preceded by VR number and number of measurement points.
In the case of **signal points**, this data file contains a block of the used method parameters followed by the sweep block of X and Y values preceded by the number of measurement points.
The ***.txt** files can be imported into spreadsheet programs like Microsoft Excel.

***.xml** **Text file in .xml-format** (ASCII file) for data export
Results can be stored as .xml-file. The three files CT797.css, CT797.xsd and CT797.xsl will be exported along. They are needed for viewing the results in a web browser.
The .xml-files are also used for data import into a LIMS (Labor Information Management System).

## 1.6 Context sensitive menus

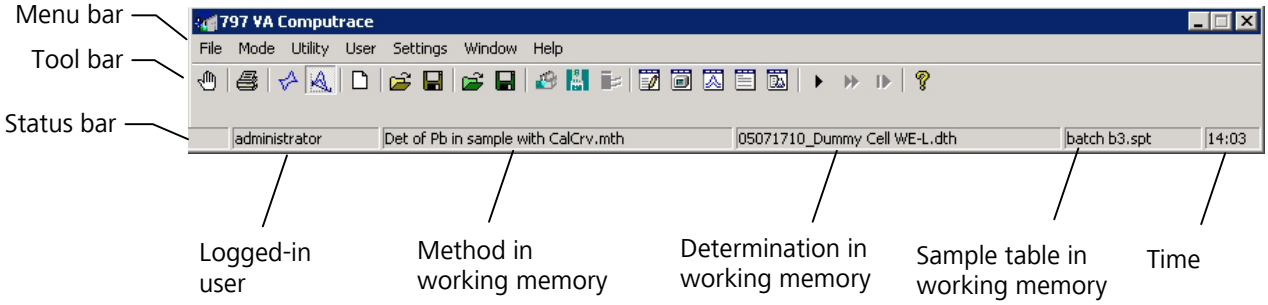
Most of the menu functions of the program windows are also accessible by clicking on the desired window or item and pressing the **right mouse button**. The pop up windows have different contents and functions depending on the selected active window or item type.

# 2 Main window

## 2.1 Main window overview

### Main window elements

The **MAIN WINDOW** is the center of the 797 VA Computrace Software 1.3.x. Its elements are the menu bar, the tool bar and the status bar indicating user, method and determination.




### Main window menus

| | |
|---|---|
| **File** | Loading, saving and export of method, determination and signal files; printing of reports and curves, loading and saving of determinations with the Autodatabase |
| **Mode** | Switching between exploratory and determination mode |
| **Utility** | VA Computrace stand control; Dosino control; pump control; film deposition and cleaning procedure for solid state electrodes |
| **User** | Login, user rights entry and overview |
| **Settings** | General settings for saving, Autodatabase, automation, Dosing Devices, relay box, remote control, GLP |
| **Window** | Tiling, opening and closing of program windows |
| **Help** | Call context-sensitive Help and Help contents |

## Main window icons

It depends on the selected mode (exploratory or determination) whether the following icons are displayed in the **MAIN WINDOW** or not.


Exit the VA Computrace program.


Print reports and curves.


Switch to exploratory mode.


Switch to determination mode.


Load default parameters for exploratory or determination mode.


Load existing method or signal file.


Save method or signal file.


Load existing determination file.


Save determination file.


Manual control of 797 VA Computrace stand.


Manual control of Dosing Devices connected to the 797 VA Computrace stand.


Manual control of pumps.


Open or close **WORKING METHOD SPECIFICATIONS** or **EXPLORATORY SPECIFICATION** window.


Open or close **DETERMINATION CURVES** window.


Open or close **MONITOR** window for determinations.


Open or close **EXPLORATORY CURVES** window.


Open or close **RESULTS** window for determinations.


Open or close **SAMPLE TABLE** window.


Start measurement.


Stop measurement.


Hold measurement.

 Continue measurement.

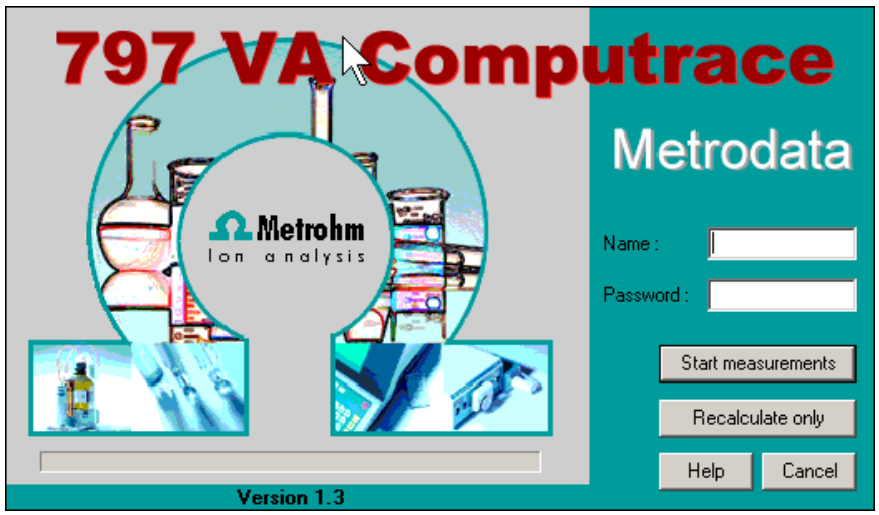
 Go to next step in operation sequence.

 Help.

## 2.2 Starting/closing the program

### Starting the VA Computrace program


**Start the Program**
Double-click the **797 VA Computrace** icon or the **Ct797.exe** file to start the 797 VA Computrace program. The **797 VA COMPUTRACE LOGIN** window appears.




Enter **Name** and **Password** and select the desired option **Start measurements** for starting measurements or **Recalculate only** for recalculation.

**Note**: After software installation, the program can be started without entering **Name** and **Password**. For the definition of users, see *section 2.6 User rights*.

### Closing the VA Computrace program

**MAIN WINDOW / File / Exit**
Exit the VA Computrace program.

The program is also quit by clicking on  in the upper right part of the **MAIN WINDOW**.

## 2.3 File menu

### Method files

Method files (***.mth**) contain all the specifications and parameters for running a determination. They can only be loaded or saved in the determination mode.

**MAIN WINDOW / File / New method (Ctrl+N)**
Load a standard template with the selected mode for creating a new method.

**MAIN WINDOW / File / Load method (Ctrl+O)**
Load an existing method file. Normally, method files are stored in the **Method** folder.

**MAIN WINDOW / File / Save method (Ctrl+S)**
Save the current method loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save method as ...**
Save the current method loaded in the working memory in a new file. Enter name and directory for storage of the method file.

**797 VA COMPUTRACE / File / Export method ...**
Save the current method loaded in the working memory into an ASCII file (extension ***.txt**). This file contains all method parameters.

### Determination files

Determination files (***.dth**) contain the measurement data and the specifications of the method used for the determination. They can only be loaded or saved in the determination mode.

**MAIN WINDOW / File / Load determination**
Load an existing determination file. Normally, determination files are stored in the **Data** folder.

**MAIN WINDOW / File / Save determination**
Save the current determination loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save determination as ...**
Save the current determination loaded in the working memory in a new file. Enter name and directory for storage of the determination file.

**MAIN WINDOW / File / Export determination points**
Save the measurement points of all sweeps of the current determination loaded in the working

memory into a data file (extension ***.txt**). This data file contains a block of the used method parameters followed by the sweep blocks of X and Y values each preceded by VR number and number of measurement points. The data files can be imported into spreadsheet programs like Microsoft Excel.

**MAIN WINDOW / FILE / EXPORT EXTENDED DETERMINATION POINTS...**

In the case of **extended determination point export**, this data file contains a block of the used method parameters followed by the voltammetric parameters, a block peak evaluation, a block baseline, a block solutions, a block export options and the sweep blocks of X and Y values each preceded by VR number and number of measurement points.

**MAIN WINDOW / FILE / EXPORT RESULTS / CURRENT DETERMINATION...**

Save the results report of the current determination loaded in the working memory into an ASCII file with extension ***.txt**, ***.csv**, or ***.xml**. This file can be imported into spreadsheet programs like Microsoft Excel (*.txt und *.csv) or in a LIMS (*.csv and *.xml).

**MAIN WINDOW / FILE / EXPORT RESULTS / DETERMINATIONS...**

Save the results report of the selected determination into an ASCII file with extension ***.txt**, ***.csv**, or ***.xml**. This file can be imported into spreadsheet programs like Microsoft Excel (*.txt und *.csv) or in a LIMS (*.csv and *.xml).

## Export/Import of Data with Autodatabase

**MAIN WINDOW / File / Export To Database / Current Determination**

Export the data from the current determination to the database.

Procedure after starting **Export To Database / Current Determination**:
If **Ask for database file..** is activated for **Manual Transfer Mode** on the **Database** tab in the **GENERAL SETTINGS** window, the **SELECT DETERMINATION DATABASE FILE** window opens, and you choose the database file where the current determination is stored.
If **Use default database file..** is activated, the current determination is stored automatically in the **Default database file**.

**MAIN WINDOW / File / Export To Database / Determination Files..**

Export previously saved determination data to the database.

Procedure after starting **Export To Database / Determination Files..**
The **Select Determination Files** window opens, choose the determination(s) you want to export and click <Open>.
If **Ask for database file..** is activated for **Manual Transfer Mode** on the **Database** tab in the **GENERAL SETTINGS** window, the **SELECT DETERMINATION DATABASE FILE** window opens, and you choose the database file where the selected determination(s) is(are) stored.
If **Use default database file..** is activated, the selected determination(s) is(are) stored automatically in the **Default database file**.

**Note:** If you work with the new program version «797 VA Computrace Software 1.3.x» and try to export to a database created with an old program version «797 VA Computrace Software 1.X», an error message appears (see *Error message "Please select a new database file"*). If you work with the «797 VA Computrace Software 1.3.x», export only to databases created with «797 VA Computrace Software 1.3.x».

**MAIN WINDOW / File / Import from Database..**
Import a determination from the database.

**Note:** Before importing: In your Autodatabase software, open database file from which you want to export a determination. Open next a report template in the report window of your Autodatabase software. Select then the determination in the **EXPLORER** window first, before clicking on the **REPORT** window to activate it (highlighted).

## Signal files

Signal files (***.sig**) contain the measurement data and specifications of a signal recorded in the exploratory mode. They can only be loaded or saved in this mode.

**MAIN WINDOW / File / New parameters**
Load default parameters for selected electrode and measurement mode.

**MAIN WINDOW / File / Load signal**
Load an existing signal file. Normally, signal files are stored in the **Data** folder.

**MAIN WINDOW / File / Save signal as ...**
Save the current signal loaded in the working memory in a new file. Enter name and directory for storage of the signal file.

**MAIN WINDOW / File / Export signal points**
Save the measurement points of the sweep of the current signal loaded in the working memory into a data file (extension ***.txt**). This data file contains a block of the used method parameters followed by the sweep block of X and Y values preceded by the number of measurement points. The data files can be imported into spreadsheet programs like Microsoft Excel.

### Printing of reports and curves

**MAIN WINDOW / File / Print (Ctrl+P)**
Print reports and/or curves. Depending on the mode selection, a window appears for selection of the items to be printed (see *section 4.4 Printing in exploratory mode* for exploratory mode, and *section 5.7 Printing in determination mode* for determination mode).

**MAIN WINDOW / File / Printer setup**
Selection of a printer and definition of paper size and format.

**MAIN WINDOW / File / Print GLP report**
Print a GLP report created with the GLP Wizard.

### Program exit

**MAIN WINDOW / File / Exit**
Quit the VA Computrace program.

The program is also quit by clicking on  in the upper right part of the **MAIN WINDOW**.

## 2.4 Mode menu

### Exploratory mode selection

**MAIN WINDOW / Mode / Exploratory**
Switching to the exploratory mode for recording and displaying of signals (see *section 4*).

### Determination mode selection

**MAIN WINDOW / Mode / Determination**
Switching to the determination mode for recor-

ding and displaying of determinations (see *section 5*).

## 2.5 Utility menu

### Computrace control selection

**MAIN WINDOW / Utility / Computrace control**

Start manual control of 797 VA Computrace stand (details see *section 7.1*).

### Dosing Device control selection

**MAIN WINDOW / Utility / Dosino control**

Control of Dosing Devices (Possible: 700/800 Dosinos; 685/805 Dosimats) connected to the 797 VA Computrace stand or to the 846 Dosing Interface (details see *section 7.2*).

### Pump control selection

**MAIN WINDOW / Utility / Pump control**

Start manual control of Pumps connected to the 797 VA Computrace stand. (details see *section 7.3*).

### Film deposition selection

**MAIN WINDOW / Utility / Film deposition**

Start Hg film deposition for solid state electrodes in the 797 VA Computrace stand (details see *section 7.4*).

### Cleaning procedure selection

**MAIN WINDOW / Utility / Cleaning procedure**

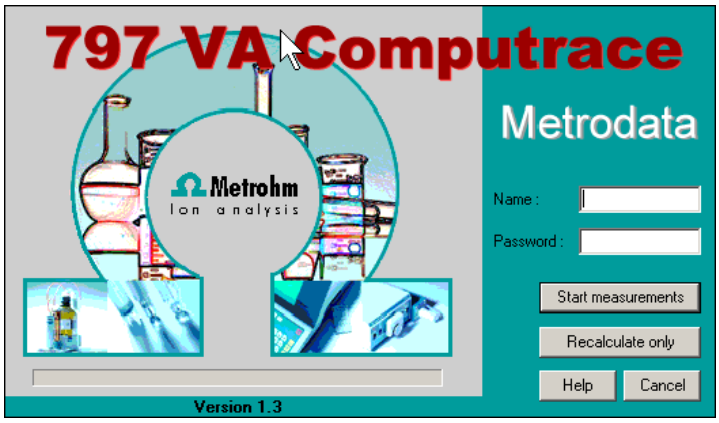
Start cleaning procedure for solid state electrodes in the 797 VA Computrace stand (details see *section 7.5*).

## 2.6 User menu

### Login

**MAIN WINDOW / User / Login**

The **797 VA COMPUTRACE LOGIN** window appears.




Enter the desired **Name** and **Password** to login as a new user and click **OK**.

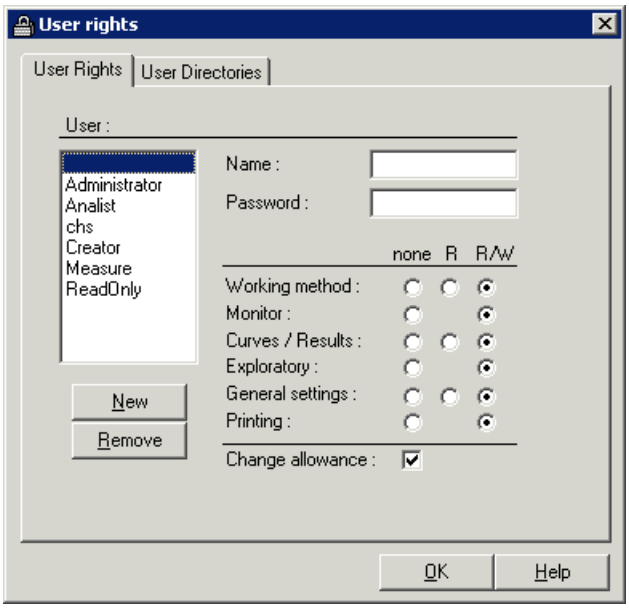
**Note:** In case that the firmware of your 797 VA Computrace stand is version 3.01 or older, the firmware update dialog starts automatically after login. To update the firmware, confirm each step with <**OK**> or <**Next**>. The information about the version of the firmware can be gathered from the window Info (this window can be opened via **MAIN WINDOW / Help / About 797 VA Computrace ...** ).

## User rights

The «VA Computrace» program has a security system based on a list of user rights. For every user or user category, a password and different access levels can be defined. We recommend to make a new user list and enter passwords as a first action after system installation.

**MAIN WINDOW / User / User rights**

The **USER RIGHTS** window appears. It contains the two tabs **User Rights** and **User Directories**.




**User**

List of all users. The user rights are displayed for the selected and highlighted user. The following users with blank passwords are defined as default examples:

**Administrator**
Access to all program parts and allowance to change the user rights.

**Analist**
Read only access to working method, curves/results and general settings.

**Creator**
Only access to Working method and Exploratory mode.

**Measure**
Read only access to working method, curves/results, no access to general settings and printing.

**ReadOnly**
Read only access to working method, curves/results and general settings.

**" "** (empty)
Blank user. Access to all program parts and allowance to change the user rights.

**Name**

Display of user name (read only). For addition of a new user name click the **<New>** button.

**Password [ max. 21 characters ]**
Change password for user. A " * " is displayed for each character entered.

**User rights**

The different user rights options can be changed for the selected user:

**none** No access to this program part.

**R** Permission to read in this program part.

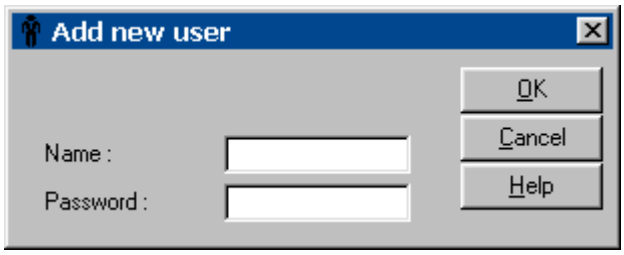
**R/W** Permission to read/write in this program part.

**Change allowance**

Permission to edit the user rights.

New

Add a new user to the users list. The **ADD NEW USER** window appears.




**Name [ max. 13 characters; ]**

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

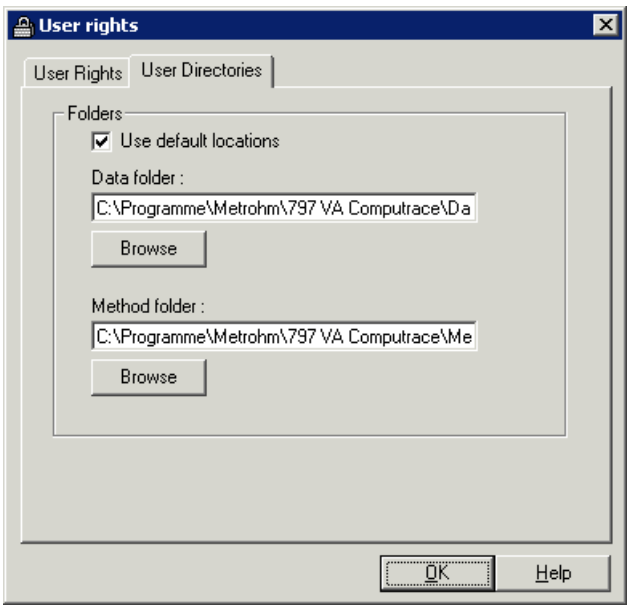
**Password [ max. 21 characters ]**

Enter password for user. A " * " is displayed for each character entered.

Remove

Remove a user from the users list.

**Note:** GLP can only be started if there is no blank user. Blank user has to be removed to apply GLP.



**Use default locations**

Set default directories for **Data folder** and **Method folder**.

**Data folder**

User specific folder for determination and signal files. Use **<Browse>** to change the folder.

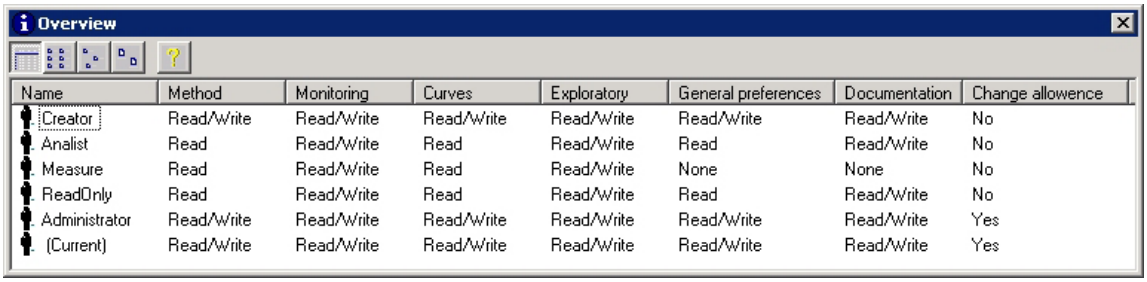
**Method folder**

User specific folder for method files. Use **<Browse>** to change the folder.

### User rights overview

**MAIN WINDOW / User / Overview**

The **OVERVIEW** window displaying the list of all users appears.




 Detailed user list with all user rights.

 User list without user rights.

 User list with small icons.

 User list with large icons.

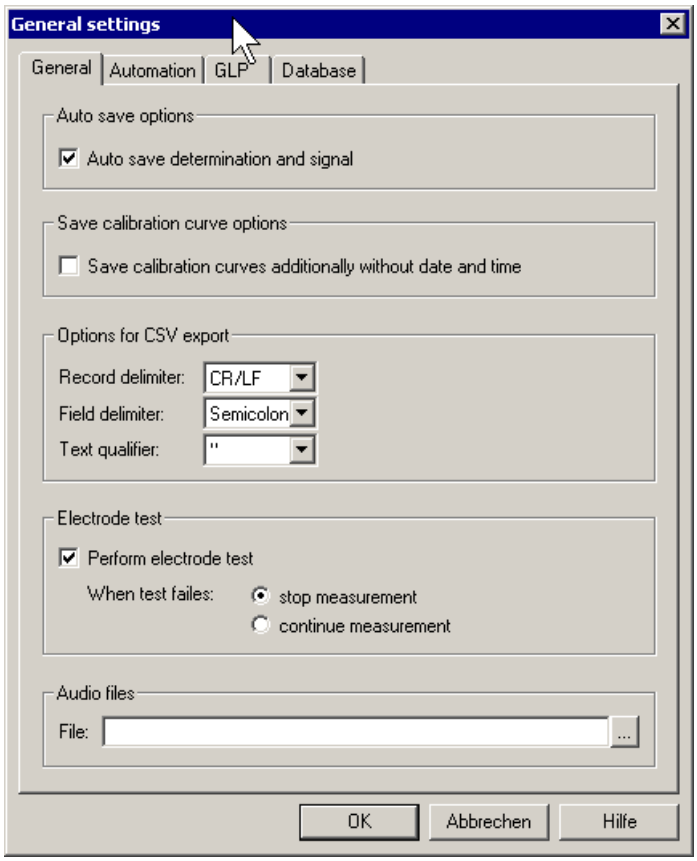
 Help.

## 2.7 Settings menu

### General settings

**MAIN WINDOW / Settings / General Settings**

On the **General** tab of the **GENERAL SETTINGS** window general settings can be defined, e.g. for automatic storage or for conducting electrode tests.




**Auto save options**

**Auto save determination and signal**

If this option is enabled, every signal or determination file is stored automatically in the data folder (defined in the **User Directories** tab of the **USER RIGHTS** window) after the end of the measurement.

**Save calibration curves additionally without date and time**

If this option is enabled, every determination will be saved twice, once with date/time and the defined Sample ID (e.g. "07181430_Calibration-Lead.dth"), and once only with the Sample ID (e.g. "CalibrationLead.dth"). That enables automatically overwriting of files.
Activation of this option enables automatic (re)calibration of methods during an automated sample run with a sample changer. It also enables automatic re-determination of the "Intercept value" with the **LAT** technique for analyzing electroplating baths.
This possibilities apply for the **VA-Calibration** technique "Record calibration curve"; and the electroplating bath **Calibration** techniques "DT Record calibration curve", "LAT Record intercept value" and "RC Record response curve".

**Options for CSV export**

Basic settings for the csv export.

**Record delimiter**

Selection of the characters which will separate the determinations resp. results:

**CR/LF**
Carriage Return and Line Feed (standard)

**CR**
Only Carriage Return

**LF**
Only Line Feed

**Field delimiter**

Selection of the characters which will separate the data fields:

**Semicolon**
Semicolon (standard)

**Comma**
Comma

**Tab**
Tabulator

**Text qualifier**

Selection of the character which defines a string as text:

**"**
Double quote (standard)

**'**
Single quote

**none**
no character

**Electrode test**

Selection of the electrode test settings.

**Perform electrode test**

If this option is activated, an electrode test is conducted automatically before each determination:

**When test fails**

Wahl was bei missglücktem Test geschehen soll:

**stop measurement**
Stop determination.

**continue measurement**
Continue determination.

**Audio files**

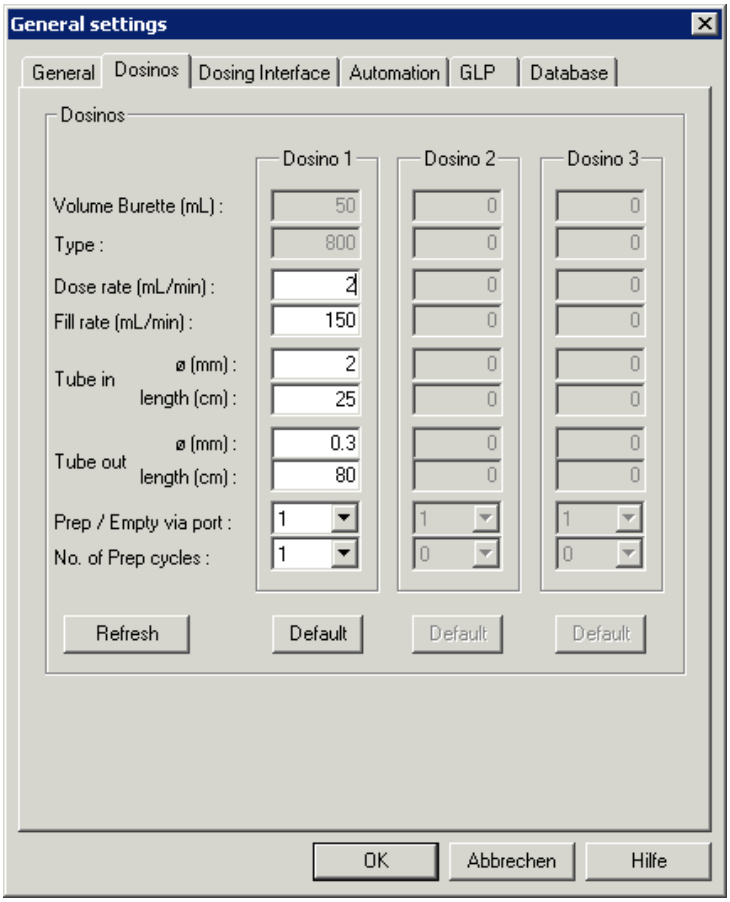
Selection of the sound which should remind a user of taking an action.

## Dosing settings

**MAIN WINDOW / Settings / General Settings**

On the **Dosinos** tab of the **GENERAL SETTINGS** windows, the default settings for Dosing Devices which are connected to the 797 VA Computrace can be defined.

On the **Dosing Interface** tab of the **GENERAL SETTINGS** windows, the default settings for Dosing Devices which are connected to the 846 Dosing Interface can be defined. This tab is only displayed if a 846 Dosing Interface is connected.




**Dosinos / Dosing Interface**

Settings for the Dosing Devices (possible: 700/800 Dosino, 685/805 Dosimat) connected to the 797 VA Computrace stand or the 846 Dosing Interface (details see *section 1.3 Installation of Dosing Devices*).

**Dosino no.**

Defined by the number of the used MSB-port.

| Dosino | Device | MSB |
|---|---|---|
| 1 | 797 VA Computrace | MSB1 |
| 2 | 797 VA Computrace | MSB2 |
| 3 | 797 VA Computrace | MSB3 |

| Dosino | Device | MSB |
|---|---|---|
| 4 | 846 Dosing Interface | MSB1 |
| 5 | 846 Dosing Interface | MSB2 |
| 6 | 846 Dosing Interface | MSB3 |
| 7 | 846 Dosing Interface | MSB4 |

**Volume Burette (mL) [read only]**

Volume of the exchange unit of the Dosing Device.

**Type [read only]**

Which Dosing Device is connected (possible: 700/800 Dosino, 685/805 Dosimat).

**Dose rate (mL/min) [ 0.01 ... 166 mL/min (depending on dosing/exchange unit); 2 mL/min ]**

Dosing rate of the Dosing Device. The dose rate is limited by the 3.333 fold volume of the burette per minute.

---

**Note**: If the diameter of **Tube out** is smaller than 1 mm, the maximum **Dose rate** is generally limited to 4 mL/min.

---

**Fill rate (mL/min) [ 0.01 ... 166 mL/min (depending on dosing/exchange unit); 3 * Volume Burette / min ]**

Filling rate of Dosing Device.

**Tube in**

**ϕ (mm)**

Diameter of the tube going in the Dosing Device (Dosino: Port 2).

**length (cm)**

Length of the tube going in the Dosing Device (Dosino: Port 2).

**Tube out**

**ϕ (mm)**

Diameter of the tube going out the Dosing Device (Dosino: Port 1).

**length (cm)**

Length of the tube going out the Dosing Device (Dosino: Port 1).

---

**Note**: If a tube is removed and replaced by a tube with a different diameter, change first the parameter **Tube (in/out) ϕ (mm)**, and afterwards the parameter **Dose rate (mL/min)**.

---

**Prep / Empty via port [ 1, 3 ; 1 ]**

Choose the port which is used for the functions "Prep" and "Empty". Recommended is **Port 3** (does not lead to the measuring cell but to a

waste container). Using **Port 3** you can reduce contamination of the measuring cell and the electrode. Moreover the emptying can be conducted faster.

**Note:** If you choose **Port 3** for menu item **Prep/Empty via port**, you must install an **FEP Tubing Connection 6.1805.530** from Port 3 to a waste container.

**No. of Prep cycles [ 0, 1, ... ,5 ; 0 ]**

Define the number of "Prep-Cycles" for the respective Dosino.
If you work **with a sample table**, the defined number of "Prep Cycles" is conducted at the beginning of the sample table. **Exception**: With the two **DT Calibration** techniques "DT Record calibration curve" and "DT Suppressors with calibration curve", **Dosino 3** is "preped" at the beginning of every determination (with or without sample table).
If you work **without sample changer**, the defined number of "Prep Cycles" is conducted at the beginning of each determination. If you work without sample changer it is recommended to set this parameter on 0, and conduct "Preps" manually.


**Refresh**

Update of the Dosing Device connections.


**Default**

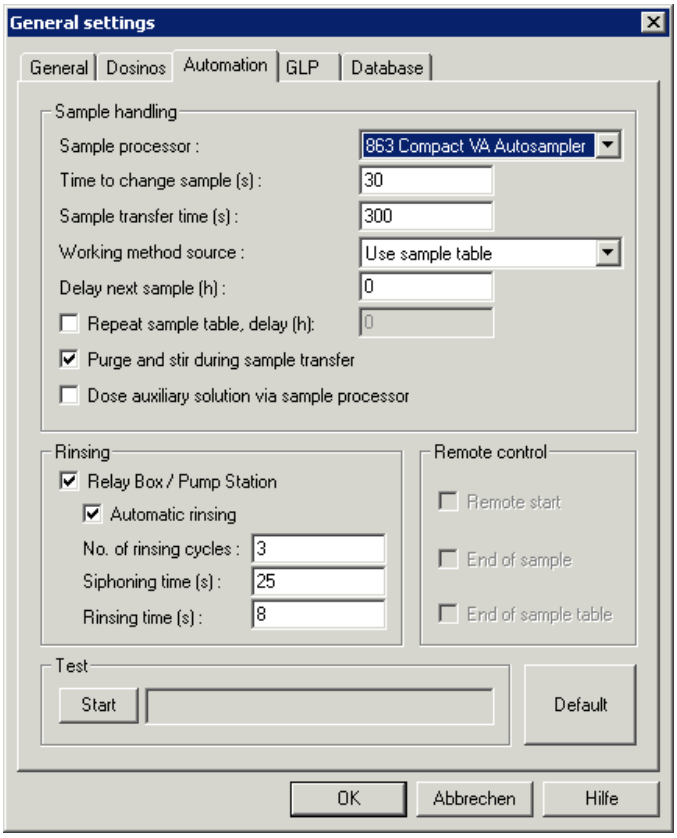
Set the Dosing Device parameters back to their default values.

## Automation

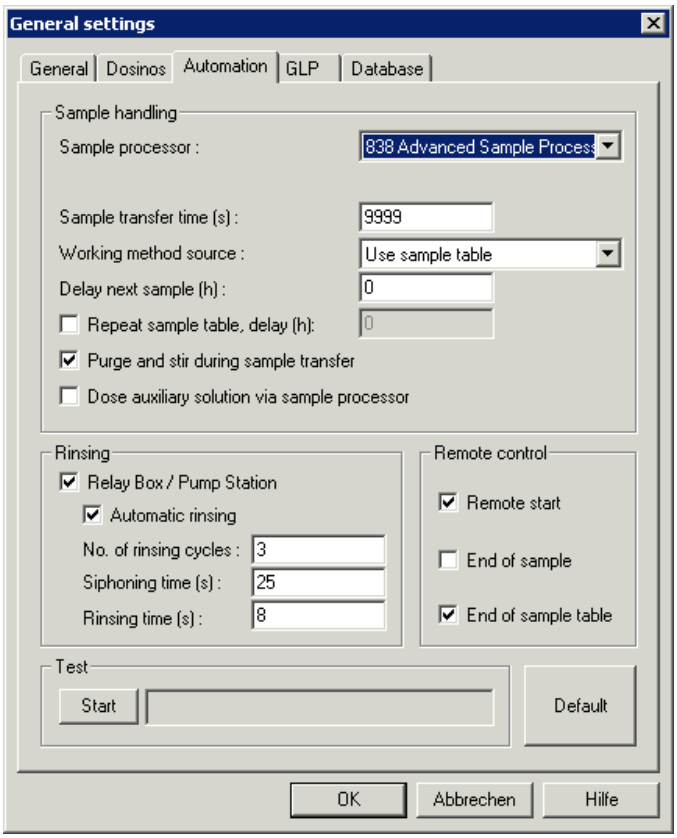
**MAIN WINDOW / Settings / General Settings**

In the **GENERAL SETTINGS** window default settings for the operation of a **863 Compact VA Autosampler / 838 Advanced Sample Processor** and the **731 Relay Box** to control two **772 Pump Units / 823 Membrane Pump Units** or the **843 Pump Station** can be defined with the **Automation** tab.

With 843:




With 838:



**Sample handling**

Define the default settings of a connected used automation unit.

**Sample processor [ read only ]**
Select the connected sample processor.

**Time to change sample [ > 25 s ; 30 s ]** (only with the 863 Compact VA Autosampler)
During that time, the rack is changed to the next position and the needle is immersed into the sample solution. It is the time between first and second remote signal that are sent from 797 Computrace to the Autosampler (see *863 Manual*).

**Sample transfer time (s) [ > 20 s ; 300 s** (with 863) **/ 9999 s** (with 838) **]**
With **863**: Time to transfer the sample solution from the sample vessel to the measurement vessel using the peristaltic pump of the 863 Compact VA Autosampler.
With **838**: During that time the 797 Computrace waits for an incoming signal (Handshake) from the 838 Advanced Sample Processor. That signal indicates that the sample has been changed **and** transferred to the measuring vessel.

**Working method source [ use sample table, repeat current method ]**
Define the sample sequence. With **use sample table**, the working method can be defined individually for each sample. With **repeat current method** the current working method is taken for all samples.

**Delay next sample**
Define the waiting period between measuring two samples.

**Repeat sample table, delay (h)** (only applicable with **use sample table**)
Check the checkbox if you want to repeat the sample sequence, and define the waiting period.

**Number of samples (-1 for infinity)** (only with **repeat current method**)
Define the number of samples you want to measure.

**Purge and stir during sample transfer**
Check the checkbox if you want to purge the sample during transfer to the measurement vessel.

**Dose auxiliary solution via sample processor**
If you want to add solutions via Dosinos connected to the 838 Advanced Sample Processor, this box **must** be checked to ensure the operation

of the program at the 838 Advanced Sample Processor.

**Rinsing**

Define the default settings of a possibly used pump unit.

**Relay box / Pump Station**
Check the checkbox if a 843 Pump Station or a 731 Relay Box with 772 Pump Units or 823 Membrane Pump Units is connected.

**Automatic rinsing**
Check the checkbox to rinse automatically.

**Note**: If **Automatic rinsing** is activated, the measuring cell is siphoned off at the beginning of every determination. If you work with manual sample addition, the sample should not be added until the siphoning process has finished and the message window **PLACE SAMPLE** appears.

**No. of rinsing cycles**
Number of rinsing cycles.
Default: 3

**Siphoning time (s)**
For each rinsing cycle, the measuring vessel is siphoned off during that time, using a 843 Pump Station (or 823 Membrane Pump Unit).
Default: 25 s

**Rinsing time (s)**
For each rinsing cycle, the measuring vessel is rinsed during that time, using a 772 Pump Unit (or 823 Membrane Pump Unit).
Default: 8 s

**Remote control** (not accessible with 863 Compact VA Autosampler)
Define the communication with connected devices.

**Remote start**
797 VA Computrace waits for an incoming signal to start the measurement.

**End of sample**
Send a signal after measuring the sample.

**End of sample table**
Send a signal at the end of the sample table (only accessible if **use sample table** is activated for **Working method source**) (the signal stops the 838 Advanced Sample Processor).

Test

Test the **863 Compact VA Autosampler**, or **838 Advanced Sample Processor** with the set automation parameters.

**Note**: Before starting the test, switch on either 863 Compact VA Autosampler(set Method **2**) or the 838 Advanced Sample Processor (set method **VA**, and enter the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad), and place two sample vessels filled with water on the sample rack.

For details on the use of the **863 Compact VA Autosampler**, or the **838 Advanced Sample Processor** see *863 Manual*, *838 Manual.*

## GLP

### GLP Settings

**MAIN WINDOW / Settings / General Settings**

The GLP settings for the Computrace and Dosing Devices can be defined on the **GLP** tab of the **GENERAL SETTINGS** window.

**Computrace**

**GLP Control**
Check the checkbox to apply GLP control to the Computrace.

**Validation interval (days)**
Define the period between two validations.

**Display a message [ .. ] days before the validation expires.**
Define, how long before the expiring date a warning message is displayed.

**Action, if validation expires**
You can choose between just showing a warning **Show warning only**, or stopping the measurements **Stop measurements**.

GLP Wizard Starts the GLP Wizard

**Note**: Clicking GLP Wizard resets the validation interval.

**Dosinos**

**GLP Control**
Check the checkbox to apply GLP control to the Dosing Devices (Testing of Dosing Devices can only be done by your Metrohm agency).

**Next certification of Dosino no. 1..7 (days)**
Displays days left to next certification of the specific Dosing Device.

**Display a message [ .. ] days before the certification expires.**

Define, how long before the expiring date a warning message is displayed.

**Action, if validation expires**
You can choose between just showing a warning **Show warning only**, or stopping the measurements **Stop measurements**.

**Note**: GLP can only be started if there is no "blank user". "Blank user" has to be removed to apply GLP.

## GLP Wizard

Clicking the GLP Wizard button on the **GLP** tab of the **GENERAL SETTINGS** window starts the GLP Wizard. The GLP Wizard window opens, and you can check which parts you want to execute.

**Diagnostics**

Performs several tests of the hardware of your instrument. You can choose which test should be performed in the **DIAGNOSTICS** window.

**Note**: Occasional purging and stirring tests should be done as "**Check the purging**"(see *section 8.10 Check the purging*) or "**Check the stirring**" (see *section 8.10 Check the stirring*), and not with the GLP Wizard (not to overwrite GLP data). It is also possible to do the whole Diagnostics procedure outside of the GLP Wizard: Click **DIAGNOSTICS** in **MAIN WINDOW / HELP** to open the **DIAGNOSTICS** window.

**Dummy cell tests**

Performs an electronic validation of the 797 VA Computrace.

**Note**: Occasional linearity and peak tests should be done as "**Perform a linearity test with the dummy cell**"(see *section 8.10 Perform a linearity test with the dummy cell*) or "**Perform a peak test with the dummy cell**" (see *section 8.10 Perform a peak test with the dummy cell*), and not with the GLP Wizard (not to overwrite GLP data).

**Electrode test**

Performs a validation of all three electrodes of the 797 VA Computrace.

**Note**: Occasional electrode tests should be done with Electrode Test in the **COMPUTRACE CONTROL** window and not with the GLP Wizard (not to overwrite GLP data).

**Validation of a chosen method**

Performs a validation of accuracy and precision using Standard Operating Procedures (SOP).

**Note**: When the GLP Wizard is executed, the current GLP data that is stored in the software and in the 797 VA Computrace instrument is overwritten.

## GLP Diagnostics

1. If you check (only) the **Diagnostics** checkbox on the **GLP Wizard** page of the **GLP WIZARD** window and press <**continue**>, you get to the **Diagnostics** page of the **GLP WIZARD** window.
2. Press <**continue**> one more time, and the **DIAGNOSTICS** window opens.
3. In the **DIAGNOSTICS** window you can choose manually or with the menu **select** which tests will be done. Press <**Start**> to get the testing started.
4. After completion you can save the data with **Save Report as** in the **File** menu. You can print it with Print Report in the File menu.
5. Leave the **DIAGNOSTICS** window with **Exit** in the **File** menu.
6. The **Summary of GLP validation** page of the **GLP WIZARD** window opens.
7. Press <**Finish**>.

**Note**: Metrohm recommends to check all 4 procedures on the **GLP Wizard** page of the **GLP WIZARD** window . The tests are progressed in the order as listed. It is also possible to do the whole Diagnostics procedure outside of the GLP Wizard: Click **Diagnostics** in **MAIN WINDOW / HELP** to open the **DIAGNOSTICS** window.

## GLP Dummy Cell Tests

1. If you check (only) the **Dummy cell tests** checkbox on the **GLP Wizard** page of the **GLP WIZARD** window and press <continue>, you get to the **Dummy Cell Test_L** page of the **GLP WIZARD** window.
2. Proceed as described and press <**continue**> one more time; the **MONITOR** window opens.

3. After testing, the results are shown In the **Dummy Cell Test_L** page of the **GLP WIZARD** window.
4. Press <**continue**> one more time; the **Dummy Cell Test_D** page of the **GLP WIZARD** window opens.
5. Proceed as described and press <**continue**> one more time; the **MONITOR** window opens.
6. After testing, the results are shown In the **Dummy Cell Test_D** page of the **GLP WIZARD** window.
7. Press <**continue**> one more time; the **Summary of GLP validation** page of the **GLP WIZARD** window opens.
8. Press <**Finish**>.

**Note**: Metrohm recommends to check all 4 procedures on the **GLP Wizard** page of the **GLP WIZARD** window . The tests are progressed in the order as listed.

### GLP Electrode tests

1. If you check (only) the **Electrode test** checkbox on the **GLP Wizard** page of the **GLP WIZARD** window and press <**continue**>, you get to the **Electrode Test** page of the **GLP WIZARD** window.
2. Proceed as written and press <**continue**> one more time; the **Result** part of the **Electrode Test** page of the **GLP WIZARD** window opens.
3. Press <**continue**> one more time; the **Summary of GLP validation** page of the **GLP WIZARD** window opens.
4. Press <**Finish**>.

**Note**: Metrohm recommends to check all 4 procedures on the **GLP Wizard** page of the **GLP WIZARD** window . The tests are progressed in the order as listed.

### GLP Validation of a chosen method

1. If you check (only) the **Validation of a chosen method** checkbox on the **GLP Wizard** page of the **GLP WIZARD** window and press <**continue**>, you get to the **Validation of Standard Method** page of the **GLP WIZARD** window.
2. Choose the method **Test Pb in standard solution.mth** (or any other predefined method from the Method folder) and press <**continue**>.
3. Choose **Number of measurements**. The **Analyte content** is automatically read from the method.

**Note**: The working method parameters cannot be changed during the GLP validation. Optimization of the method should be done before the GLP validation.

4. Press <**continue**> one more time; the **PLACE SAMPLE** window opens. Fill the measurement vessel as defined and press <**Ok**>, the **MONITOR** window opens and the measurement starts.
5. The **Result** part of the **Validation of Standard Method** page of the **GLP WIZARD** window opens.
6. Press <**continue**> one more time; the **Summary of GLP validation** page of the **GLP WIZARD** window opens.
7. Press <**Finish**>.

**Note**: Metrohm recommends to check all 4 procedures on the **GLP Wizard** page of the **GLP WIZARD** window . The tests are progressed in the order as listed.

## Database settings

**MAIN WINDOW / Settings / General Settings**

The Database settings can be defined on the **Database** tab on the **GENERAL SETTINGS** window.

**Note:** If you work with the new program version «797 VA Computrace Software 1.3.x» and try to export to a database created with an old program version «797 VA Computrace Software 1.X», an error message appears (see *Error message "Please select a new database file"*). If you work with the «797 VA Computrace Software 1.3.x», export only to databases created with «797 VA Computrace Software 1.3.x».

**Manual Transfer Mode**

**Use default database file when exporting determinations**

Determinations are stored directly in the default database if you export them via **MAIN MENU / File / Export To Database**.

**Ask for database file when exporting determinations**

If you export determinations via **MAIN MENU / File / Export To Database** the **SELECT DETERMINATION DATABASE FILE** window opens, and you choose the database file where the current determination is stored.

**Note:** The automatic database export directly after determinations is defined on the sheet Export of the working method.

### Save settings

**MAIN WINDOW / Settings / Save now**
This function saves the actual settings of the software: Open windows, window position and size, general settings.

**MAIN WINDOW / Settings / Save on exit**
If this function is enabled, the software settings are stored when the software is quit.

## 2.8 Window menu

### Tiling of windows

**MAIN WINDOW / Window / Tile**
All opened windows are tiled.

### Opening and closing of program windows

**MAIN WINDOW / Window / Working method specification (F6)**
The **WORKING METHOD SPECIFICATIONS** window will be opened or (if it is already open) closed (see *section 5.2*) (F6 only works, if the Main Window is selected).

**MAIN WINDOW / Window / Monitor (F7)**
The **MONITOR** window will be opened or (if it is already open) closed (see *section 5.3*) (F7 only works, if the Main Window is selected).

**MAIN WINDOW / Window / Determination curves (F8)**
The **DETERMINATION CURVES** window will be opened or (if it is already open) closed (see *section 5.4*) (F8 only works, if the Main Window is selected).

**MAIN WINDOW / Window / Results (F9)**
The **RESULTS** window will be opened or (if it is already open) closed (see *section 5.5* (F9 only works, if the Main Window is selected)).

**797 VA COMPUTRACE / Window / Sample table (F10)**
The **SAMPLE TABLE** window will be opened or (if it is already open) closed (see *section 5.6*) (F10 only works, if the Main Window is selected).

**MAIN WINDOW / Window / Exploratory specification (F11)**
The **EXPLORATORY SPECIFICATION** window will be opened or (if it is already open) closed (see *sec-*

*tion 4.2*) (F11 only works, if the Main Window is selected).

**MAIN WINDOW / Window / Exploratory curves (F12)**

The **EXPLORATORY CURVES** window will be opened or (if it is already open) closed (see *section 4.3*) (F12 only works, if the Main Window is selected).

The opened windows are marked with a checkbox sign.

## Display settings for Main window

**MAIN WINDOW / Window / Status bar**

Switch on/off display of status bar in the **MAIN WINDOW**.

**MAIN WINDOW / Window / Toolbar**

Switch on/off display of toolbar in the **MAIN WINDOW**

# 3 General settings for exploratory and determination mode

## 3.1 Electrodes

### MME

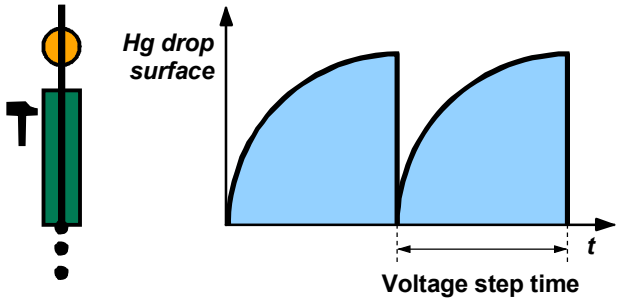
**MME** stands for **Multi-Mode Electrode** and is the working electrode commonly used in the 797 VA Computrace stand. It combines the most important polarographic and voltammetric mercury electrodes in a single construction:

| | |
|---|---|
| **DME** | Dropping mercury electrode |
| **SMDE** | Static mercury drop electrode |
| **HMDE** | Hanging mercury drop electrode |

For installation and maintenance of the Multi-Mode Electrode, see *Hardware Manual*.

### DME


**DME** is an electrode mode of the Multi-Mode Electrode and stands for **Dropping Mercury Electrode**. It is the classical mercury electrode where the mercury flows out freely from the glass capillary until the mercury drop is knocked off by a tapping mechanism after each **Voltage step time** set in the measurement mode.



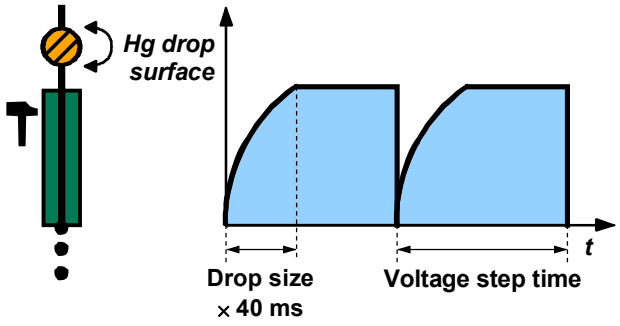

Notes:

- In the exploratory mode, the DME can be used for the measurement modes DC, NP, DP and AC. In the determination mode, the DME can be used for the measurement modes DP and AC.
- An advantage of the DME compared with the SMDE is that the MME capillary is subjected to less mechanical stress.
- A disadvantage of the DME compared with the SMDE and HMDE is the higher mercury consumption and the lower sensitivity as the electrode surface constantly changes during the measurement phase.

## SMDE


**SMDE** is an electrode mode of the Multi-Mode Electrode and stands for **Static Mercury Drop Electrode**. It combines the features of the DME and the HMDE: as with the DME, the mercury drops are constantly renewed, but during the measurement the drop surface is constant as in the HMDE case. Each mercury drop is knocked off by a tapping mechanism after the **Voltage step time** set in the measurement mode.

**Drop size [ 1...9 ; 4 ]**
Size of the mercury drop (surface 0.15 $mm^2$...0.60 $mm^2$).



Notes:

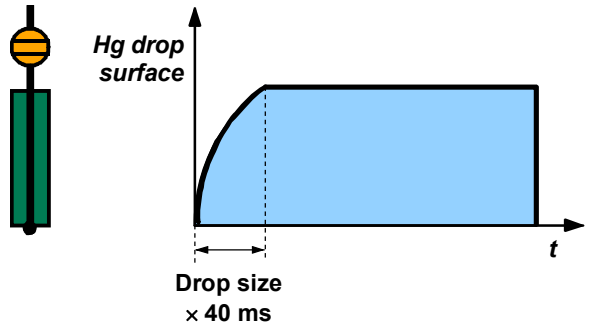
- In the exploratory mode, the SMDE can be used for the measurement modes DC, NP, DP and AC. In the determination mode, the SMDE can be used for the measurement modes DP and AC.
- An advantage of the SMDE compared with the DME is its greater sensitivity as the electrode surface and hence the baseline remains constant during the measurement. Further, less mercury is needed. On the other hand, the MME capillary is subjected to greater mechanical stress than with the DME.
- A disadvantage of the SMDE compared with the HMDE is the higher mercury consumption, in addition the MME is subjected to greater mechanical stress.

## HMDE


**HMDE** is an electrode mode of the Multi-Mode Electrode and stands for **Hanging Mercury Drop Electrode**. Four mercury drops of defined size are formed in succession at the MME. The last drop remains suspended and the entire voltage sweep is performed on this single stationary drop, in general with preceding deposition (stripping voltammetry).

**Drop size [ 1...9 ; 4 ]**

Size of the mercury drop (surface 0.15 $mm^2$...0.60 $mm^2$).




Notes:

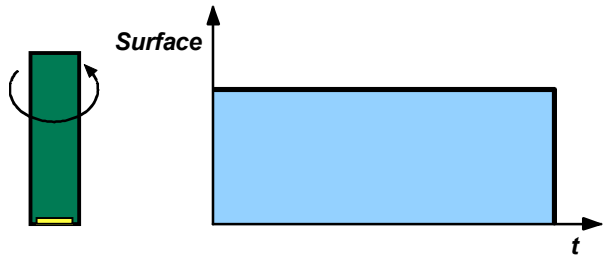
- The HMDE can be used for all measurement modes except CPVS.
- The HMDE is primarily used for very sensitive stripping voltammetry in which the analyte species is not measured until it has first been electrochemically enriched.

## RDE/SSE


**RDE** stands for **Rotating Disk Electrode** and is used for direct and stripping determinations with **Solid State Electrodes** (**SSE**).

**Stirrer/RDE (rpm) [ 0...3000 rpm ; 2000 rpm ]**

Revolutions per minute of the rotating disk electrode. The stirring of the RDE remains active during all preparation procedure steps until the start of sweep.




Notes:

- The RDE can be used for all measurement modes.
- For the 797 VA Computrace stand, a drive shaft with different electrode tips is available as an option (see *Hardware Manual*).
- For installation and maintenance of the RDE, see *Hardware Manual*.

# 3.2 VA measurement modes

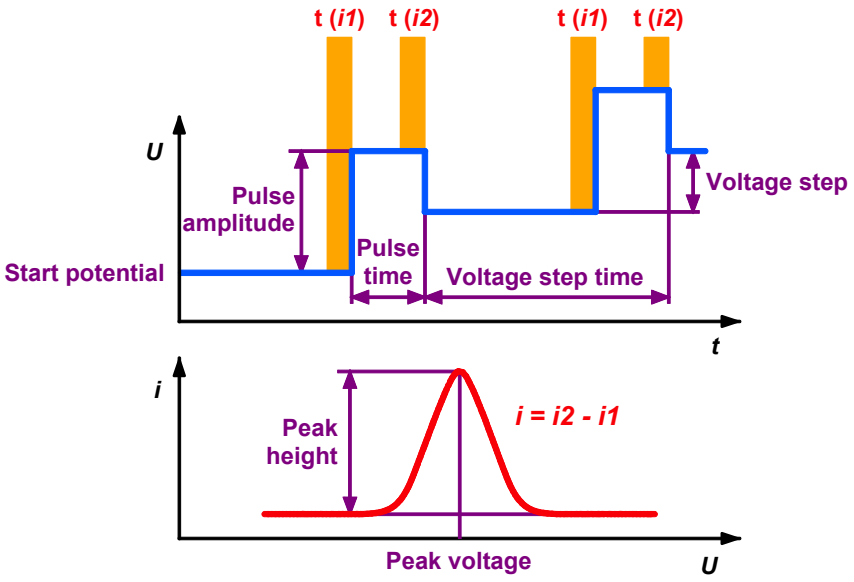
## DP – Differential Pulse

General:

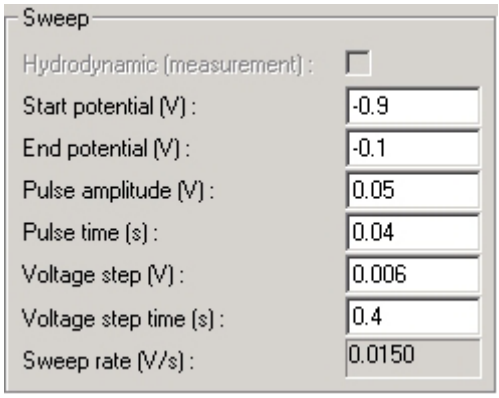
**DP** or **Differential Pulse voltammetry** is the most universal and frequently used voltammetric measurement mode. It is equally well suited for irreversible and reversible systems and offers a high sensitivity. The DP measurement mode can be set for the exploratory and determination mode by selecting **DP - Differential pulse** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For DP voltammetry, rectangular pulses with a constant amplitude are superimposed on a stepwise rising direct voltage ramp. The current ***i*** is measured as a function of the voltage ***U*** immediately before the pulse and at the end of the pulse. From the differences between the two current measurements, peak-shaped curves are obtained which are evaluated using linear, polynomial, horizontal or exponential baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the voltage sweep.

**Pulse amplitude (V) [ -1...+1 V ; 0.05 V ]**
Pulse amplitude of the voltage pulse superimposed on the direct voltage (pos. values = same direction; neg. values = reversed direction with respect to the scan direction).

**Pulse time (s) [ > 500 µs ; 0.04 s ]**
Time interval during which a voltage pulse is superimposed on the direct voltage.

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Voltage step time (s) [ > 0 s ; 0.4 s ]**
Time interval after which the voltage in the sweep is increased or decreased by the amount **Voltage step**.

**Sweep rate (V/s) [ read only ]**
Display of the ramp slope calculated as **Voltage step / Voltage step time**.

Notes:

- The DP measurement mode can be used with all types of electrodes.
- The following conditions apply to the definition of the **Voltage step time**:
  **Voltage step time > Pulse time + 10 ms** (HMDE/RDE)
  **Voltage step time > Pulse time + 220 ms** (DME)
  **Voltage step time > Pulse time + Drop size × 40 ms + 200 ms** (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  **Pulse time ≥ 40 ms → t (*i*) = 20/16.67 ms** ((power frequency 50/60 Hz)
  **Pulse time < 40 ms → t (*i*) = 0.5 × Pulse time**

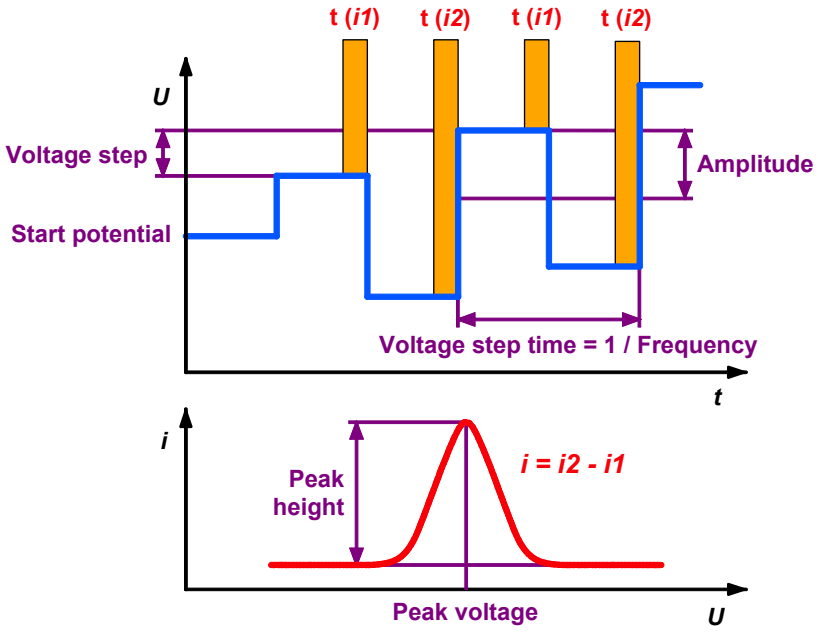
## SqW – Square Wave

General:

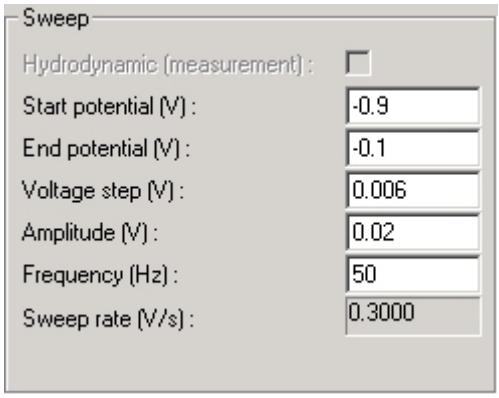
**SqW** or **Square Wave voltammetry** is primarily suitable for reversible electrode processes. It is used particularly for sensitive stripping voltammetric determinations at the HMDE or RDE. The SqW measurement mode can be set for the exploratory and determination mode by selecting **SqW - Square wave** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For SqW voltammetry, a square wave alternating voltage with a small, constant amplitude is superimposed on a stepwise rising direct voltage ramp. The current ***i*** is measured as a function of the voltage ***U*** at the maximum and minimum of the square wave voltage. The phase dependent differences between the two current measurements give peak-shaped curves which are evaluated using linear, horizontal, polynomial or exponential baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the voltage sweep.

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Amplitude (V) [ > 0...+1 V ; 0.02 V ]**
Voltage amplitude of the square wave voltage superimposed on the direct voltage.

**Frequency (Hz) [ > 0...2000 Hz ; 50 Hz ]**
Frequency of the superimposed square wave voltage, which defines the voltage step time (**Voltage step time = 1 / Frequency**).

**Sweep rate (V/s) [ read only ]**
Display of the ramp slope calculated as **Voltage step** × **Frequency**.

Notes:

- The SqW measurement mode can only be used with HMDE or RDE electrodes.
- If your curves have high noise, put **Highest current range** and **Lowest current range** in the **POTENTIOSTAT** window on the same level (see *section 9.6 SqW Problems*)
- The following condition applies to the definition of the **Voltage step time**:
  **Frequency ≤ 2000 Hz ⇒ Voltage step time ≥ 500 µs**
- The measurement time **t (*i*)** is defined as follows:
  **Voltage step time ≥ 80 ms → t (*i*) = 20/16.67 ms** (power frequency 50/60 Hz)
  **Voltage step time < 80 ms → t (*i*) = 0.5 × Voltage step time**

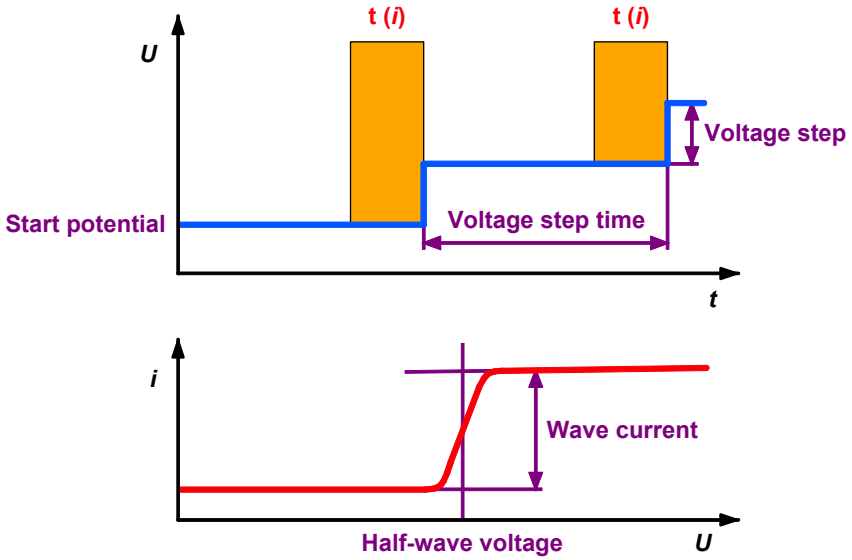
## DC – Sampled Direct Current

General:

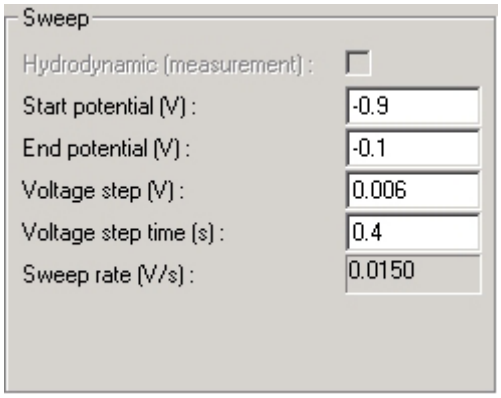
**DC** or **Sampled Direct Current voltammetry** is the classic, simplest voltammetric measurement mode with limited sensitivity. It is mainly used for the investigation of reversible redox systems. The DC measurement mode can be set for the exploratory and determination mode by selecting **DC - Sampled direct current** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For DC voltammetry, the direct voltage applied to the working electrode is continuously changed and the resultant current ***i*** which flows measured as a function of the voltage ***U***. For DME and SMDE this normally provides wave-shaped curves which can be evaluated in the exploratory mode using the tangent method.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the voltage sweep.

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Voltage step time (s) [ > 0 s ; 0.4 s ]**
Time interval after which the voltage in the sweep is increased or decreased by the amount **Voltage step**.

**Sweep rate (V/s) [ read only ]**
Display of the ramp slope calculated as **Voltage step / Voltage step time**.

Notes:

- The DC measurement mode can be used with all types of electrodes except for DME and SMDE in the determination mode.
- The following conditions apply to the definition of the **Voltage step time**:
  **Voltage step time > 270 µs** (HMDE/RDE)
  **Voltage step time > 220 ms** (DME)
  **Voltage step time > Drop size × 40 ms + 200 ms** (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  **t (*i*) = 20/16.67 ms** (power frequency 50/60 Hz)

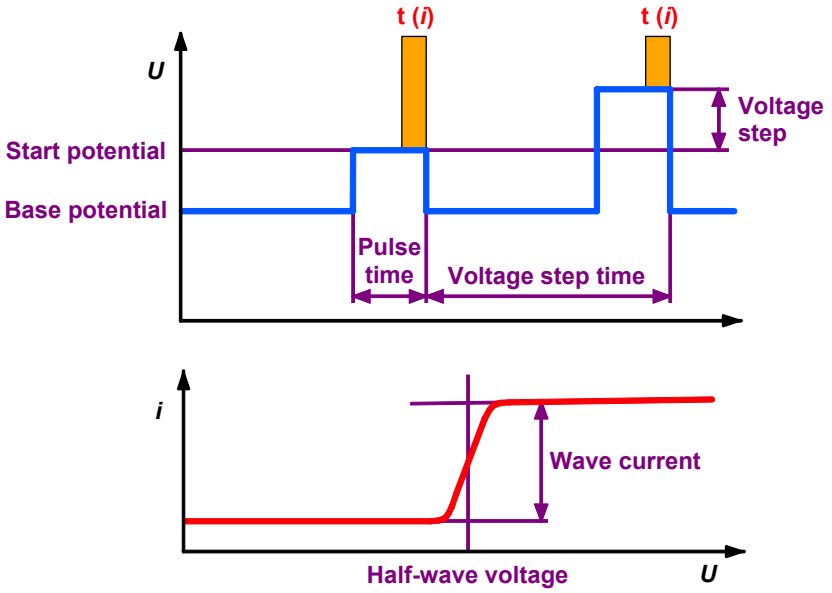
## NP – Normal Pulse (for "Exploratory" only)

General:

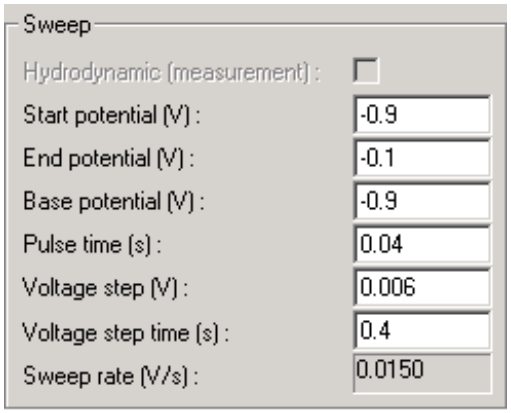
**NP** or **Normal Pulse voltammetry** is the classic pulse voltammetric measurement mode with direct recording of the current. It is equally well suited for irreversible and reversible systems and offers a higher sensitivity than the DC voltammetry. The NP measurement mode can only be set for the exploratory mode by selecting **NP - Normal pulse** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** window.

Description:

For NP voltammetry, square-wave pulses with an increasing amplitude are superimposed on a constant base voltage. The current ***i*** is measured as a function of the voltage ***U*** at the end of the pulse. This normally provides wave-shaped curves which can be evaluated using the tangent method.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the voltage sweep.

**Base potential (V) [ -5...+5 V ; -0.9 V ]**
Base voltage for voltage sweep.

**Pulse time (s) [ ≥ 500 µs ; 0.04 s ]**
Time interval during which an increasing voltage pulse is superimposed on the base voltage.

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Voltage step time (s) [ > 0 s ; 0.4 s ]**
Time interval after which the voltage in the sweep is increased or decreased by the amount **Voltage step**.

**Sweep rate (V/s) [ read only ]**
Ramp slope calculated as **Voltage step / Voltage step time**.

Notes:

- The NP measurement mode can be used with all types of electrodes (but only in the exploratory mode!).
- The following conditions apply to the definition of the **Voltage step time**:
  **Voltage step time > Pulse time + 10 ms** (HMDE/RDE)
  **Voltage step time > Pulse time + 220 ms** (DME)
  **Voltage step time > Pulse time + Drop size × 40 ms + 200 ms** (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  **Pulse time ≥ 40 ms → t (*i*) = 20/16.67 ms** (power frequency 50/60 Hz)
  **Pulse time < 40 ms → t (*i*) = 0.5 × Pulse time**

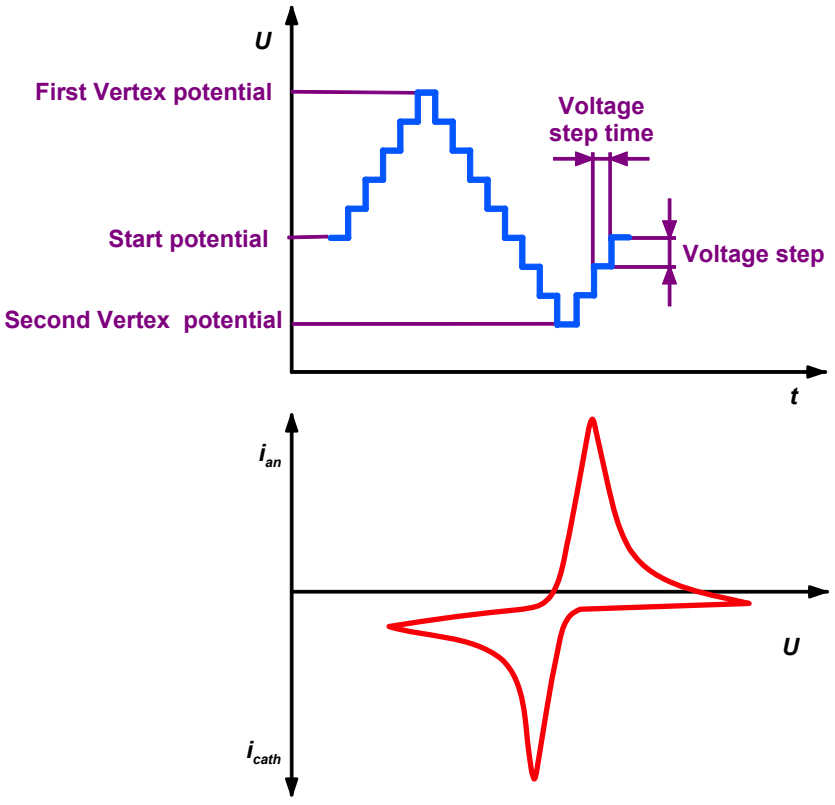
## CV – Cyclic Voltammetry

General:

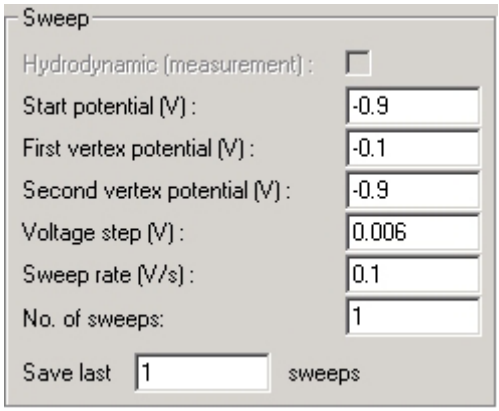
**CV** or **Cyclic voltammetry** is mainly used to investigate the reversibility of electrode processes and for kinetic studies. The CV measurement mode can be set for the exploratory and determination mode by selecting **CV - Cyclic voltammetry** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For cyclic voltammetry, the voltage is once or several times changed at a constant sweep rate to the end potential and then decreased at the same rate back to the start potential. The current ***i*** is measured as a function of the voltage ***U***. The curve registered in the last cycle is stored and its peaks can be evaluated using linear, polynomial, horizontal or exponential baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**First vertex potential (V) [ -5...+5 V ; -0.1 V ]**
First turning point for the potential sweep.

**Second vertex potential (V) [ -5...+5 V ; -0.9 V ]**
Second turning point for the potential sweep (Can be different from the **Start potential**).

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Sweep rate (V/s) [ > 0 V/s ; 0.1 V/s ]**
Ramp slope = **Voltage step / Voltage step time**.

**No. of sweeps [ > 0 ; 1 ]**
Number of cyclic sweeps to be performed.

**Save last ... sweeps]**
Number of cycles to be saved.

**Note**: Total number of saved sweeps is number of **Save last sweeps** multiplied with **No. of replications**.

Notes:

- The CV measurement mode can only be used with HMDE or RDE electrodes.
- The following condition applies to the definition of **Voltage step** and **Sweep rate**:
  **Voltage step time = Voltage step / Sweep rate > 270 µs**
- The measurement time **t (i)** is defined as follows:
  **Voltage step time ≥ 80 ms → t (i) = 20/16.67 ms** (power frequency 50/60 Hz)
  **Voltage step time < 80 ms → t (i) = Voltage step time / 4** (Voltage step time = Voltage step / Sweep rate)

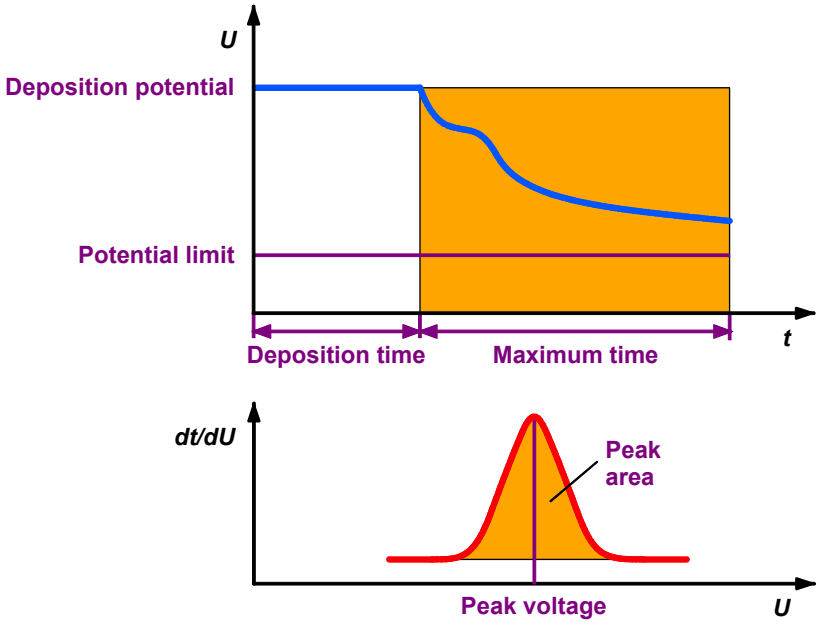
## PSA – Potentiometric Stripping Analysis

General:

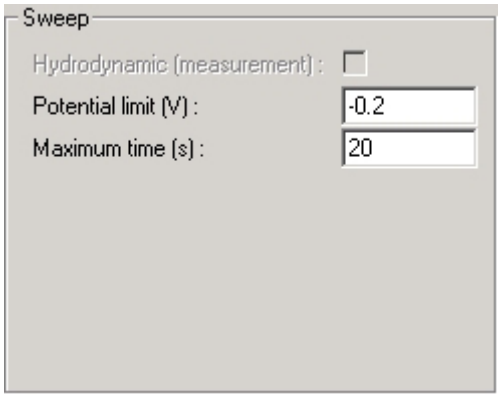
**PSA** or **Potentiometric stripping analysis** with chemical oxidation is mainly used to determine substances in an organic matrix with the aid of mercury film electrodes without prior digestion. The PSA measurement mode can be set for the exploratory and determination mode by selecting **PSA - Potentiometric stripping analysis** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

In PSA measurement mode, the analytes are deposited at the working electrode with the constant **Deposition potential** during a predetermined **Deposition time**. Then the applied deposition potential is switched off and the voltage ***U*** is measured as a function of the time ***t*** with a sampling rate of 69.69 kHz. The measurement time is limited either by the set **Potential limit** or the **Maximum time**. The voltage measurement ***U*** vs ***t*** is used to calculate the retention times ***dt/dU*** vs ***U***. This results in peak-shaped curves which can be evaluated. The **Peak voltage** is characteristic of the substance, the **Peak area** is proportional to its concentration.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Potential limit (V) [ -5...+5 V ; -0.2 V ]**
Voltage limit for PSA sweep.

**Maximum time (s) [ > 0 ; 20 s ]**
Time limit for PSA sweep.

Notes:

- The PSA measurement mode should only be used with RDE electrodes (mainly with Hg film).

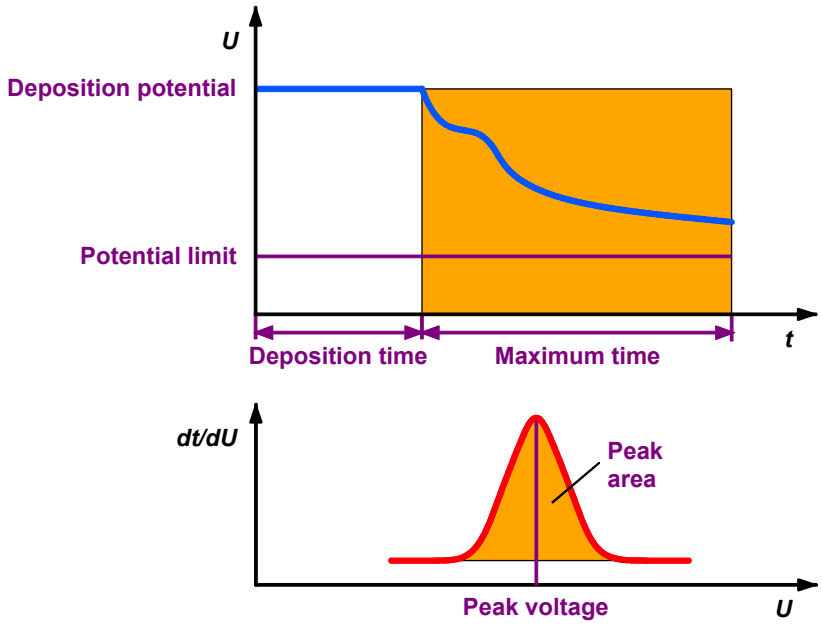
## CCPSA – Constant Current Potentiometric Stripping Analysis

General:

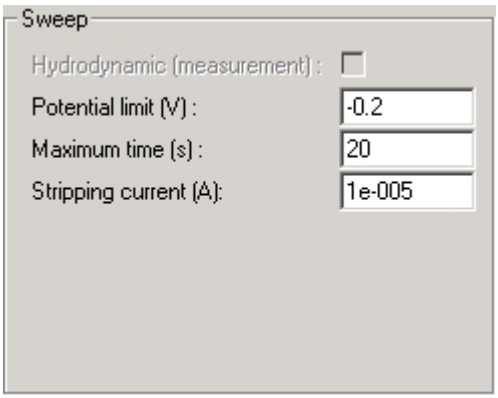
**CCPSA** or **Constant Current Potentiometric stripping analysis** with oxidation by an applied constant current is mainly used to determine substances in an organic matrix with the aid of mercury film electrodes without prior digestion. The CCPSA measurement mode can be set for the exploratory and determination mode by selecting **CCPSA – Constant Current Potentiometric stripping analysis** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

In CCPSA measurement mode, the analytes are deposited at the working electrode with the constant **Deposition potential** during a predetermined **Deposition time**. Then the applied deposition potential is switched off and a constant current is applied. The voltage **U** is measured as a function of the time **t** with a sampling rate of 69.69 kHz. The measurement time is limited either by the set **Potential limit** or the **Maximum time**. The voltage measurement ***U*** vs ***t*** is used to calculate the retention times ***dt/dU*** vs ***U***. This results in peak-shaped curves which can be evaluated. The **Peak voltage** is characteristic of the substance, the **Peak area** is proportional to its concentration.




Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Potential limit (V) [ -5...+5 V ; -0.2 V ]**
Voltage limit for PSA sweep.

**Maximum time (s) [ > 0 ; 20 s ]**
Time limit for PSA sweep.

**Stripping current (A) [ > 4e-009 ; 1e-005 ]**
Constant current, applied for stripping after switching off the potential.

Notes:

- The CCPSA measurement mode should only be used with RDE electrodes (mainly with Hg film).

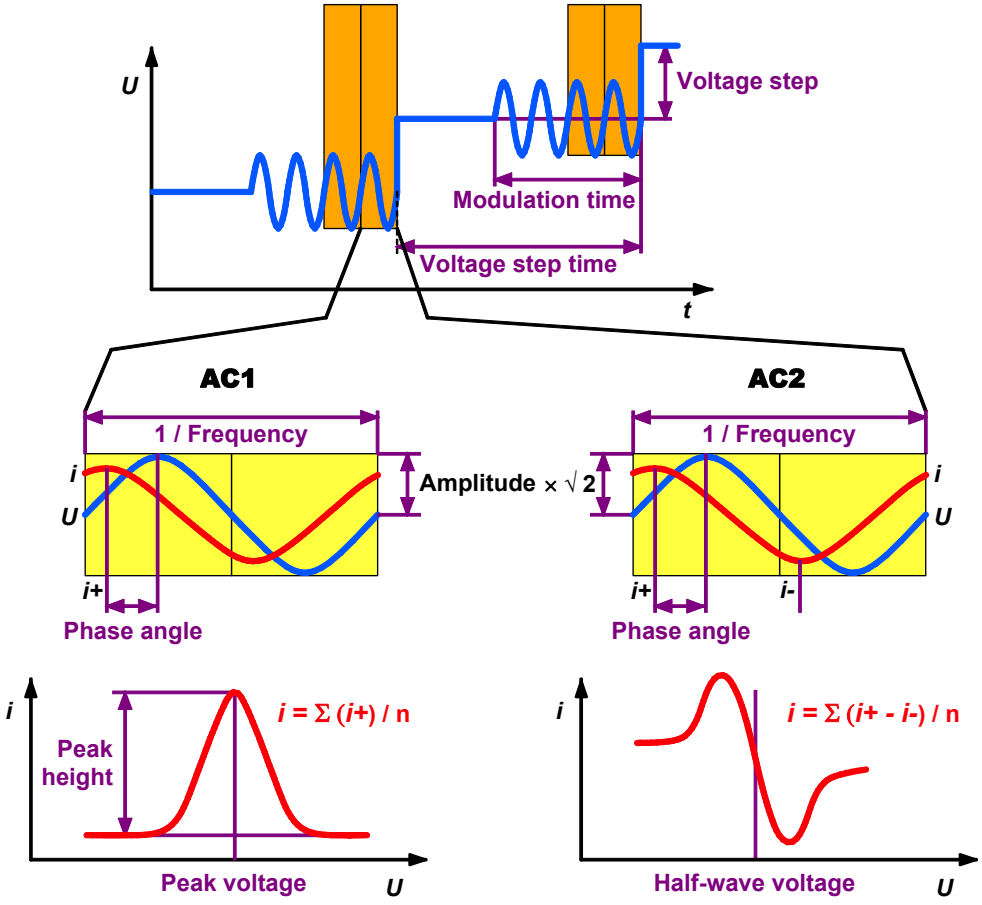
## AC – Alternating Current Voltammetry

General:

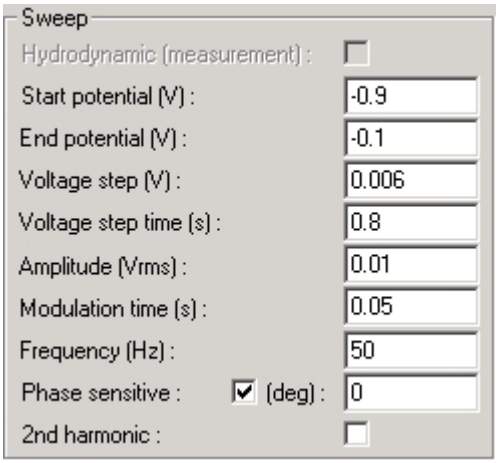
**AC** or **Alternating Current voltammetry** is primarily suitable for reversible electrode reactions. It is virtually completely insensitive to irreversible reactions. The AC measurement mode can be set for the exploratory and determination mode by selecting **AC - Alternating current voltammetry** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For AC voltammetry, a digitally generated sinusoidal alternating voltage with a small, constant amplitude and a low frequency is superimposed on a stepwise rising direct voltage ramp. The first or second harmonic wave of the alternating current component ***i*** produced by the alternating voltage is measured as a function of the voltage ***U***. The current measurements give peak-shaped (AC1) or sinusoidal shaped (AC2) curves which can be evaluated using linear, polynomial, horizontal or exponential baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; off ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; -0.9 V ]**
Start voltage for the voltage sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the voltage sweep.

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Voltage step time (s) [ > 0 s ; 0.8 s ]**
Time interval after which the voltage in the sweep is increased or decreased by the amount **Voltage step**.

**Amplitude (V) [ -1...+1 V ; 0.01 V ]**
Voltage amplitude of the sine wave voltage superimposed on the direct voltage (rms value).

**Modulation time (s) [ > 0 s ; 0.05 s ]**
Time period during which the sine wave voltage is superimposed on the direct voltage.

**Frequency (Hz) [ > 0...2000 Hz ; 50 Hz ]**
Frequency of the superimposed sine wave voltage.

**Phase sensitive [ on, off ; on ]**
Enable/disable phase sensitive current measurement.

**(deg) [ -180/-90...+180/+90° ; 0° ]**
Phase shift of the alternating current in regard to the alternating voltage. For AC1 the maximum phase angle is ± 180°, for AC2 ± 90°.

**2nd harmonic [ on, off ; off ]**
Enable/disable second harmonic current measurement (AC2).

Notes:

- The AC measurement mode can be used with all types of electrodes.
- The following condition applies to the definition of the **Modulation time**:

**Voltage step time > Modulation time + 450 ms** (HMDE/RDE)
**Voltage step time > Modulation time + 470 ms** (DME)
**Voltage step time > Modulation time + Drop size * 40 ms + 450 ms** (SMDE)

- **Modulation time > 2 / Frequency**
- The measurement time **t (*i*)** is defined as follows:
  **t (*i*) = Modulation time / 2**

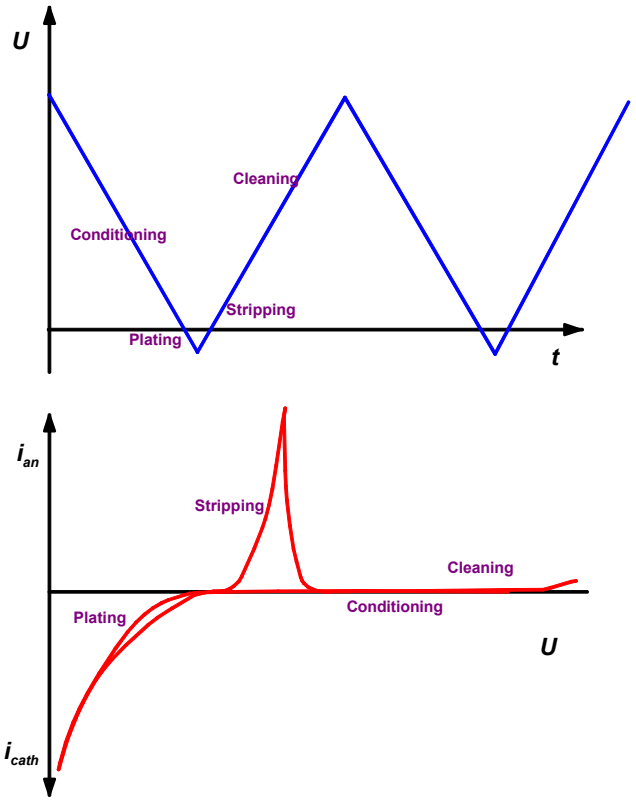
## CVS - Cyclic Voltammetric Stripping

General:

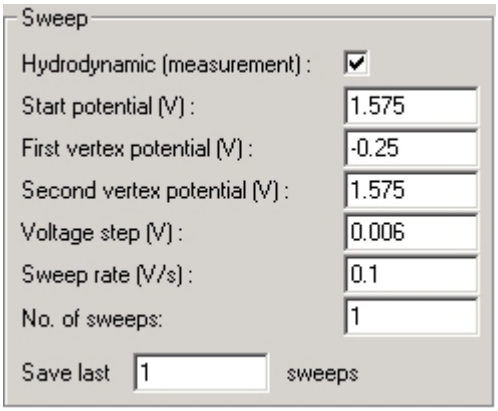
**CVS** or **Cyclic Voltammetric Stripping** is used to determine organic additives in electroplating electrolytes. The CVS measuring mode can be set for the exploratory and determination mode by selecting **CVS - Cyclic Voltammetric Stripping** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For Cyclic Voltammetric Stripping, the potential of an RDE (e.g. Pt) is cycled at a constant rate in a plating bath. The current ***i*** is measured as a function of the voltage ***U***. The curves registered in the last cycles are stored and its peaks can be evaluated using linear, polynomial, horizontal or exponential baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; on ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Start potential (V) [ -5...+5 V ; 1.625 V ]**
First turning point for the potential sweep.

**Note**: The Start potential needs to be between the **First vertex potential** and the **Second vertex potential**.

**First vertex potential (V) [ -5...+5 V ; -0.175 V ]**
First turning point for the potential sweep.

**Second vertex potential (V) [ -5...+5 V ; 1.625 V ]**
Second turning point for the potential sweep (Can be different from the **Start potential**).

**Voltage step (V) [ > 0 V ; 0.006 V ]**
Voltage step for direct voltage ramp.

**Sweep rate (V/s) [ > 0 V/s ; 0.1 V/s ]**
Ramp slope = **Voltage step / Voltage step time**.

**No. of sweeps [ > 0 ; 3 ]**
Number of cyclic sweeps to be performed.

**Save last ... sweeps [ > 0 ; 2 ]**
Number of cycles to be saved.

**Note**: Total number of saved sweeps is number of **Save last sweeps** multiplied with **No. of replications**.

Notes:

- The CVS measurement mode is mainly used with RDE electrodes. HMDE is possible.
- The following condition applies to the definition of **Voltage step** and **Sweep rate**:
  **Voltage step time = Voltage step / Sweep rate > 270 µs**
- The measurement time **t (i)** is defined as follows:
  **Voltage step time ≥ 80 ms → t (i) = 20/16.67 ms** (power frequency 50/60 Hz)
  **Voltage step time < 80 ms → t (i) = Voltage step time / 4** (Voltage step time = Voltage step / Sweep rate)

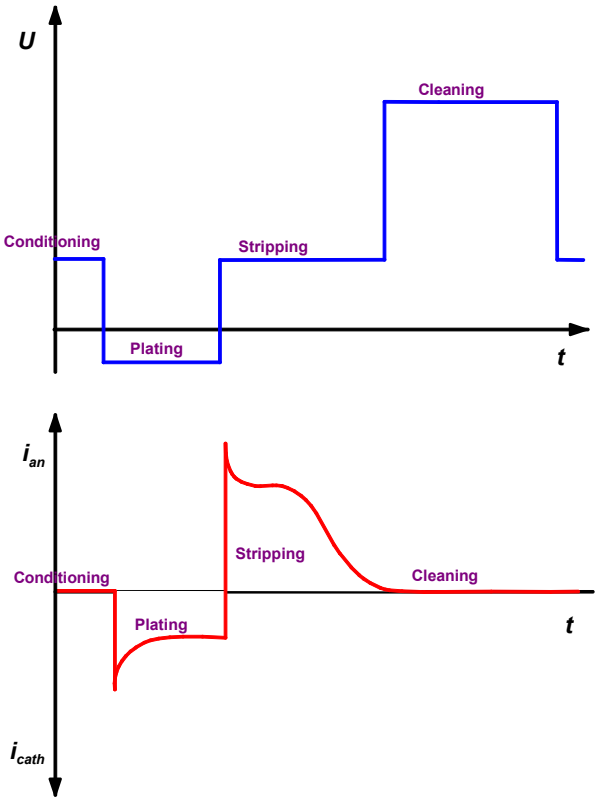
## CPVS - Cyclic Pulse Voltammetric Stripping

General:

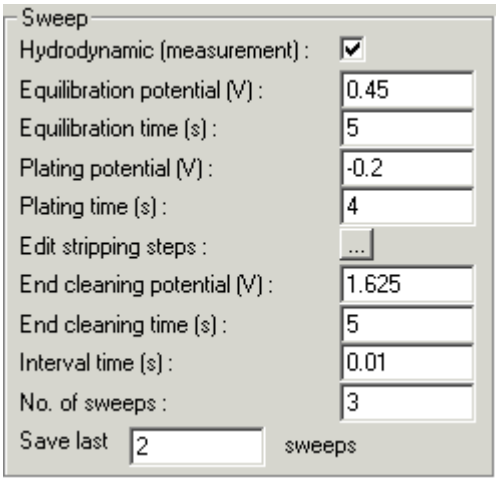
**CPVS** or **Cyclic Pulse Voltammetric Stripping** is used to determine organic additives in electroplating electrolytes. The CPVS measuring mode can be set for the exploratory and determination mode by selecting **CPVS - Cyclic Pulse Voltammetric Stripping** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION** or **WORKING METHOD SPECIFICATIONS** window.

Description:

For Cyclic Pulse Voltammetric Stripping, the potential of an RDE (e.g. Pt) is changed between different potentials in pulsed, discrete steps in a plating bath. The current ***i*** is measured as a function of the time ***t***. The curves registered in the last cycles are stored and its peaks can be evaluated using linear or horizontal baselines.



Sweep parameters:




**Hydrodynamic (measurement) [ on, off ; on ]**
Enable/disable stirring of the RDE/SSE during the sweep.

**Equilibration potential (V) [ -5...+5 V ; 0.45 V ]**
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]**
During that time, the **Equilibration potential** is applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Plating potential (V) [ -5...+5 V ; -0.25 V ]**
Set voltage for the plating period.

**Plating time (s) [ > 0 s ; 4 s ]**
Length of plating period.

**Edit stripping steps** 

Edit the stripping steps. Check a checkbox to establish a stripping step, define a potential **Potential (V) (default: 0.25**, **1.125**, **1.475**, **1.625 V)** and a step time **Step time (s) (default: 10**, **1**, **1**, **5 s)**.

**End cleaning potential (V) [-5...+5 V; 1.625 V ]**
Voltage of the cleaning period.

**End cleaning time (s) [ > 0 s ; 5 s ]**
Voltage of the cleaning period.

**Interval time (s) [ 0.001...1 s ; 0.01 s ]**
Interval time between to data points.

**No. of sweeps [ > 0 ; 3 ]**
Number of cyclic sweeps to be performed.

**Save last ... sweeps [ > 0 ; 2 ]**
Number of cycles to be saved.

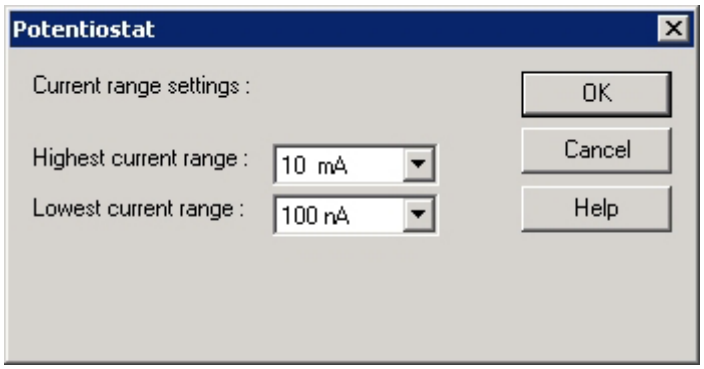
**Note**: Total number of saved sweeps is number of **Save last sweeps** multiplied with **No. of replications**.

Notes:

- The CPVS measurement mode can only be used with RDE electrodes.
- The measurement time **t (i)** is defined as follows:
  **Interval time ≥ 100 ms → t (i) = 20/16.67 ms** (power frequency 50/60 Hz)
  **Interval time < 100 ms → t (i) = Interval time / 4**

## 3.3 Potentiostat

The potentiostat built-in in the 797 VA Computrace stand normally works with full sensitivity for current measurements from 5 pA to 80 mA. Depending on the measured current, the current range will be selected automatically between the lowest and the highest current range. For fast measurements with CV, CVS, SqW or DC is helpful to limit the highest and/or lowest current range in order to avoid disturbing current leaps.




**Highest current range [ 10 nA, 1/10/100 µA, 1/10 mA ; 10 mA ]**
Limitation of the highest current range.

**Lowest current range [ 10 nA, 1/10/100 µA, 1/10 mA ; 100 nA ]**
Limitation of the lowest current range.

---

**Note**: If you work with the SqW mode, you should define a fixed current range to avoid detecting problems caused by quick sweeping and high current. Put **Highest current range** and **Lowest current range** in the **POTENTIOSTAT** window on the same level (see *section 9.6 SqW Problems*).

---

Because of the limited bandwidth of some current ranges, it is not possible to freely select any **Voltage step time** or **Frequency** for a distinct current range on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

The following table shows the possible values for the modes DP, SqW**, AC, NP, DC, CV*, CVS*:

| *Current range* | *Voltage step time* |
|---|---|
| 10 nA | > 50 ms |
| 100 nA | > 5 ms |
| 1 µA | > 0.5 ms |
| 10 µA | > 0.5 ms |
| 100 µA | > 0.5 ms |
| 1 mA | > 0.5 ms |
| 10 mA | > 0.5 ms |

* CV and CVS: Voltage step time = Voltage step / Sweep rate

** SqW: Voltage step time = 1 / Frequency

## 3.4 General operation sequence

### Overview of operation sequence

The general operation sequence for measurements is identical for both the exploratory and the determination mode and includes the following steps:

1. **Electrode test**
   Testing of the electrodes (only for oerating mode «Determination»).
2. **Stirring**
   Optional stirring of the sample solution during preparation procedures until start of the equilibration time (details see *Stirring*).
3. **Purging**
   Optional purging of the sample solution during the **Initial purge time** (details see *Purging*).
4. **Drop formation**
   Hg drop formation at the MME if **DME**, **SMDE** or **HMDE** is selected (details see *section 3.1*).
5. **Conditioning cycles**
   Optional conditioning of solid state electrodes by applying cyclic conditioning sweeps (details see *Conditioning of solid state electrodes*).
6. **Cleaning**
   Optional cleaning of solid state electrodes by applying a cleaning potential during the **Cleaning time** (details see *Pretreatment*).
7. **Deposition**
   Optional electrochemical deposition for stripping voltammetry during the **Deposition time** (details see *Pretreatment*).
8. **Equilibration time**
   Waiting time before starting the sweep; with start potential applied to the electrodes. If the checkbox **Hydrodynamic (meas-**

**urement)** is not checked, the stirrer is switched off during that time (details see *Pretreatment*).

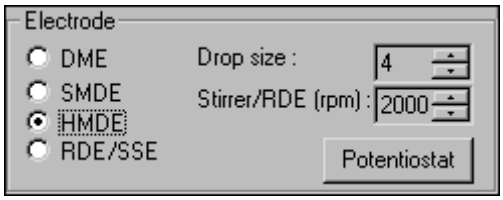
9. **Voltage sweep**
   Start of the voltage sweep which depends on the selected measurement mode (details see *VA measurement modes, section 3.2*).

10. **Stand-by potential**
    Optional apply of a **Stand-by potential** before the start and after the end of the voltage sweep (details see *Stand-by potential*).

**Note**: If you work with the electroplating bath modes CVS and CPVS, the operation sequence is different (see *section 8.6 Operate a sequence in Electroplating Bath VA*)

## Stirring

If switched on (**Stirrer > 0 rpm**), the solution in the sample vessel at the 797 VA Computrace stand is stirred during all preparation procedure steps until the start of the equilibration time.
**Exception**: Hydrodynamic measurements in the CV mode, where the stirring continues during measurement.




**Stirrer (rpm) [ 0...3000 rpm ; 2000 rpm ]**
Revolutions per minute of the stirrer.

## Purging

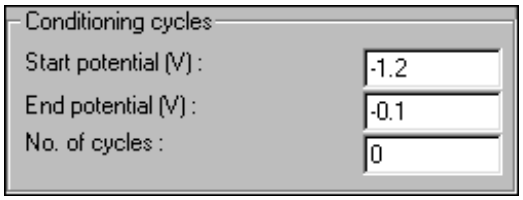
Purging means saturation of the analysis solution with an inert gas and is used to remove the electrochemically active and hence interfering oxygen. With the inert gas flow rate of ca. 20 l/h set on the 797 VA Computrace stand, a purging time of ca. 3...5 min. usually suffices. For an effective purging of the analysis solution, the solution should also be stirred.


**Initial purge time (s) [ 0...80600 s ; 300 s ]** (**Initial mixing time** with CVS and CPVS, see *section 6.3 Initial mixing time with CVS and CPVS*)

Time of inert gas purging before the first measurement of the sample solution.

## Conditioning of solid state electrodes

Solid state electrodes (particularly carbon electrodes) can be electrochemically regenerated by a freely selectable number of conditioning cycles. For every cycle, the voltage is changed at a sweep rate of 1 V/s to the **end potential** and then decreased at the same rate back to the **start potential**.




**Start potential (V) [ -5...+5 V ; -1.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

---

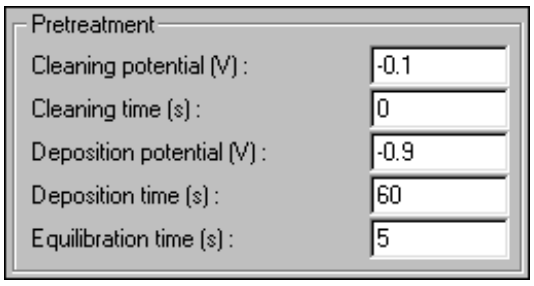
**Note**: With the electroplating bath modes different default values are set (see *section 6.3 Conditioning cycles with CVS and CPVS*)

---

## Pretreatment

The pretreatment of the electrode before starting a sweep can consist of the following three steps:

- The **cleaning potential** can be used to clean solid state electrodes with a stationary surface which are contaminated with the products of the electrode redox processes.
- The **deposition potential** is used for electrochemical enrichment in stripping voltammetry.
- During the **Equilibration time**, the start potential of the sweep is applied to the electrode.



**Cleaning potential (V) [ -5...+5 V ; -0.1 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Deposition potential (V) [ -5...+5 V ; -0.9 V ]**
Voltage applied to the electrodes during the **Deposition time**.

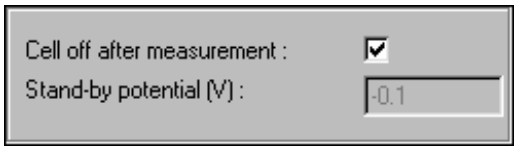
**Deposition time (s) [ 0...80600 s ; 60 s ]**
Time during which the **Deposition potential** is applied to the electrodes.

**Equilibration time (s) [ 0...80600 s ; 5 s ]**
Waiting time before starting the sweep; with start potential applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Achtung:** In the CVS and CPVS mode, no deposition is possible, and an own Equilibration potential can be defined (see Pretreatment with CVS and CPVS). With CPVS, it is part of the sweep.

## Stand-by potential

The **stand-by potential** can be applied to the electrodes at the end of the measurement. It remains in force until it is switched off manually in the **COMPUTRACE CONTROL** window or until a new voltage is applied to the electrodes in the next measurement.




**Cell off after measurement [ on, off ; on ]**
Enable/disable the switching off of the voltage applied to the electrodes after measurement.

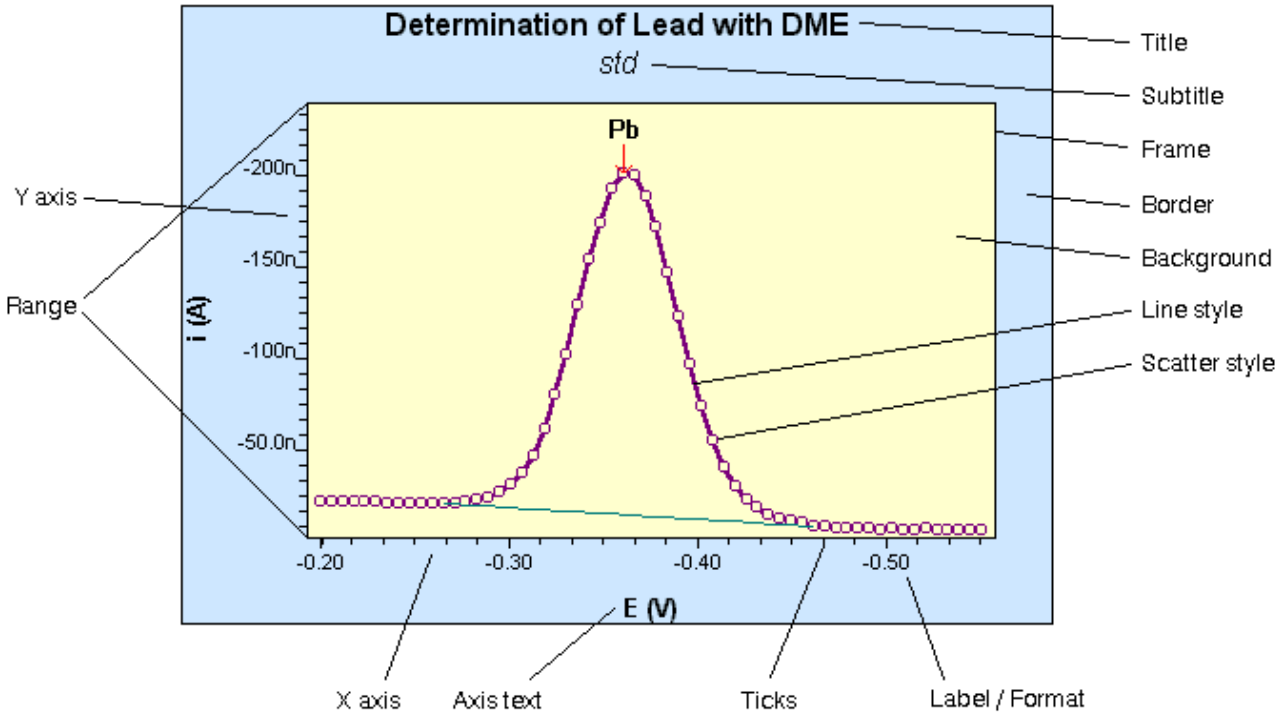
**Stand-by potential (V) [ -5...+5 V ; -0.1 V ]**
Voltage to be applied to the electrodes after measurement if the **Cell off after measurement** box is not activated.

**Note**: If **Cell off after measurement** is not checked, and you want to remove any electrode cable, the **Stand-by potential** must be turned off by clicking the Cell button on the **COMPUTRACE CONTROL** window.

# 3.5 Graphical settings

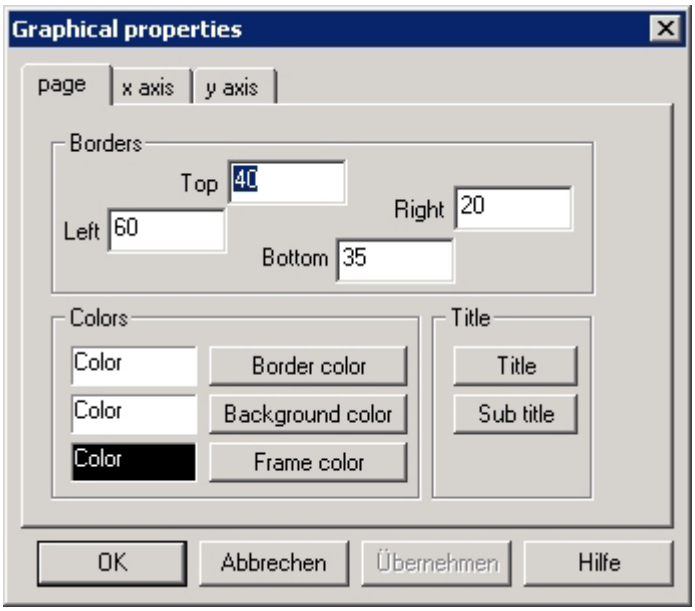
## Curve window elements

All curve windows in the **EXPLORATORY CURVES** window, the **DETERMINATION CURVES** window and in the **MONITOR** window have the same elements which can be changed as desired in the **GRAPHICAL PROPERTIES** and the **LINE PROPERTIES** window (see below).




## Page properties

The page properties of all curve windows can be set with the **page** tab of the **GRAPHICAL PROPERTIES** window.




**Borders**

**Top [ ≥ 0 pt ; 40 pt (for determination curves)]**

**Left [ ≥ 0 pt ; 60 pt (for determination curves)]**

**Right [ ≥ 0 pt ; 20 pt (for determination curves)]**

**Bottom [ ≥ 0 pt ; 35 pt (for determination curves)]**
Border size in points (distance between the curve window frame and the graphical window frame inside the curve window).

**Colors**

Border color
Color of border in the curve window.

Background color
Color of curve background in the curve window.

Frame color
Color of frame of the curve window.

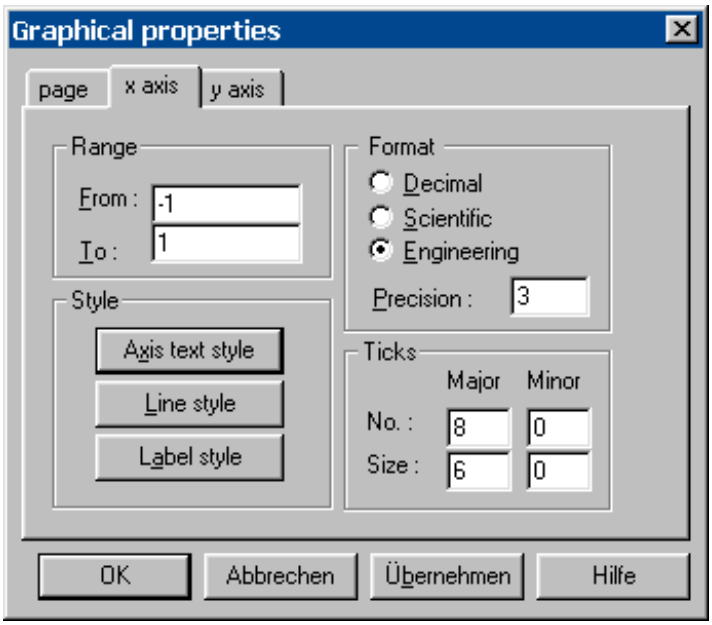
**Title**

Title
Font for title in the curve window (no function in the **MONITORING** window).

Sub title
Font for subtitle in the curve window (no function in the **EXPLORATORY CURVES** and **MONITORING** window).

## Axis properties

The axis properties for the x and y axis of all curve windows can be set with the **x axis** or **y axis** tab of the **GRAPHICAL PROPERTIES** window.




**Range (for x axis)**

**From [ -5...+5 ; -1 V ]**
Lower limit for x axis (voltage)
(t(s) for CPVS, U(V) for all other measurement modes)

**To [ -5...+5 ; -1 V ]**
Upper limit for x axis (voltage)
(t(s) for CPVS, U(V) for all other measurement modes)

**Range (for y axis)**

**From [ > 0 ; -1e-10 ]**
Lower limit for y axis
(dt/dU (s/V) for PSA and CCPSA; I(A) for all other measurement modes).

**To [ > 0 ; 1e-10 ]**
Upper limit for y axis
(dt/dU (s/V) for PSA and CCPSA; I(A) for all other measurement modes).

**Style**

Axis text style
Font for description of the x or y axis.

Line style
Selection of line style of the x or y axis in the **LINE PROPERTIES** window (see *section 3.5 Line properties*).

Label style
Font for labels of the x or y axis.

**Format**

Format for labels of the x or y axis. Check one of the following options:

**Decimal**
**± ##.###** (floating point number)

**Scientific**
**± #.### e ± ###**

**Engineering**
**± ###.## + prefix**

**Precision [ ≥ 0 ; 3 ]**
Total number of significant digits for labels of the x or y axis.

**Ticks**

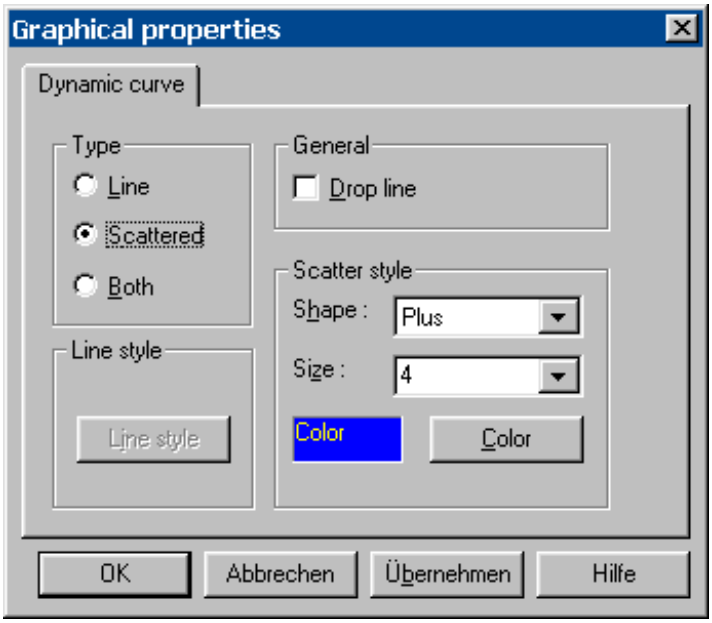
Definition of major and minor ticks for x or y axis.

**No. [ ≥ 0 ; 8 ]**
Number of major or minor ticks for x or y axis. In some cases this number will not be applied exactly but be fitted automatically to the next possible value for axis graduation.

**Size [ ≥ 0 pt ; 6 pt ]**
Size of major or minor ticks for x or y axis in points.

## Curve properties

The drawing properties for all curves can be set with the appropriate **..... curve** tab (**Dynamic curve**, **Selected curve** and **Other curves** for the **Exploratory curves**; **blank**, **sample** and **other curves** for the **Determination curves**; **Monitor curve** for the **Monitor curves**) of the **GRAPHICAL PROPERTIES** window.



**Type**

**Line**
Connect the measurement points by a straight line.

**Scattered**
Draw a symbol for each measurement point.

**Both**
Connect the measurement points by a straight line and draw a symbol for each point.

**Line style**

Line style

Selection of line style of the curve in the **LINE PROPERTIES** window (see *section 3.5 Line properties*).

**General**

**Drop line**
Draw vertical lines between each measurement point of the curve and bottom x axis.

**Scatter style**

**Shape [ Dot, Box, Circle, Plus, X, Asterisk ; Plus ]**
Selection of the symbol for drawing the measurement points.

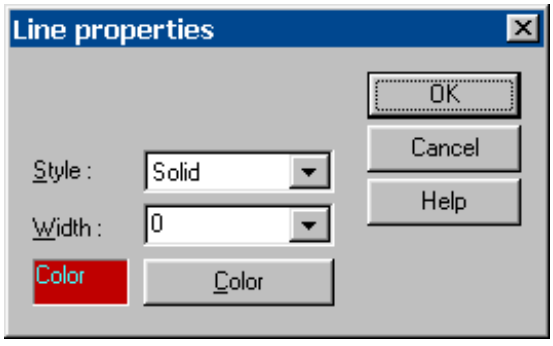
**Size [ 1...12 ; 4 ]**
Size of the symbol in points.

Color

Color of the symbol.

## Line properties

Definition of line properties for axes or curve lines. To get to the window **LINE PROPERTIES** click Line style in the window **GRAPHICAL PROPERTIES**.




**Style [ different styles ; Solid ]**
Style of the line.

**Width [ 0...8 ; 0 ]**
Width of the line in points (**0** = hair line).


Color of the line.

# 4 Exploratory mode

## 4.1 Exploratory mode overview

### Exploratory mode features

The program part "Exploratory" has been especially designed for practice-oriented **qualitative voltammetric analysis**. It comprises ten different measurement techniques and is curve oriented. You are shown voltammograms and the associated parameters in two windows next to each other. The various voltammograms can be superimposed on one another thus making comparison of the curves extremely simple.

Peaks or waves of the measured curves can be evaluated automatically or manually after setting the base points. Tracing the curves with a cursor allows the measured current and voltage values to be accessed.

Thanks to its possibilities, this program part is helpful in the development and optimization of methods for the quantitative determination of substances. The optimized voltammetric parameters can be transferred directly to the working method in the program part "Determination".

### Exploratory mode selection

**MAIN WINDOW / Mode / Exploratory**
Switching to the exploratory mode for recording and displaying of signals.

### Exploratory mode windows

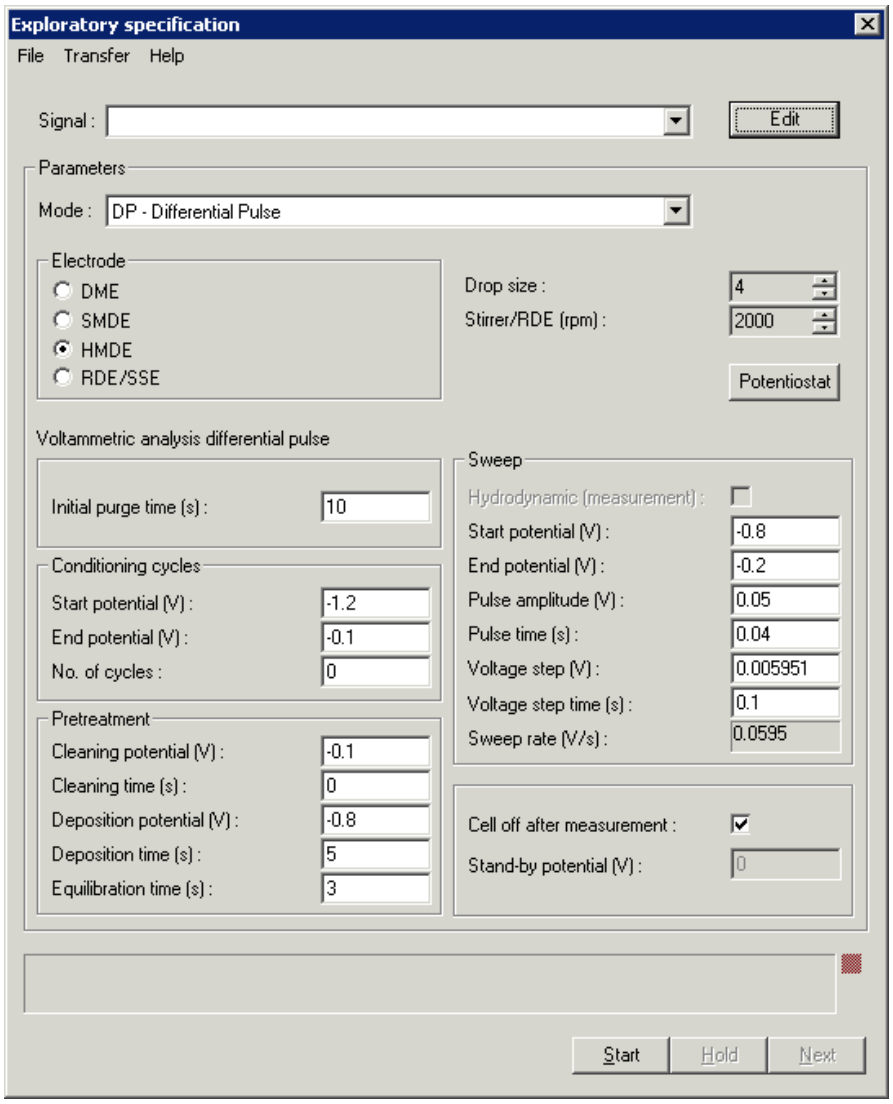
**MAIN WINDOW / Window / Exploratory specification (F11)**
The **EXPLORATORY SPECIFICATION** window will be opened or (if it is already open) closed.

**MAIN WINDOW / Window / Exploratory curves (F12)**
The **EXPLORATORY CURVES** window will be opened or (if it is already open) closed.

# 4.2 Exploratory specification window

## Exploratory specification settings

The **EXPLORATORY SPECIFICATION** window contains all settings for performing measurements in the exploratory mode. Most of the settings are identical for exploratory and determination mode and are therefore described in *section 3*.




**Signal** Selection of a signal file to be shown with the **Selected signal properties**. As long as a signal is selected, the settings can not be edited.

Edit By clicking the button <**Edit**>, the currently loaded settings can be changed. The selection of the signal is repealed. The settings can be transferred to the window **WORKING METHOD SPECIFICATION**.

**Mode** Selection of VA measurement mode, see *VA measurement modes section 3.2*

**Electrode** see *Electrodes*, *section 3.1*

**Drop size** see *Electrodes*, *section 3.1*

**Stirrer** see *Stirring*, *section 3.4*

Potentiostat see *Potentiostat*, *section 3.3*

**Initial purging time** (Initial mixing time with CVS and CPVS)
see *Purging section 3.4*, and *Initial mixing time with CVS and CPVS section 6.3*)

**Conditioning cycles** see *Conditioning of solid state electrodes section 3.4*, and *Conditioning cycles with CVS and CPVS section 6.3*

**Pretreatment** see Pretreatment *section 3.4*, and *Pretreatment with CVS and CPVS section 6.3*

**Sweep** Parameters of the selected VA measurement mode, see *VA measurement modes section 3.2*

**Cell off after measurement**
Enable/disable the switching off of the voltage applied to the electrodes after measurement.

**Stand-by potential** see *Stand-by potential*, *section 3.4*

## Load/save signals

Signal files (***.sig**) contain the measurement data and specifications of a signal recorded in the exploratory mode.

**EXPLORATORY SPECIFICATION / File / New parameters**
Load default parameters for selected electrode and measurement mode.

**EXPLORATORY SPECIFICATION / File / Load signal**
Load an existing signal file. Normally, signal files are stored in the **Data** folder.

**EXPLORATORY SPECIFICATION / File / Save signal ...**
Save the signal whose parameters are loaded in the working memory into a new file (this is only possible for a signal marked with an asterisk *****). Enter name and directory for storage of the signal file.

**EXPLORATORY SPECIFICATION / File / Export signal points**
Save the measurement points of the sweep of the current signal loaded in the working memory into a data file (extension ***.txt**). This data file contains a block of the used method parameters followed by the sweep block of X and Y values preceded by the number of measurement points. The data files can be imported into spreadsheet programs like Microsoft Excel.

**EXPLORATORY SPECIFICATION / File / Export voltammetric parameters ...**
Save the voltammetric parameters of the current signal loaded in the working memory into an ASCII file (extension ***.txt**). The files can be imported into spreadsheet programs like Microsoft Excel or into text programs like Microsoft Word.

## Transfer parameters and data

Measurement parameters and/or data points of signal files can be transferred between the exploratory mode and the determination mode.

**EXPLORATORY SPECIFICATION / Transfer / Parameters / To working method**
Transfer measurement parameters from the **EXPLORATORY SPECIFICATION** window to the **WORKING METHOD SPECIFICATIONS** window.

**EXPLORATORY SPECIFICATION / Transfer / Parameters / From working method**
Transfer measurement parameters from the **WORKING METHOD SPECIFICATIONS** window to the **EXPLORATORY SPECIFICATION** window.

**EXPLORATORY SPECIFICATION / Transfer / Parameters / From determination method**
Transfer measurement parameters from the **EDIT DETERMINATION METHOD PARAMETERS** window to the **EXPLORATORY SPECIFICATION** window.

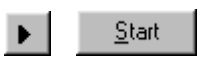
**EXPLORATORY SPECIFICATION / Transfer / Data to determination**
Transfer measurement data of the loaded signal file to the loaded determination file. The data set to which the measurement data should be transferred has to be specified as VR code (number of variation and replication).

Variation: 0, 1, 2 … (0 = blank, 1 = sample, 2 = first addition, …)

Replication: 1, 2, 3 …

## Performing exploratory measurements

Measurements in the exploratory mode can be performed using the following icons (in the **MAIN WINDOW**) or buttons (in the **EXPLORATORY SPECIFICATION** window):




### Start measurement

The operation sequence (see *section 3.4*) defined in the **EXPLORATORY SPECIFICATION** window is started. Each step of the operation sequence is listed in the first line of the status window beside the **<Start>** button.


For the running voltage sweep there is a live display in the **EXPLORATORY CURVES** window with automatic scaling of the axes. Manual rescaling can be done by pressing the <F4> button.

The red light at the left side of the **<Stop>** button indicates a current overload. In this case, stop the measurement and change the measurement parameters.

In the second line of the status window comments or error messages concerning the running measurement are displayed.

A running measurement can be stopped, interrupted and continued. Each step in the operation sequence can be abbreviated by clicking the **<Next>** button.


**Stop measurement**
Stop running measurement immediately.


**Hold measurement**
Interrupt running measurement.

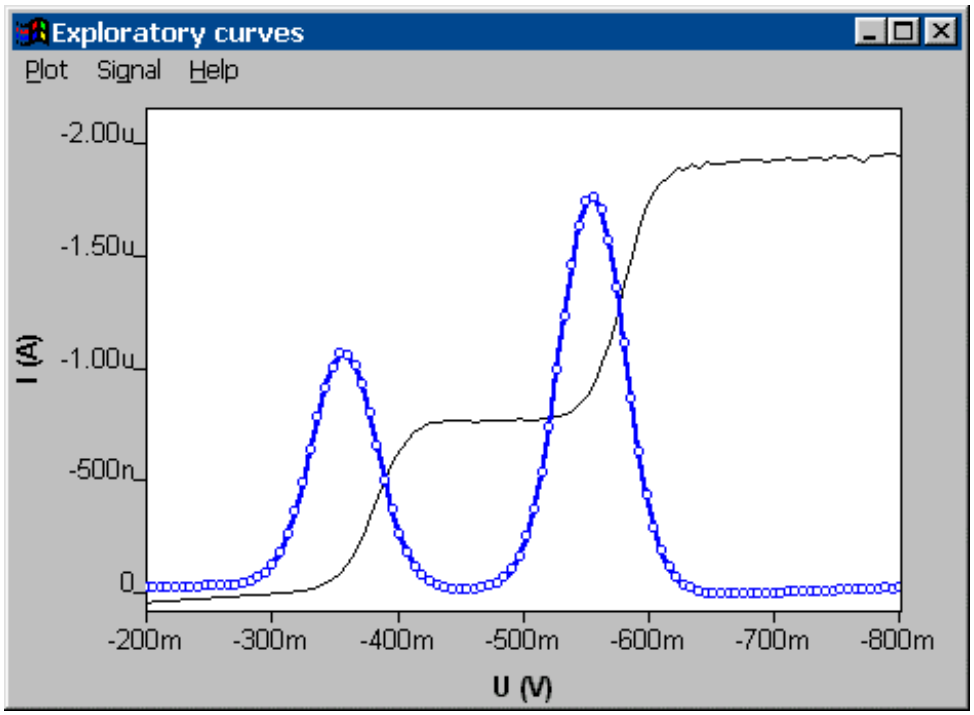

**Continue measurement**
Continue an interrupted measurement.


**Next step**
Go to next step in operation sequence.

## 4.3 Exploratory curves

### Exploratory curves window

The **EXPLORATORY CURVES** window shows all curves of the signals loaded and (if a voltage sweep is running) the live curve.




If a signal file is loaded or measured, the axes have the following orientation:

**x axis** The previously loaded or measured signal is displayed from the left to the right. For cyclic sweeps, the forward sweep is displayed from the left to the right.

**y axis** The y axis is displayed with positive values at the top.

## Load signal curves

The signal curves are loaded into the **EXPLORATORY CURVES** window by loading the signal files (***.sig**) in the **EXPLORATORY SPECIFICATION** window.

**EXPLORATORY SPECIFICATION / File / Load signal**
Load one or several (Ctrl + Click) existing signal file(s) with its measurement parameters. Normally, signal files are stored in the **Data** folder.

## Select signal curves

One of the signal curves loaded into the **EXPLORATORY CURVES** window is always shown with **Selected signal properties** which can be set different from all other curves loaded (see *Curve properties, section 3.5*). The selection of this signal file is done in the **Signal** field of the **EXPLORATORY SPECIFICATION** window. An asterisk * in this field marks the signal file whose parameters are loaded in the **EXPLORATORY SPECIFICATION** window. Only this signal file can be stored.

## Zooming

Curve regions in the **EXPLORATORY CURVES** window can be enlarged by zooming the desired area while pressing the left mouse button ("drag a box"; reset see *Auto scaling*).

## Auto scaling

**EXPLORATORY CURVES / Plot / Auto scale (F4)**
Reset zooming and scale x and y axes so that all measurement points of all signal curves are visible. This function is also active during measurement for the live display.

## Swap axes

**EXPLORATORY CURVES / Plot / Swap axis / abscissa**
Swap x axis for the current signal curve.

**EXPLORATORY CURVES / Plot / Swap axis / ordinate**
Swap x axis for the current signal curve.

## Graphical properties for exploratory curves

**EXPLORATORY CURVES / Plot / Page properties**
The page properties of the **EXPLORATORY CURVES** window can be set with the **page** tab of the **GRAPHICAL PROPERTIES** window (details see *Page properties*, *section 3.5*).

The properties of the x and y axis can be set with the **x axis** and **y axis** tab of the **GRAPHICAL PROPERTIES** window (details see *Axis properties*, *section 3.5*).

**EXPLORATORY CURVES / Plot / Dynamic signal properties**
The properties of the dynamic signal curve (live curve) can be set with the **Dynamic curve** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**EXPLORATORY CURVES / Plot / Selected signal properties**
The properties of the selected signal curve can be set with the **Selected curve** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**EXPLORATORY CURVES / Plot / Other signal properties**
The properties of all other signal curves can be set with the **Other curves** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**Note**: The line properties for axis or signal curve lines can be set with in the **LINE PROPERTIES** window (details see *Line properties*, *section 3.5*)

## Copy to clipboard

**EXPLORATORY CURVES / Plot / Copy to clipboard**
Copy the current content of the **EXPLORATORY CURVES** window to the clipboard.

## Save as enhanced metafile

**EXPLORATORY CURVES / Plot / Save as enhanced metafile**
Saves the current content of the **EXPLORATORY CURVES** window as an enhanced metafile (*.emf).

## Change labels

**EXPLORATORY CURVES / Plot / Change Y axis text**
Modify text label for y axis.

**EXPLORATORY CURVES / Plot / Change title**
Modify title text, which is displayed above the curve.

## Clear signal curves

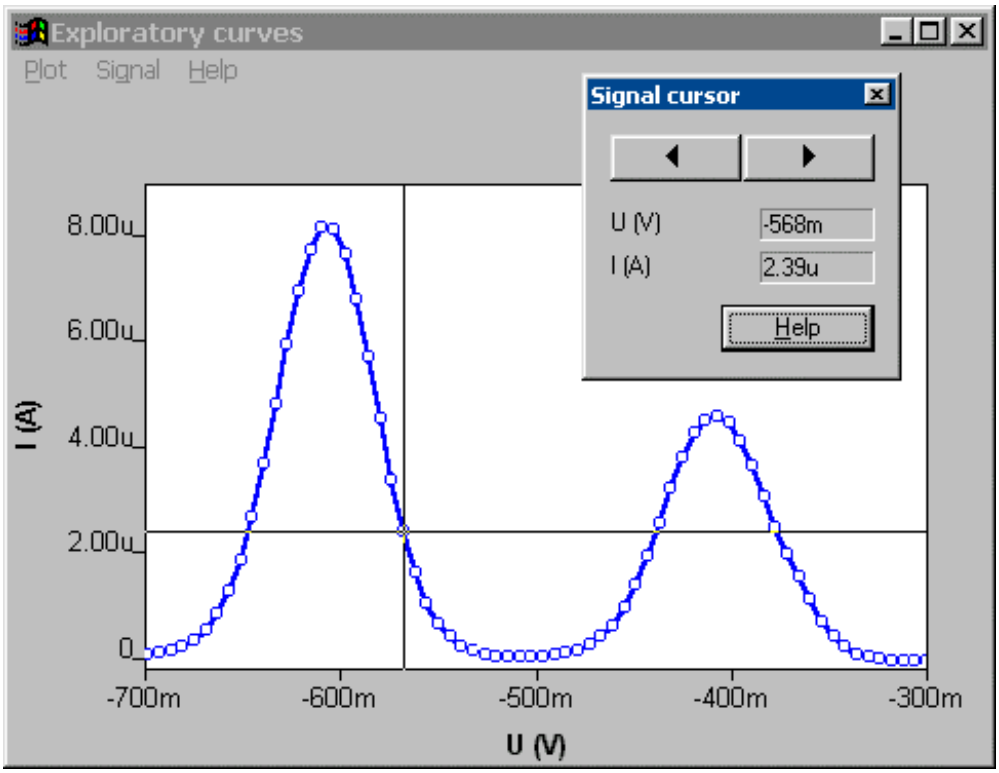
A single or all signal curves loaded into the **EXPLORATORY CURVES** window can be cleared by selecting the appropriate menu point in the **EXPLORATORY CURVES** window.

**EXPLORATORY CURVES / Signal / Clear**
Remove the selected signal curve from the **EXPLORATORY CURVES** window.

**EXPLORATORY CURVES / Signal / Clear all**
Remove all signal curves from the **EXPLORATORY CURVES** window.

## Signal cursor

**EXPLORATORY SPECIFICATION / Signal / Signal cursor**
Open the **SIGNAL CURSOR** window for selection of measurement points. The X and Y value of the selected point is displayed in the window.



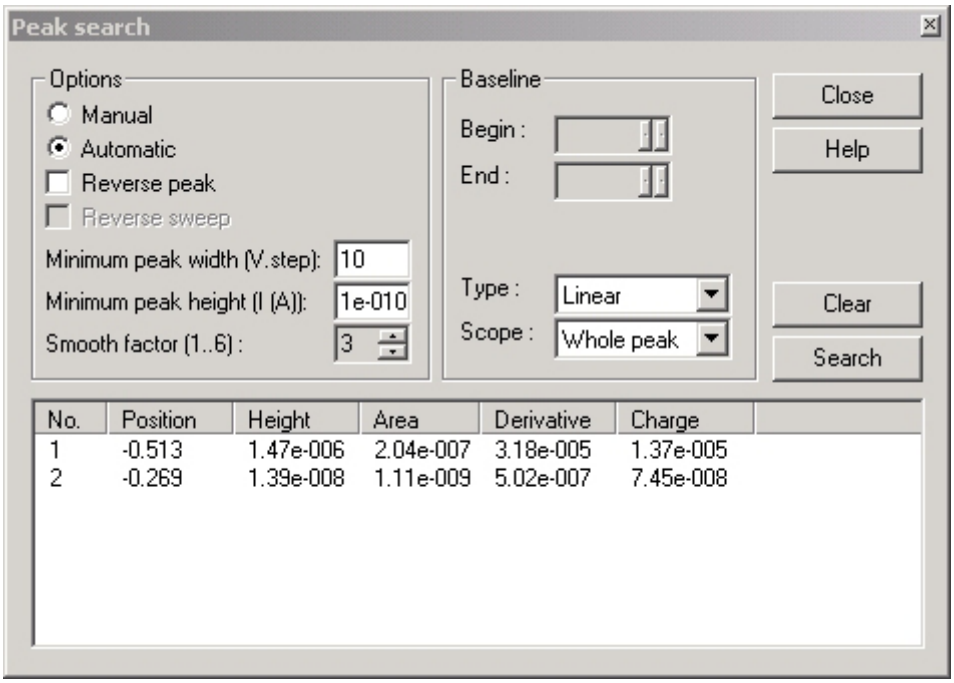

Move cursor to the next or to the preceding measurement point on the selected signal.

## Peak search

Automatic or manual peak evaluation of recorded signal curves. The results (peak position, height, area, derivative) are listed in the table of results, the calculated baselines and peak positions are also displayed in the **EXPLORATORY CURVES** window.

**EXPLORATORY SPECIFICATION / Signal / Peak search**

Open the **PEAK SEARCH** window for starting the quantitative peak evaluation.




**Options** General parameters for peak evaluation.

**Manual**
Manual peak evaluation. The base points for baseline evaluation must be set manually.

**Automatic**
Automatic peak evaluation. The base points for baseline evaluation are evaluated automatically.

**Reverse peak**
Enable peak evaluation of reverse peaks (peaks with opposite direction compared to the sweep direction: negative peaks with anodic sweeps; positive peaks with cathodic sweeps).

**Reverse sweep**
Enable peak evaluation of the reverse sweep of cyclic voltammograms (only available with CV and CVS).

**Minimum peak width (V.step) [ ≥ 0 ; 10 ]**
Minimum peak width for peak recognition by number of **Voltage steps** (= number of measurement points).

**Minimum peak height (A) [ > 50 pA ; 100 pA ]**
Minimum peak height for peak recognition.

**Smooth factor [ 1...6 ; 3 ]**
Smoothing power for the Savitzky/Golay smoothing of the baseline (**1** = minimum smoothing, **6** = maximum smoothing).

**Baseline** Parameters for baseline evaluation.

**Begin (V)** (for CPVS: **s**) **[ Start potential...End potential ; - ]**
Manual setting of the start base point for baseline evaluation. The values can be increased or decreased by clicking the buttons of the field or by clicking the field and pressing the ↑ or ↓ key. If the automatic peak evaluation is selected, **n/a** is displayed and the field can not be edited.

**End (V)** (for CPVS: **s**) **[ Start potential...End potential ; - ]**
Manual setting of the end base point for baseline evaluation. The values can be increased or decreased by clicking the buttons of the field or by clicking the field and pressing the ↑ or ↓ key. If the automatic peak evaluation is selected, **n/a** is displayed and the field can not be edited.

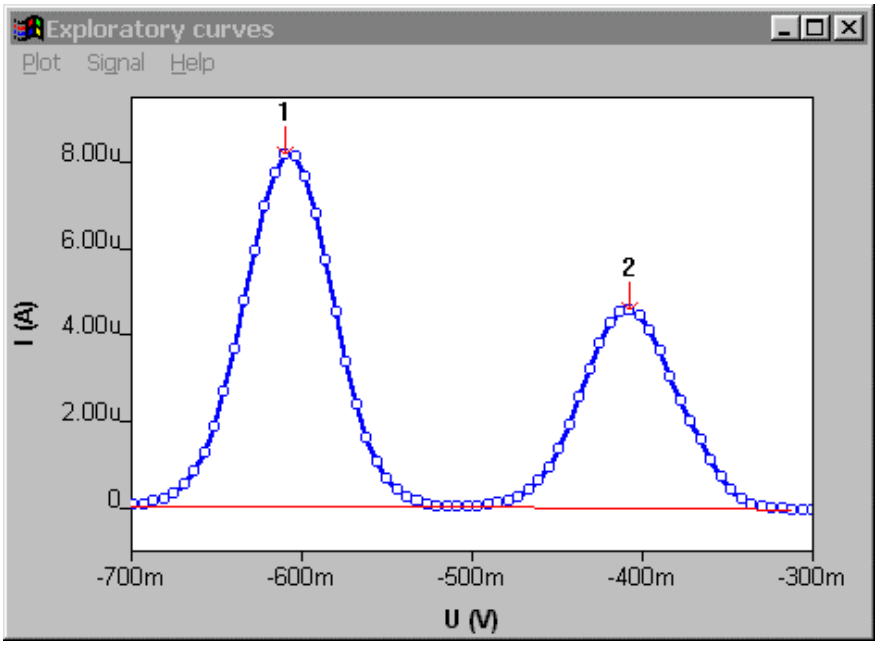
**Type [ Linear, Polynomial, Exponential , Horizontal ; Linear ]**
Selection of the baseline type. Automatic peak evaluation is only possible with baseline types linear and horizontal.

**Scope [ Whole peak, Front end, Rear end ; Whole peak ]**
Selection of the range for baseline evaluation. This field can only be edited if the **Linear** baseline type is selected.

Close — Close the **PEAK SEARCH** window.

Clear — Clear all the peak evaluation results entered in the peak table and the **EXPLORATORY CURVES** window.

Search — Start peak evaluation with the current parameters entered in the **PEAK SEARCH** window. The calculated baselines and peak maximum positions are displayed in the **EXPLORATORY CURVES** window.




## Table of results

Display of peak evaluation results.

**No.**
Number of evaluation result. This number is also displayed in the **EXPLORATORY CURVES** window. Clicking this number with the right mouse button offers the following menu:

**Edit baseline**
Open the **EDIT BASELINE** window for further modifying the peak evaluation for the selected peak (see *Edit baseline*, *section 4.3*).

**Copy**
Copy the selected results line of the table to the clipboard.

**Copy Peak List**
Copy all result lines of the table to the clipboard.

**Copy Graphed Results**
Copy the current content of the **EXPLORATORY CURVES** window to the clipboard.

**Position (V)**
Calculated peak voltage at the peak maximum.

**Height (A)**
Calculated peak height from the baseline to the peak maximum.

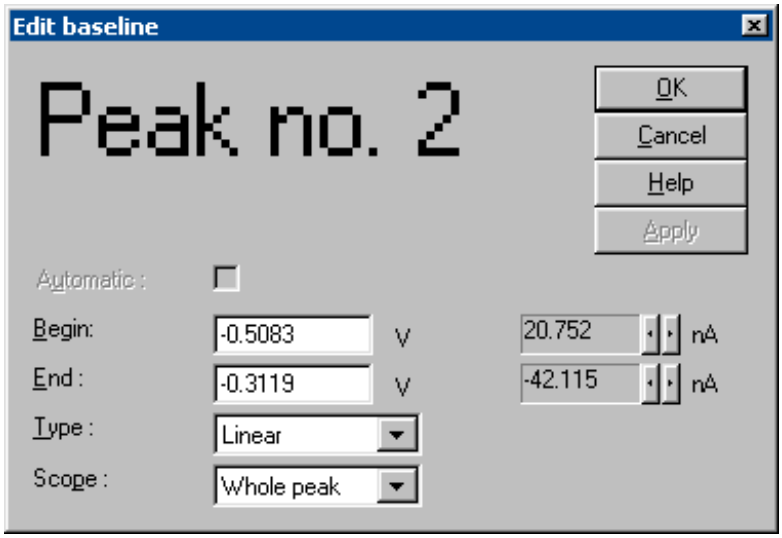
**Area (W)**
Calculated peak area between peak curve and calculated baseline.

**Derivative**
Calculated difference between the positive and negative maximum of the first derivative of the voltammogram.

**Charge (C)**
Calculated charge transmitted during this peak (is depending from sweep rate and current).

## Edit baseline

Modify the peak evaluation of an already found peak. The results are displayed in the **PEAK SEARCH** window. This window is opened by clicking the number of a found peak in the **PEAK SEARCH** window with the right mouse button and selecting the menu point **Edit peak**.




**Begin**
Manual setting of the start base point for baseline calculation. The base point can be moved either by manually changing the voltage value (time with CPVS) in the first field or by clicking the buttons of the second field indicating the current value.

**End**
Manual setting of the end base point for baseline calculation. The base point can be moved either by manually changing the voltage value (time with CPVS) in the first field or by clicking the buttons of the second field indicating the current value.

**Type of baseline [ Linear, Polynomial, Exponential , Horizontal ; Linear ]**
Selection of the baseline type.

**Scope [ Whole peak, Front end, Rear end ; Whole peak ]**
Selection of the range for baseline evaluation. This field can only be edited if the **Linear** baseline type is selected.

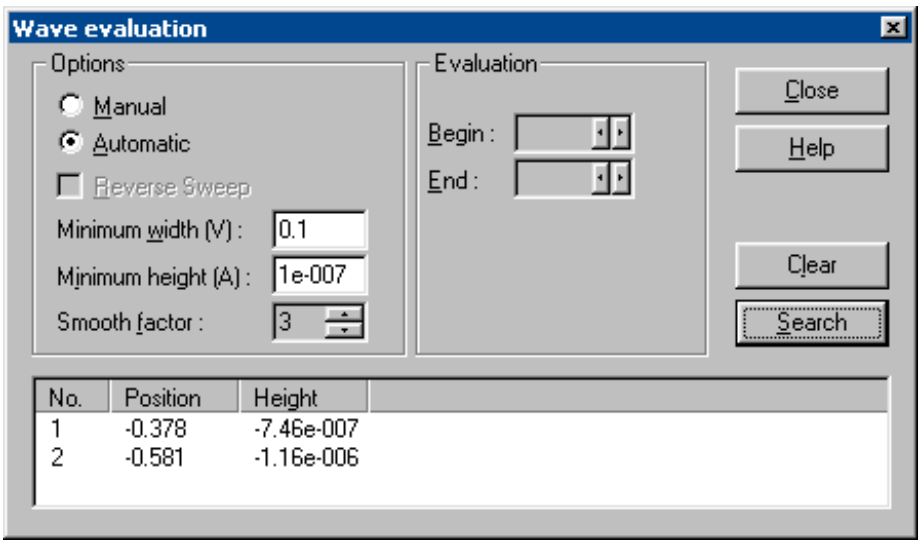
Apply
Start peak evaluation with the current parameters entered in the **EDIT PEAK** window.

## Wave evaluation

Automatic wave evaluation of recorded DC or NP signal curves. The results (position of half-wave potentials and wave height) are listed in the table of results, the calculated tangents and positions of the half-wave potential are displayed in the **EXPLORATORY CURVES** window.

**EXPLORATORY SPECIFICATION / Signal / Wave evaluation**

Open the **WAVE EVALUATION** window for starting the quantitative wave evaluation.




**Options** General parameters for wave evaluation.

**Manual**
Manual wave evaluation. The base points for tangent evaluation must be set manually.

**Automatic**
Automatic wave evaluation. The base points for tangent evaluation are evaluated automatically.

**Minimum width (V) [ > 0...5 V ; 0.1 V ]**
Minimum width for wave recognition.

**Minimum height (A) [ > 50 pA ; 100 nA ]**
Minimum wave height for wave recognition.

**Smooth factor [ 1...6 ; 3 ]**
Smoothing power for the Savitzky/Golay smoothing of the wave (**1** = minimum smoothing, **6** = maximum smoothing).

Close — Close the **WAVE EVALUATION** window.

Clear — Clear all the wave evaluation results entered in the results table and the **EXPLORATORY CURVES** window.

Search — Start wave evaluation with the current parameters entered in the **WAVE EVALUATION** window. The

calculated positions of the half-wave potentials and tangents are displayed in the **EXPLORATORY CURVES** window.

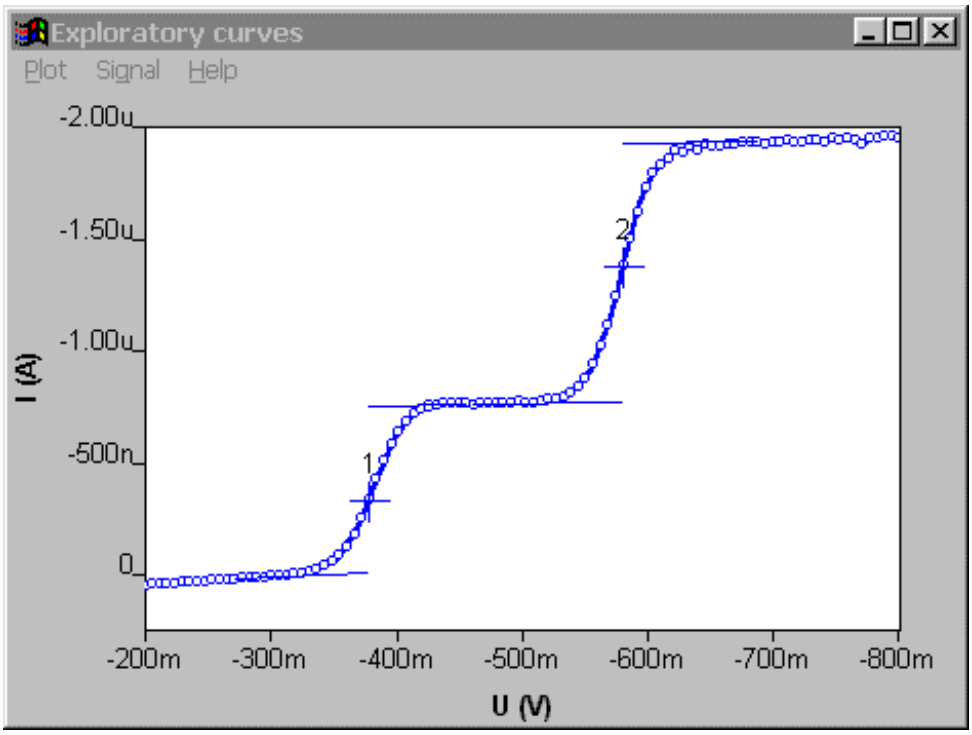



**Table of results**

Display of wave evaluation results.

**No.** Number of evaluation result. This number is also displayed in the **EXPLORATORY CURVES** window. Clicking this number with the right mouse button offers the following menu points:

**Copy**
Copy the selected result line to the clipboard.

**Copy All** or **Copy Wave List**
Copy all result lines of the table to the clipboard.

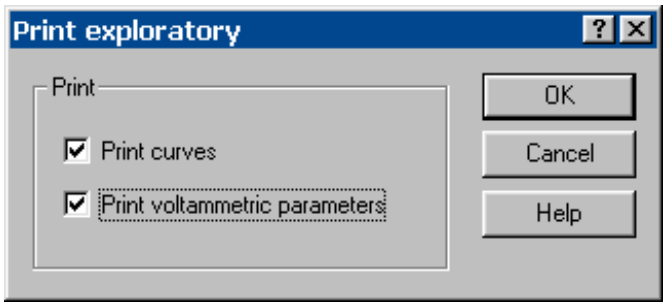
**Copy Graphed Results**
Copy the current content of the **EXPLORATORY CURVES** window to the clipboard.

**Position (V)**
Calculated half-wave potential of the wave.

**Height (A)**
Calculated wave height between the tangents at the half-wave potential position.

## 4.4 Printing in exploratory mode

**MAIN WINDOW / File / Print (Ctrl+P)**
Print exploratory specifications and/or curves. The **PRINT EXPLORATORY** window appears for selection of the items to be printed.




With **Print curves** enabled, the content of the **EXPLORATORY CURVES** window is printed on the upper half of the page if the portrait format is selected for the printer or on the whole page, if landscape format is selected.

With **Print voltammetric** parameters enabled, the voltammetric parameters defined in the **EXPLORATORY SPECIFICATION** window are printed.

Curves and voltammetric parameters are always printed on separate pages.

# 5 Determination mode

## 5.1 Determination mode overview

### Determination mode features

The program part "Determination" is used for **quantitative voltammetric analysis** of inorganic and organic substances. It comprises nine different measurement modes and the possibility for stripping techniques. Quantitative evaluation can be performed via standard addition or calibration curve.

The **peak evaluation** is automatic, various functions (linear, polynomial, horizontal and exponential) can be selected for the baseline approximation. In case of asymmetric peaks, there is a possibility to evaluate only the front or rear peak half.

Peak evaluation and result calculation are documented in an individually compilable **report** which can also contain voltammograms and calibration curves.

The parameters of the voltammetric analysis are stored in a method file. The method loaded into the working memory is the **working method** which is used for performing new determinations. The **determination method** is the method which was used for the recording of the loaded determination and which is stored together with the measurement data in a determination file.

### Determination mode selection

**MAIN WINDOW / Mode / Determination**

Switching to the determination mode for recording and displaying of determinations.

### Determination mode windows

**MAIN WINDOW / Window / Working method specification (F6)**

The **WORKING METHOD SPECIFICATIONS** window will be opened or (if it is already open) closed. It contains the specifications of the method loaded into the working memory.

**MAIN WINDOW / Window / Monitor (F7)**

The **MONITOR** window will be opened or (if it is

already open) closed. It serves to start a determination using the working method and shows the live display of the running determination curves.

**MAIN WINDOW / Window / Determination curves (F8)**
The **DETERMINATION CURVES** window will be opened or (if it is already open) closed. It contains determination and calibration curves of the loaded determination and offers the possibility for recalculation and modification of the loaded determination.

**MAIN WINDOW / Window / Results (F9)**
The **RESULTS** window will be opened or (if it is already open) closed. It contains the full report of the loaded determination.

**MAIN WINDOW / Window / Sample table (F10)**
The **SAMPLE TABLE** window will be opened or (if it is already open) closed. (Only visible, if in **GENERAL SETTINGS/Automation** tab **Use sample table** is chosen for **Working method source**).

## 5.2 Working method specifications

### Load/save methods

Method files (***.mth**) contain all the specifications and parameters for running a determination.

**MAIN WINDOW / File / New method (Ctrl+N)**
Load a standard template with DP mode for creating a new method into the working memory.

**MAIN WINDOW / File / Load method (Ctrl+O)**
Load an existing method file into the working memory. The name of the method loaded is displayed in the status bar of the **MAIN WINDOW**.

**MAIN WINDOW / File / Save method (Ctrl+S)**
Save the current method loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save method as ...**
Save the current method loaded in the working memory as a new file. Enter name and directory for storage of the method file. If the file name already exists, windows asks if you want to overwrite the existing file.

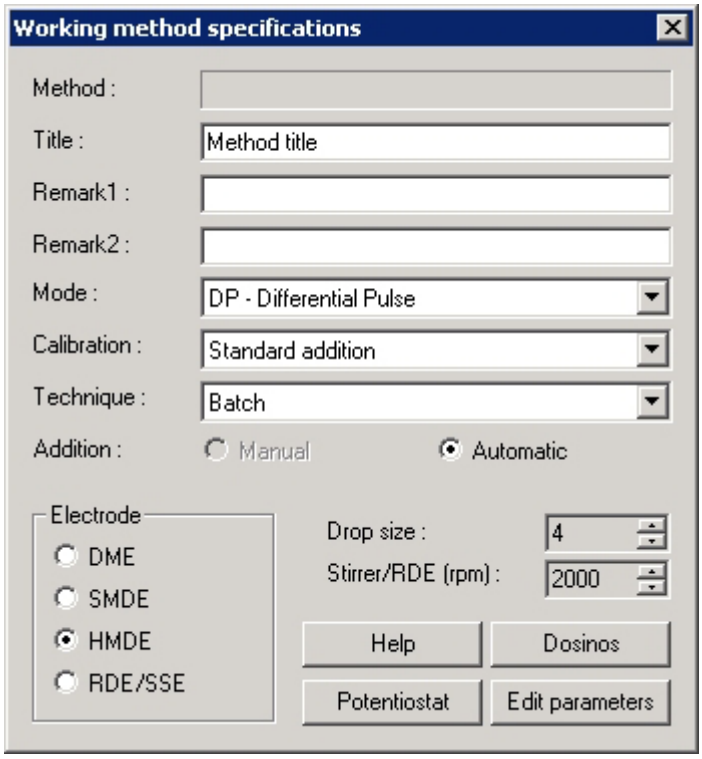
**797 VA COMPUTRACE / File / Export results ...**
Save the full report of the current determination

loaded in the working memory as an ASCII file (***.txt**). This file can be imported into spreadsheet programs like Microsoft Excel or into text programs like Microsoft Word.

**Note**: The default folder where methods are saved or loaded from is set in the **User directories** tab of the **USER RIGHTS** window.

## Working method specifications window

The **WORKING METHOD SPECIFICATIONS** window contains the main specifications for the working method (method loaded in the working memory). The rest of the settings and parameters for the working method can be accessed by clicking the **<Edit parameters>**, **<Potentiostat>** and **<Dosinos>** button.




**Method [ read only ]**
File name of the method loaded in the working memory (only visible if the method has already been saved).

**Title [ 0...68 characters ; "Method title" ]**
Method title.

**Remark1 [ 0...68 characters ; ]**
Remark 1 regarding the method.

**Remark2 [ 0...68 characters ; ]**
Remark 2 regarding the method.

**Mode**
Selection of VA measurement mode (see *VA measurement modes*, *section 3.2*).

**Calibration [ *see below* ; Standard addition manual ]**

Selection of calibration mode (see also *Calibration techniques with CVS and CPVS*, *section 6.2*):

**Standard addition**

Standard addition. The number of additions is defined in the **Determination** tab, the standard addition solutions are defined in the **Substances** tab, and the Dosing Devices are defined in the **DOSINOS** window.

**Sample with calibration curve**

Sample determination using previously recorded calibration curves. The determination with the recorded calibration curves must be defined in the **Determination** tab.

**Record calibration curve**

Recording of calibration curves. The number of additions is defined in the **Determination** tab, the addition solutions are defined in the **Substances** tab, and the Dosing Devices are defined in the **DOSINOS** window.

---

**Note**: For the electroplating bath modes **CVS** and **CPVS** the **Calibration** techniques are different. See *Calibration techniques with CVS and CPVS*, *section 6.2*).

---

**Technique [ *see below* ; Batch ]**

Selection of measurement technique:

**Batch**

Measurement without solution exchange.

**Batch with solution exchange**(not selectable with **CVS** and **CPVS** modes)

Measurement with solution exchange for every addition or calibration level.

**Taken from calibration curve**

This option is used automatically if **Sample with calibration curve** is selected.

**Addition [ Manual, Automatic ; Manual ]**

Selection of manual or automatic standard addition or recording of calibration curves:

**Manual**

Manual standard addition resp. recording of calibration curves using a pipette.

**Automatic**

Automatic standard addition resp. recording of calibration curves using one or several Dosing Devices.

**Electrode** Selection of electrode (see *Electrodes*, *section 3.1*).

**Drop size** Drop size for SMDE or HMDE (see *Electrodes*, *section 3.1*).

**Stirrer** Stirrer settings (see *Stirring*, *section 3.4*).

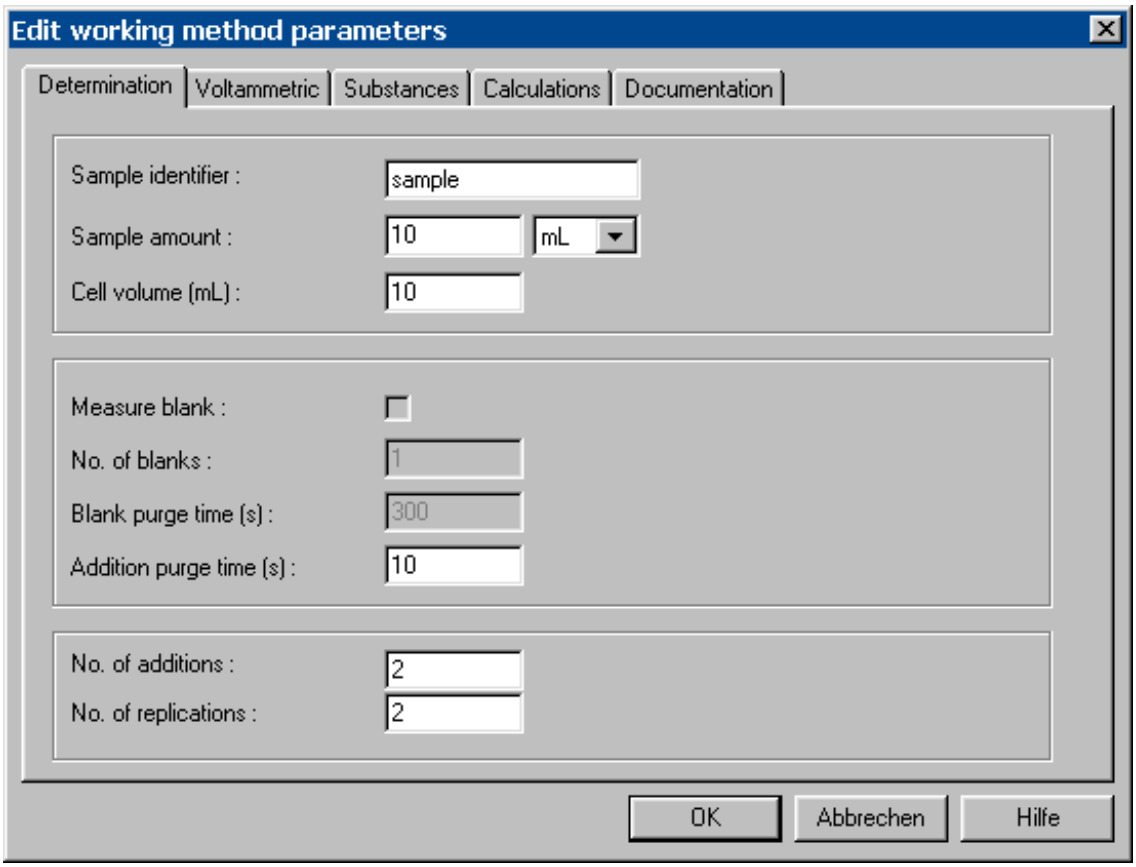

Dosing Device settings (see *Dosing Devices*, *section 5.2*).


Potentiostat settings (see *Potentiostat*, *section 3.3*).


Edit working method parameters (see *Determination*, *Voltammetric*, *Substances*, *Calculations* and *Documentation*).

## Determination

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**.




**Sample identifier [ 32 characters ; "sample" ]**

Identification for sample. The

**Note**: The **Sample identifier** is used for the file name. To make sure that (for automated operations with a sample processor) always the latest calibration file is taken for the calculation; the **Sample identifier** defined for recording the calibration curve (with **Calibration** technique "Record calibration curve"), must match with the file name of the calibration file chosen for parameter **Calibration curve** (see below) for the determination of the sample (with **Calibration** technique "Sample with calibration curve").

Example for **Sample identifier**: CalibrationLead

**Sample amount (mL) [ > 0 mL ; 10 mL ]**

Amount of sample added to the measuring vessel.

**Sample unit [ mL, g ; mL ]**

Selection of unit for sample amount.

**Note**: The sample unit chosen in the **EDIT WORKING METHOD PARAMETERS/Determination** tab determines the selecting list for **Final Unit** in the **CALCULATION** window.

mL → #g / #L [g/L]
g → #g / #g [g/kg]

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Total volume of solution (sample + auxiliary solution, e.g. buffer (added manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination. The sample concentrations **Conc.** calculated refer to this cell volume.

---

**Note**: The sample and solution parameters (**Sample identifier**, **Sample amount**, **Sample unit**, **Cell volume**) are different with the CVS or CPVS mode.

---

**Measure blank [ on, off ; off ]**
Measure a blank solution before sample determination. The blank curve is then automatically subtracted from all subsequent measured curves. This background compensation is mainly used to reduce interference due to the supporting electrolyte. Such interference includes both the presence of the analyte (blank value) and that of foreign substances electroactive in the same range.

**No. of blanks [ 1...5 ; 1 ]**
Number of measurements to determine the blank curve. If the blank solution is measured several times, a mean blank curve is determined from the different measurements.

**Blank purge time [ 0...80600 s ; 300 s ]**
Time of inert gas purging before measurement of the blank solution.

**Addition purge time [ 0...80600 s ; 10 s ]**
Time of inert gas purging for all measurements after determination of the sample (standard addition) or of the first calibration solution if **Batch** is selected for **Technique** (for the first measurement, the **Initial purge time** is used).

---

**Note**: The blank measurements parameters (**Measure blank**, **No. of blanks**, **Blank purge time**, **Addition purge time**) are different with the **CVS** or **CPVS** mode.

---

**Cell purge time [ 0...80600 s ; 10 s ]**
Time of inert gas purging after solution exchange if **Batch with solution exchange** is selected for **Technique**.

**No. of additions [ 0...28 ; 2 ]**
Number of additions of standard addition solutions resp. calibration solutions if **Batch** is selected for **Technique**.

**No. of cells [ 0...28 ; 2 ]**

Number of solutions to be measured if **Batch with solution exchange** is selected for **Technique**.

**Calibration curve [ path + file name ; ]**

Selection of the determination file that contains the desired calibration curves. Accessible if **Sample with calibration curve** is selected for **Calibration**. Also accessible with **Calibration** technique "DT Suppressors with calibration curve" in the CVS and CPVS mode.

---

**Note**: To make sure that (for automated operations with a sample processor) always the latest calibration file is taken for the calculation; the file name of the calibration file chosen for parameter **Calibration curve** for the determination of the sample (with **Calibration** technique "Sample with calibration curve"), must match with the **Sample identifier** (see above) defined for recording the calibration curve (with **Calibration** technique "Record calibration curve").

---

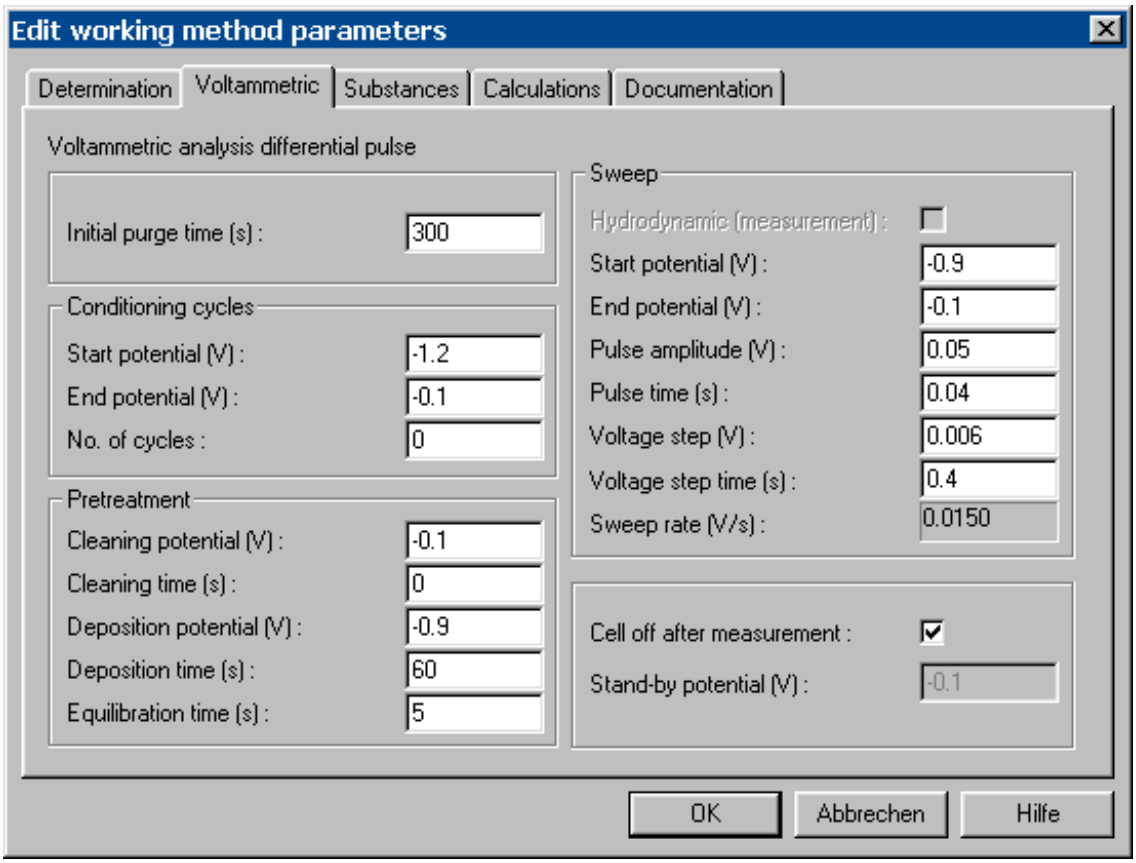
Example for **Calibration curve**:
C:\Program files\Metrohm\797 VA Computrace\-Data\CalibrationLead.dth

**No. of replications [ 0...10 ; 2 ]**

Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

## Voltammetric

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window.




For a detailed description of these parameters see *section 3.4 General operation sequence*, and *section 3.2 VA measurement modes*.

If you work with the electroplating bath modes **CVS** or **CPVS**, see *section 8.6 Operate a sequence in Electroplating Bath VA*.

**Note:** For **Calibration** technique "Sample with calibration curve" the **Voltammetric** tab parameters are not editable. To make sure that the **Voltammetric** parameters defined for the determination of the sample match with the **Voltammetric** parameters defined for recording the calibration curve (with **Calibration** technique "Record Calibration curve"), following procedure is recommended:

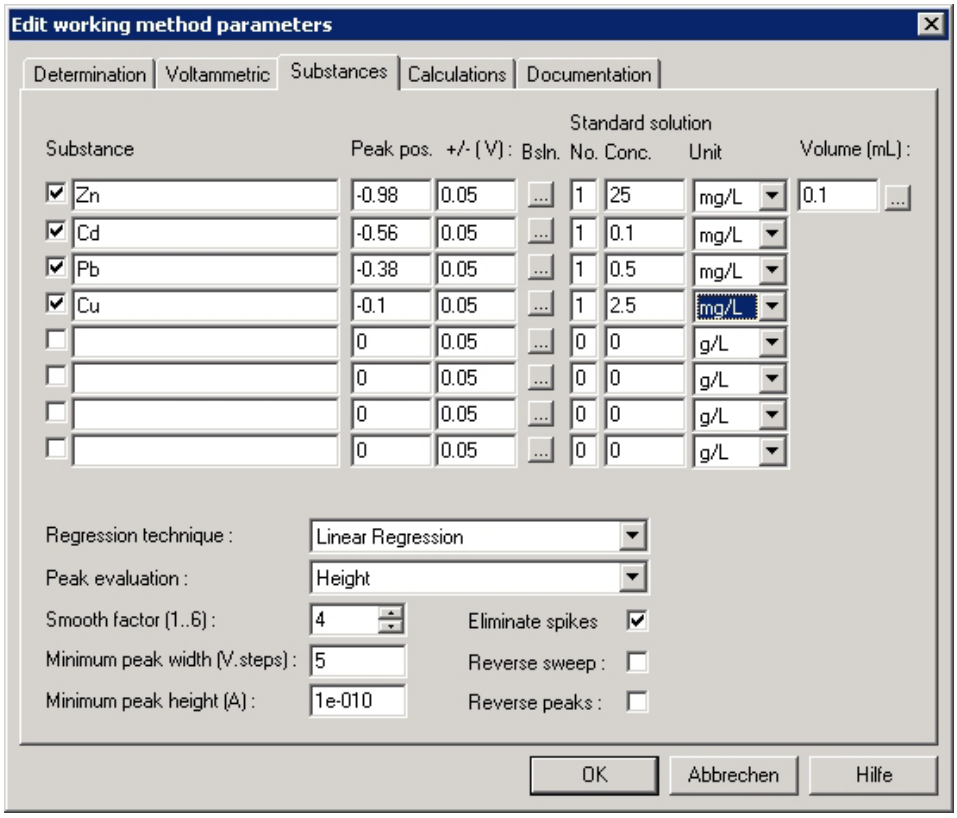
1. Load the determination of the calibration curve (**FILE / Load determination**)
2. Open window **DETERMINATION CURVES**
3. Copy the parameters to the working method (**EDIT / Copy parameters to working method**)

The same procedure is recommended for the Suppressor determination (see **Voltammetric** tab with **Calibration** technique "DT Suppressors with calibration curve").

## Substances

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed de-

pend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window.




**Substance [ 24 characters ; ]**

Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

**Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**

Position of the peak voltage for the substance and tolerance for this verification voltage.

**Bsln.**

Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Standard solution**(**Additive solution** with CVS and CPVS)

Definition of addition solutions for standard addition or recording of calibration curves. These parameters are not displayed if **Batch with solution exchange** is selected for **Technique**.

**No. [ 0...8; 0 ]**

Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number. If a mixed standard solution is used, the number of this solution must be entered for each substance present in the mixed solution.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**

Value for concentration of addition solution.

**Unit [ pg/L...g/L ; g/L ]**

Unit for concentration of addition solution. With the CVS or CPVS mode: **[ fL/L...mL/L ; mL/L ]**

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**

Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **Batch with solution exchange** is selected for **Technique** or if **0** is entered as solution number.

Cell

Click this button to open the **CELL CONCENTRATIONS** window for entering the concentrations of the solutions used for standard addition or the recording of calibration curves for the selected substance (details see *Concentrations of calibration solutions*, *section 5.2*). This button is only displayed if **Batch with solution exchange** is selected for **Technique**.

**Regression technique [ see below ; Linear Regression ]**

Selection of regression technique:

**Linear Regression**

The regression is calculated with a straight line.

**Nonlinear Regression**

The regression is calculated with a nonlinear curve. This option is only available if **Record calibration curve**, **DT Record calibration curve** or **RC Record response curve** is selected for **Calibration**.

**Linear Regression (through Zero)**

The regression is calculated with a straight line forced to the zero point. This option is only available if **Record calibration curve**, **DT Record calibration curve** or **RC Record response curve** is selected for **Calibration**.

**Nonlinear Regression (through Zero)**

The regression is calculated with a nonlinear curve forced to the zero point. This option is only available if **Record calibration curve**, **DT Record ca-**

**libration curve** or **RC Record response curve** is selected for **Calibration**.

**Linear Interpolation**
The regression is calculated with a linear interpolation through 2 points. This option is only available if **Record calibration curve**, **DT Record calibration curve** or **RC Record response curve** is selected for **Calibration**.

**Quadratic Interpolation**
The regression is calculated with a nonlinear curve. This option is only available if **Record calibration curve**, **DT Record calibration curve**, **DT Suppressors with Calibration Curve** or **RC Record response curve** is selected for **Calibration**.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Height ]**
Selection of peak evaluation quantity:

**Height**
Peak height from baseline to peak maximum.

**Area**
Peak area between peak curve and calculated baseline.

**Derivative**
Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (**1** = minimum smoothing, **6** = maximum smoothing). See *Smoothing and differentiation*, *section 5.8*)

**Minimum peak width (V.step) [ ≥ 5 ; 5 ]**
Minimum peak width for peak recognition by number of **Voltage steps** (= number of measurement points).

**Minimum peak height (A) [ > 1 pA ; 100 pA ]**
Minimum peak height for peak recognition.

**Eliminate spikes**
Eliminates spikes to smooth the signal.

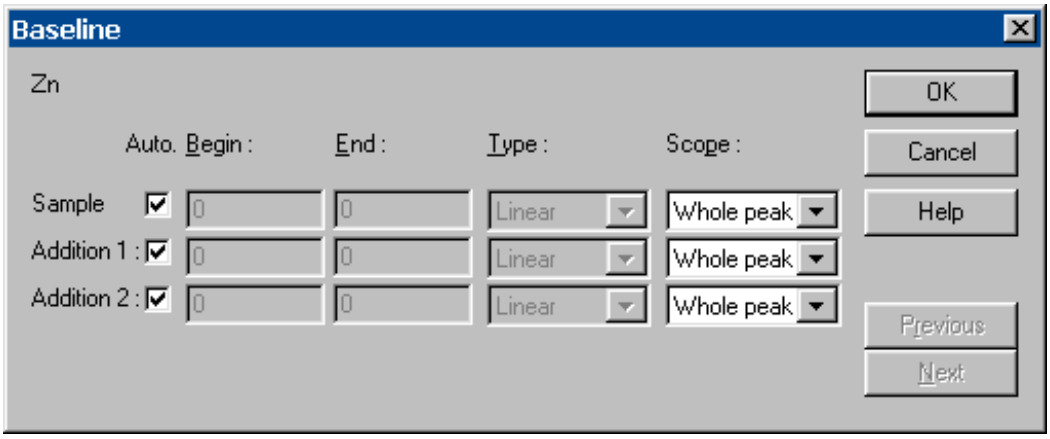
**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (only available with CV and CVS).

**Reverse peaks [ on, off ; off ]**
Enable peak evaluation of reverse peaks (peaks with opposite direction compared to the sweep or pulse direction).

**Note**: If you work with the modes CVS or CPVS the parameter list is different.

## Baseline

The **BASELINE** window contains the settings for baseline evaluation for a single "variation" measurement (= all replications of a sample, standard addition or calibration measurement) of a substance and is opened by clicking the ... button for the selected substance in the **Bsln.** column in the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.




**Auto.** **[ on, off ; on ]**
Enable/disable the automatic peak evaluation.

**Begin** **[ -5...+5 V ; 0 V ]**
Manual setting of the start base point for baseline evaluation. If **Auto** is enabled, the automatically calculated start base point is displayed and the field can not be edited.

**End** **[ -5...+5 V ; 0 V ]**
Manual setting of the end base point for baseline evaluation. If **Auto** is enabled, the automatically calculated end base point is displayed and the field can not be edited.

**Type** **[ Linear, Polynomial, Exponential , Horizontal ; Linear ]**
Selection of baseline type. If **Auto** is enabled, **Linear** is displayed and the field can not be edited.

**Scope** **[ Whole peak, Front end, Rear end ; Whole peak ]**
Selection of the range for baseline evaluation. Can only be edited with the **Type** "Linear".

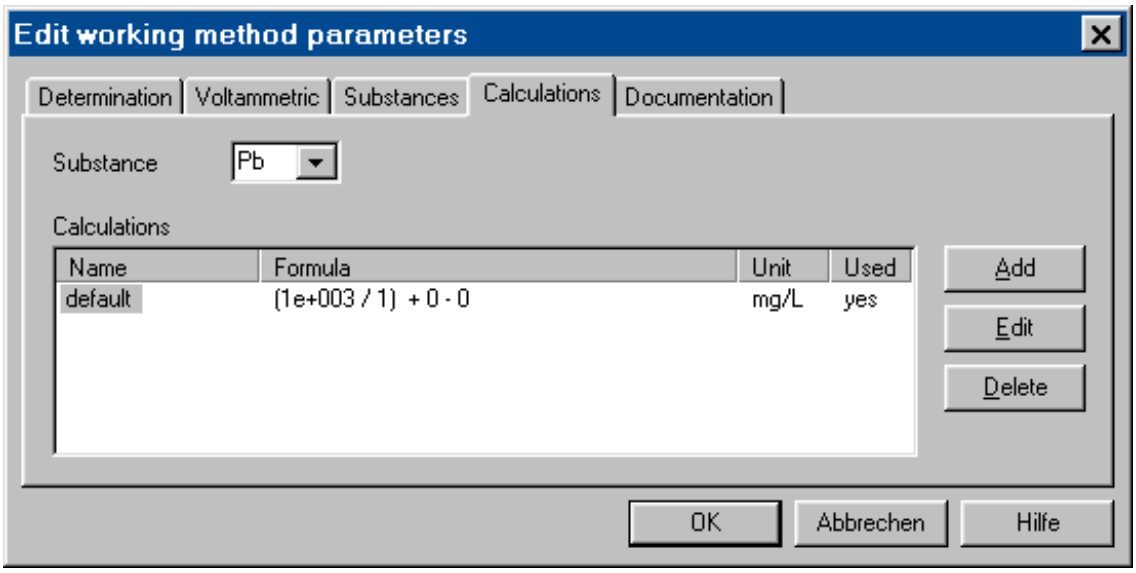
Previous — Switch to the previous page of this window.

Next — Switch to the next page of this window.

**Note**: For Electroplating Bath VA, Metrohm recommends to use a horizontal baseline with a fixed Begin and End.

## Calculations

The **Calculations** tab in the **EDIT WORKING METHOD PARAMETERS** window contains a table with all formulae used for the calculation of the final results for a substance.




**Substance**

Selection of the substance with its calculation formulae.

**Calculations**

Display of defined calculation formulae.

**Name**

Name of the calculation formula. Double-clicking the name opens the **CALCULATION** window for edition of the formula.

**Formula**

Display of calculation formula.

**Unit**

Unit of the calculation formula.

**Used**

Display whether the formula is used or not. The use of the formula can be changed by clicking the **Name** field with the right mouse button and selecting one of the menu items **Use**, **Use all** or **Use only**. In the case of **Use all**, the first formula is used to show the result in the **CALIBRATION CURVE** window.

Add

Add a new calculation formula. The **CALCULATION** window for edition of the formula is automatically opened.

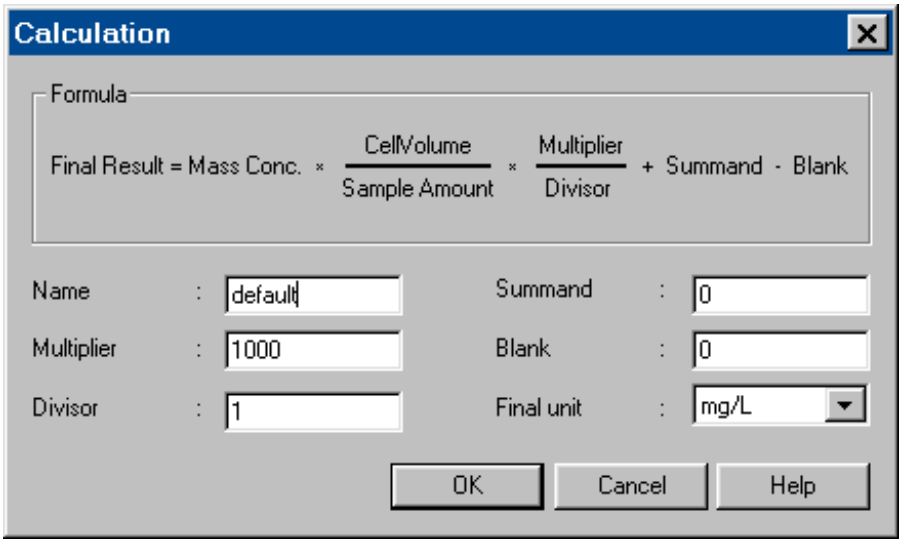
Edit — Open the **CALCULATION** window for edition of the selected formula.

Delete — Delete the selected formula.

**Note**: There is no **Calculation** tab in the **EDIT WORKING METHOD PARAMETERS** window, if you work with the CVS or CPVS modes **and** the **Calibration** technique Standard addition plating bath.

## Calculation Window

The **CALCULATION** window is opened if a new formula is added or an existing formula is edited on the **Calculations** tab of the **EDIT WORKING METHOD PARAMETERS** window. It contains the formula and parameters for the calculation of a final result for a substance.




**Formula**

General calculation formula for the final result.

**Name**

User-defined name for the calculation formula.

**Final unit**

**[ pg/L...g/L ; g/L ]**

If mL is chosen as Sample unit on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.

**[ pg/kg...g/kg ; g/kg ]**

If g is chosen as Sample unit on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.

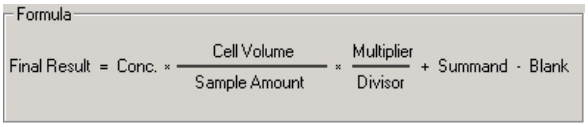
**[ fL/L...mL/L ; mL/L ]**

If you work with the modes CVS or CPVS.

Final result unit. Depending on the chosen units in the

**EDIT WORKING METHOD PARAMETER/Determination** tab.

For **Calibration** techniques not related to the Electroplating Bath VA modes, following formula is quoted:




**Final Result**
Final result of the determination, displayed on the bottom of the result sheet.

**Conc.**
The determined sample concentration, obtained through measurements and internal standard addition calculations (displayed in the Substance part of the result sheet).

**Cell Volume**
Total volume of solution (sample + auxiliary solution, e.g. buffer (added manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination (displayed in the Sample part of the result sheet).

**Sample Amount**
Amount of sample added to the measuring vessel. (displayed in the Sample part of the result sheet).

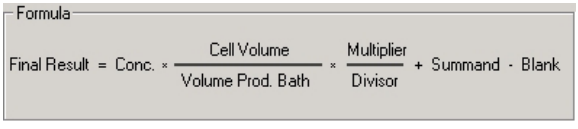
**Multiplier [ any number ; 1 ]**
Multiplier for calculation formula.

**Divisor [ any number ; 1 ]**
Divisor for calculation formula.

**Summand [ any number ; 0 ]**
Summand for calculation formula.

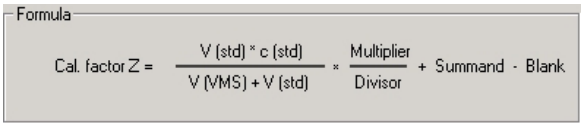
**Blank [ any number ; 0 ]**
Blank value to be subtracted from the final result.

For the Electroplating Bath VA **Calibration** techniques “LAT” and “MLAT” (for Brightener determination) as well as "RC Sample with response curve" (for Suppressor determination) following formula is quoted:




**Volume Prod. Bath**
The volume of sample bath solution added (see *Production bath solution*, *section 6.4*).

For the Electroplating Bath VA **Calibration** technique "DT Record calibration curve" (to get the "Calibration factor" for Suppressor determination), following formula is quoted:




**Cal.factor Z**

Is the "Calibration factor" to calculate the Suppressor concentration in the bath. It is determined at the "Evaluation ratio". The default unit of the **Cal.factor Z** is mL/L. For all internal calculations the unit mL/L is used even if the output unit has been changed.

**V(std)**

Is the volume of Suppressor standard solution at the "Evaluation ratio".

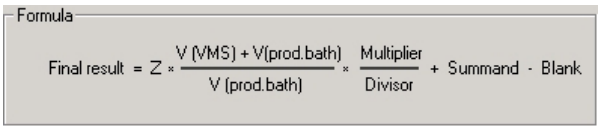
**c(std)**

Is the concentration of Suppressor standard solution.

**V(VMS)**

Is the volume of VMS (Virgin Make-up Solution).

For the Electroplating Bath VA **Calibration** technique "DT Suppressors with calibration curve" (for Suppressor determination), following formula is quoted:




**Z**

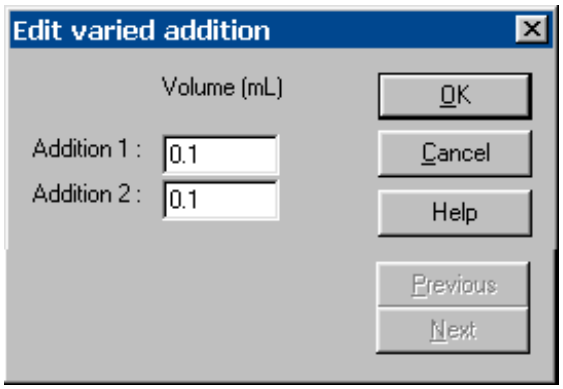
Is the "Calibration factor" to calculate the Suppressor concentration in the bath. It is determined at the "Evaluation ratio". The unit of the "Calibration factor" is mL/L.. For all internal calculations the unit mL/L is used even if the output unit has been changed.

**V (prod.bath)**

Volume of the added plating bath at the "Evaluation ratio".

## Variable addition

Variable addition volumes can be entered in the **EDIT VARIED ADDITION** window which is opened by clicking the ... button for the selected substance in the **Volume** column in the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.



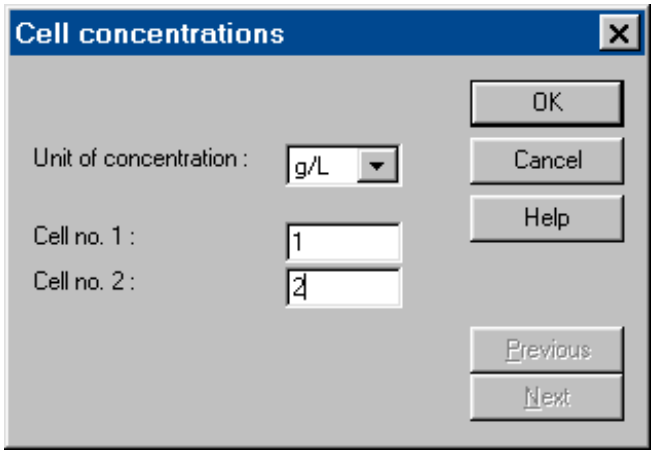

**Volume (mL) [ > 0.01 mL ; 0 mL ]**
Addition volume for each addition.

Previous — Switch to the previous page of this window.

Next — Switch to the next page of this window.

## Concentrations of calibration solutions

If **Batch with solution exchange** is selected for **Technique**, the concentrations of the calibration solutions must be entered in the **CELL CONCENTRATIONS** window which is opened by clicking the Cell button for the selected substance in the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.




**Unit of concentration [ pg/L...g/L ; g/L ]**
Unit for concentration of solution X.

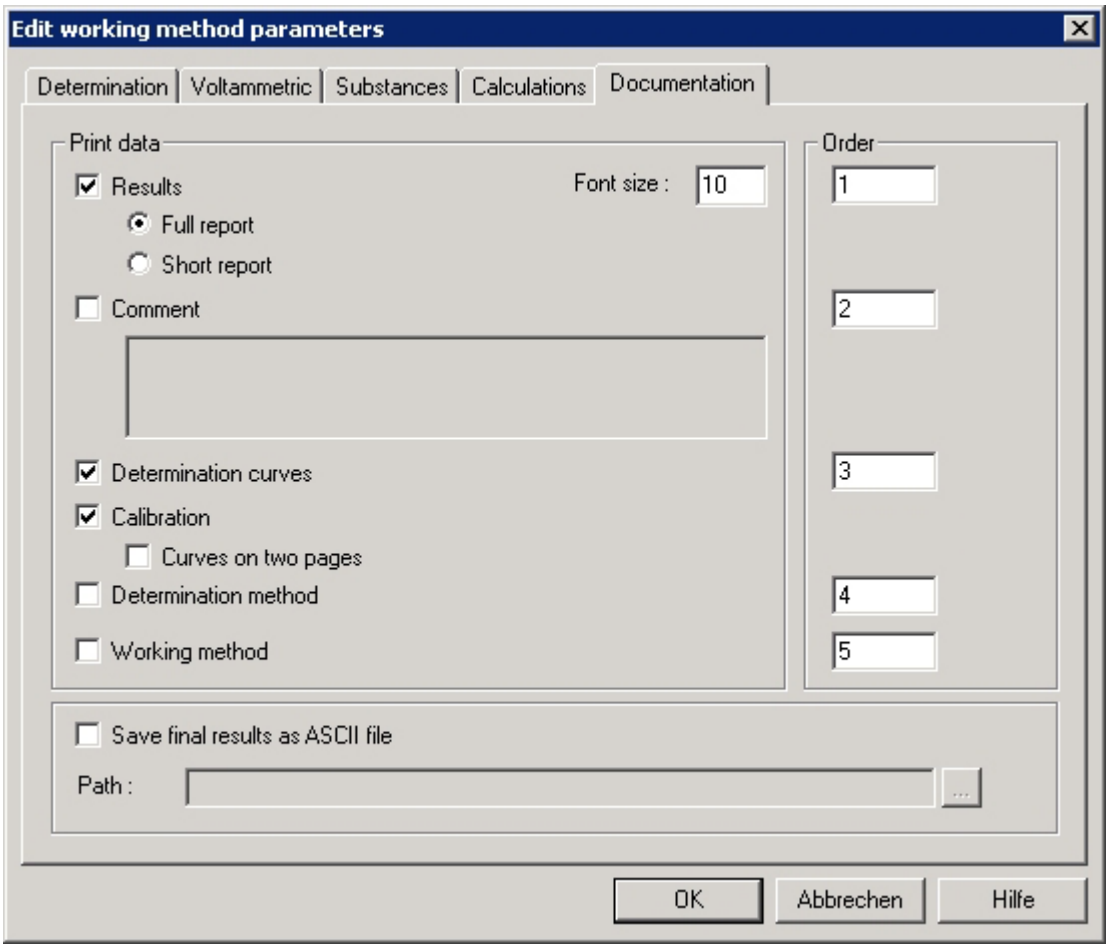
**Cell no. X [ > 0 ; 0 ]**
Value for concentration of solution X.

Previous — Switch to the previous page of this window.

Next — Switch to the next page of this window.

## Documentation

In the **Documentation** tab of the **EDIT WORKING METHOD PARAMETERS** window the elements for the automatic documentation printout at the end of the determination are defined. These settings belong to the method and are stored with it.




**Results**

Automatic printout of **Full report** or **Short report**.

**Font size**

Font size in points for report printout.

**Comment**

Automatic printout of the method comment defined in the accompanying field.

**Determination curves**

Automatic printout of all voltammograms.

**Calibration**

Automatic printout of all calibration curves.

**Curves on two pages**

If this option is checked, the determination and calibration curves are printed on two separate pages; if not, they are printed on one page.

**Determination method**

Automatic printout of the method parameters used for the determination.

**Working method**

Automatic printout of the method parameters of the working method in the working memory.

**Order [ 1...6 ; ]**

Order of printout for the element.

**Save final results as ASCII file**

Automatic storage of the full report into an ASCII file.

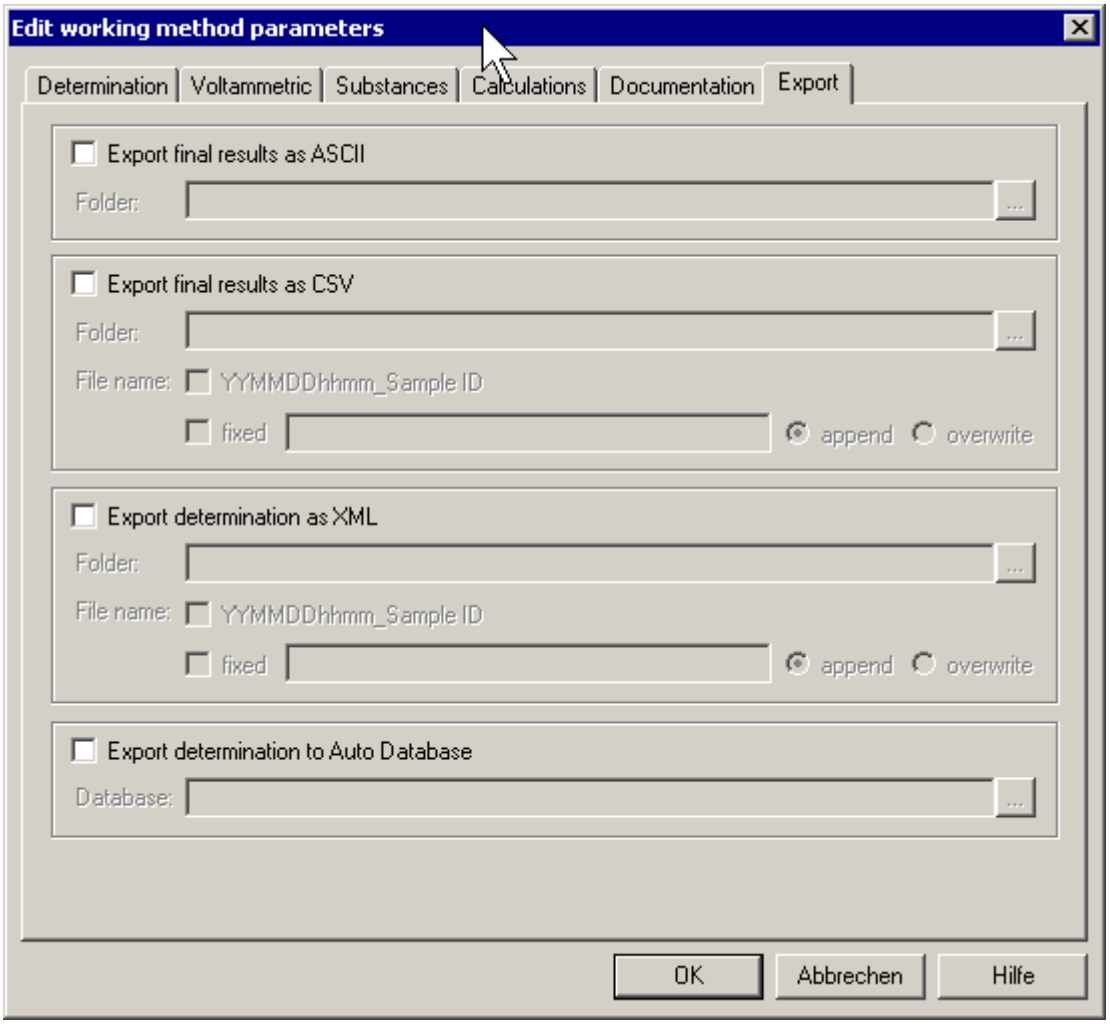
**Path**

Path for saving the selected report elements into an ASCII file. Use ... to change the path.

## Export

In the **Documentation** tab of the **EDIT WORKING METHOD PARAMETERS** windo

In the **Export** tab of the **EDIT WORKING METHOD PARAMETERS** window the settings for the export of determinations and results (which are automatically stored after determination) are defined. These settings belong to the method and are stored with it.



**Export final results as ASCII**

If this option is activated, the full report is exported as an ASCII-file.

**Folder**

Target folder for storing the ASCII-file with the selected report elements. The folder can be changed by clicking the button ... .

**Export final results as CSV**

If this option is activated, the full report is exported as a CSV-file.

**Folder**

Target folder for storing the CSV-file with the selected report elements. The folder can be changed by clicking the button ... .

**File name**

Definition of the file name

**YYMMDDhhmm_Sample ID**

If this option is activated, the CSV-file is named automatically with date and sample ID. This option is activated automatically, if **Export final results as CSV** is activated.

**Fixed**

If this option is activated, the CSV-file is named automatically with the text in the field.

**Append**

If this option is activated, the new CSV-file is appended to a (possibly) already existing CSV-file.

**Overwrite**

If this option is activated, the new CSV-file overwrites a (possibly) already existing CSV-file.

**Export determination as XML**

If this option is activated, the full report is exported as an XML-file.

**Folder**

Target folder for storing the XML-file with the selected report elements. The folder can be changed by clicking the button ... .

**File name**

Definition of the file name

**YYMMDDhhmm_Sample ID**

If this option is activated, the XML -file is named automatically with date and sample ID. This option is activated automatically, if **Export final results as XML** is activated.

**Fixed**

If this option is activated, the XML -file is named automatically with the text in the field.

**Append**

If this option is activated, the new XML -file is appended to a (possibly) already existing CSV-file.

**Overwrite**

If this option is activated, the new XML -file overwrites a (possibly) already existing CSV-file.

**Export determination to Auto Database**

If this option is activated, the determintion data is exported to a database.

**Database**

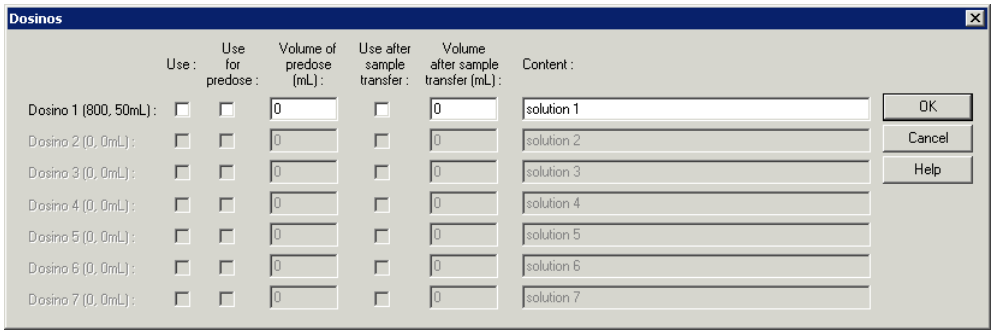
Database in which the data is to be exported. The database can be selected by clicking the button ... .

## Dosing Devices

The automatic use of Dosing Devices (possible: 700/800 Dosino, 685/805 Dosimat) for the addition of solutions has to be defined in the **DOSINOS** window that is opened by clicking the Dosinos button in **WORKING METHOD SPECIFICATIONS** window.

**Note**: Make sure that **Automatic** is selected for **Addition** on the **WORKING METHOD SPECIFICATIONS** window.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).




**Use [ on, off ; off ]**

Checkbox for Dosing Devices used for automatic addition of solutions. For the addition of standard solutions, the Dosing Devices must have the same number as the **Standard solution No.** entered on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

**Use for predose [ on, off ; off ]**
Use of a Dosing Device for addition of an auxiliary solution (e.g. buffer, or VMS for automated electroplating bath analysis) at the start of the determination.

**Volume of predose (mL) [ > 0.01 mL ; 0 mL ]**
Volume of the auxiliary solution (e.g. buffer, or VMS for automated electroplating bath analysis) to be added at the start of the determination. This volume must be accounted for the calculation of the **Cell volume**.

**Use after sample transfer [ on, off ; off ]** (only with the to electroplating bath modes CVS and CPVS and the **Calibration** technique "MLAT" or "RC Sample with response curve")
Use of a Dosing Device for addition of an auxiliary solution (e.g. Suppressor) after the sample transfer.

**Volume after sample transfer [ 0.01 ... 1000 mL ; 0 mL ]** (only with the two electroplating bath modes CVS and CPVS and the **Calibration** technique "MLAT")
Volume for addition of an auxiliary solution (e.g. Suppressor) after the sample transfer.

**Content [ 46 characters ; "solution" ]**
Remarks regarding the solution.

---

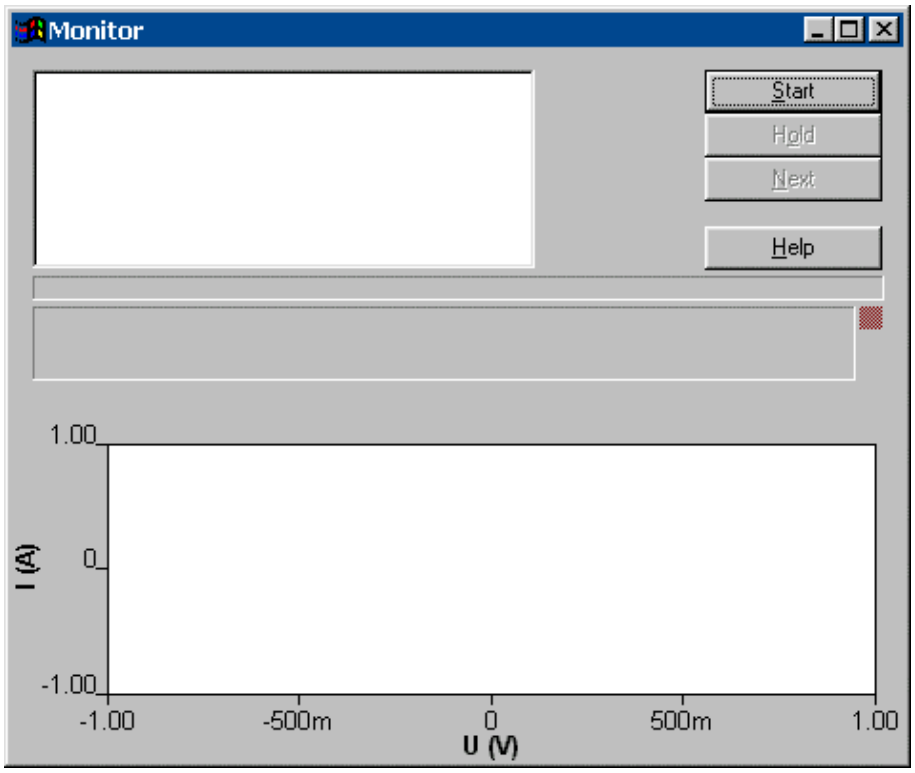
**Note**: Dosing Device parameters can only be overwritten if the checkbox **Use** is checked.

---

## 5.3 Monitor

### Start determination

If no determination is running, the **MONITOR** window is used to start a new determination with the current working method.

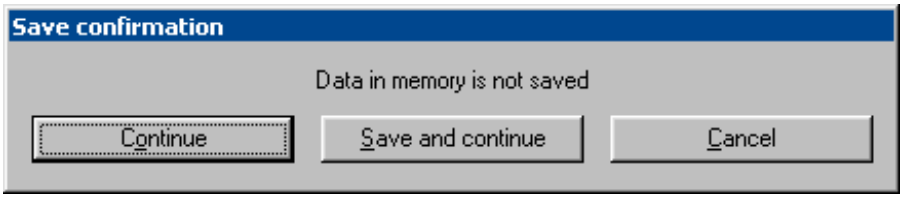




### Start determination

The operation sequence (see *section 3.4*) defined in the working method is started.

If the previous determination has not been saved, the **SAVE CONFIRMATION** window indicating **Data in memory is not saved** appears offering the following options:





Start the new determination without saving the previous determination.


Save the previous determination before starting the new determination.


Cancel the start of a new determination.

### Stop/Hold determination

A running determination can be stopped, interrupted and continued. Each step in the operation sequence can be abbreviated by clicking the **<Next>** button.


**Stop determination**
Stop running determination immediately.

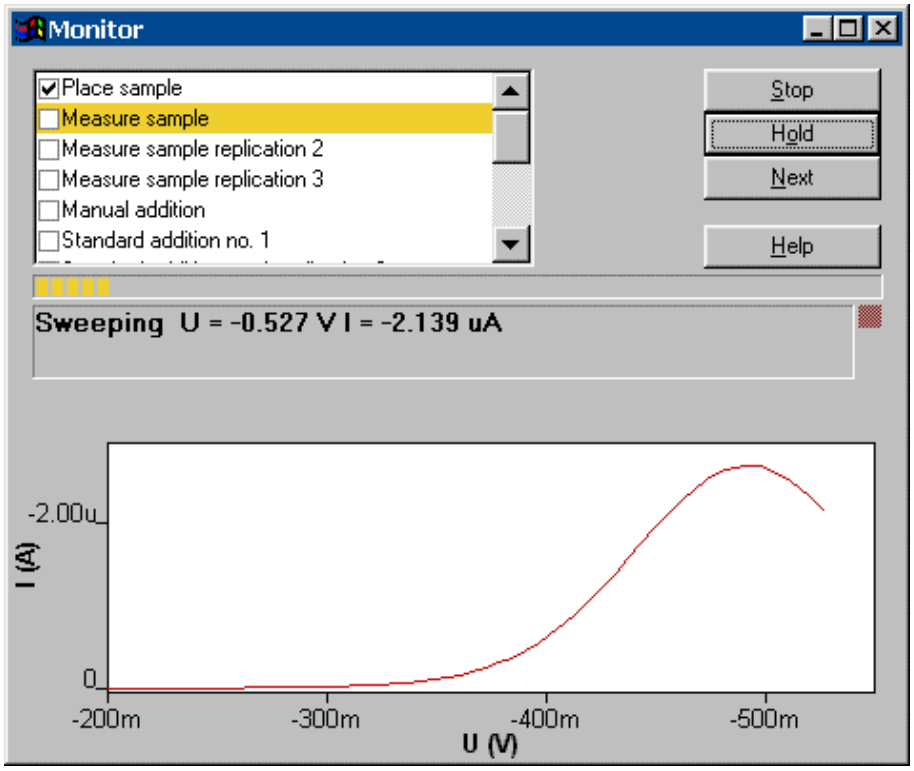

**Hold determination**
Interrupt running determination.


**Continue determination**
Continue an interrupted determination.


**Next step**
Break off the running step and go to next step of the operation sequence.

## Monitor determination

Once the determination is started, the running determination is monitored in the **MONITOR** window.




All **steps of the operation sequence** are listed in the upper field at the left side of the control buttons. All steps completed are checked, the current running step is highlighted.

The **progress indicator** below this field shows the progress of the determination.

The **details of the running operation sequence step** are displayed in the first line of the status field below the progress indicator. In the second line of the status field **comments or error messages** concerning the running determination are displayed. The red light at the right side of the status field indicates a **current**

**overload**. In this case, stop the measurement and change the measurement parameters.

For a running voltage sweep there is a live display in the **MONITORING** window with automatic scaling of the axes. Manual rescaling can be done by pressing the <F4> button or selecting the **Auto scale** option of the context sensitive menu. At the end of each voltage sweep, the recorded curve is copied into the **DETERMINATION CURVES** window.

## Message windows during determination

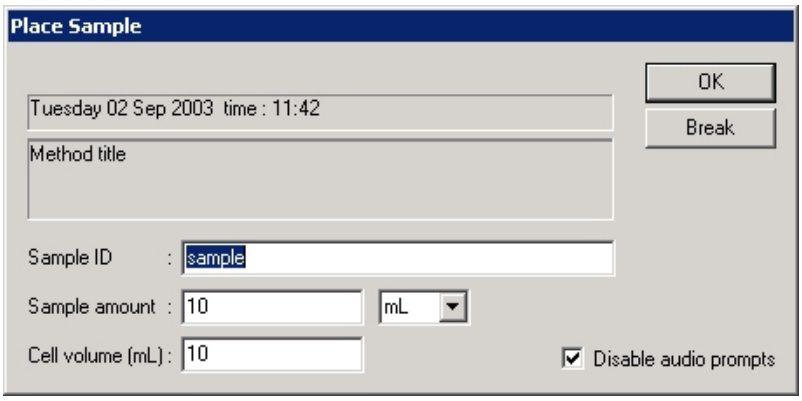
For some steps in the operation sequence additional windows demanding an action or entry of the user appear.

**PLACE BLANK**

If the **Measure blank** option in the **Determination** tab is enabled, the message **Place blank and press OK** appears. Add the blank solution into the measuring vessel and press **<OK>**.

**PLACE SAMPLE**

This window appears for all sample determinations with standard addition or calibration curve.




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 characters ; "sample" ]**

Identification for sample. The expression defined in the **Determination** tab is displayed and can be changed if desired.

**Sample amount [ > 0 ; 10 ]**

Amount of sample added to the measuring vessel. The value defined on the **Determination** tab is displayed and can be changed if desired.

**Sample unit [ mL, g ; mL ]**

Selection of unit for sample amount. The value defined on the **Determination** tab is displayed and

can be changed if desired.

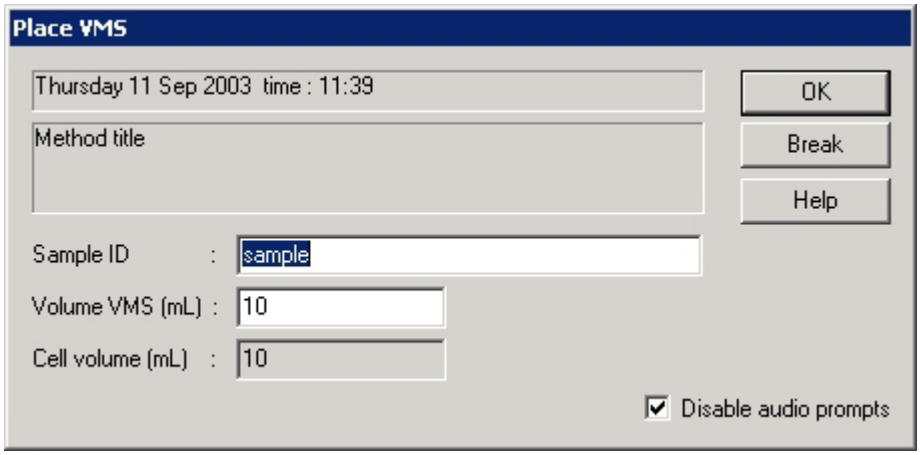
**Cell volume (mL) [ > 0 mL ; 10 mL ]**

Total volume of solution (sample + auxiliary solution, e.g. buffer (manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination. The calculated sample concentrations **Conc.** refer to this cell volume.

Add the sample solution into the measuring vessel and press **<OK>**.

**PLACE VMS**

This window appears in the Electroplating Bath VA with the **Calibration** techniques "Standard addition plating bath", "DT Suppressors with calibration curve "and "DT Record calibration curve".




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 characters ; "sample" ]**

Identification for sample. The expression defined in the **Determination** tab is displayed and can be changed if desired.

**Volume VMS (mL) [ > 0 mL ; 10 mL ]**

(only with "DT Suppressors with calibration curve" and "DT Record calibration curve")
The volume of the "Virgin Make-up Solution" (see *VMS (Virgin Make-up Solution)*, *section 6.4*) is displayed and can be changed if desired.

**Cell volume (mL) [ > 0 mL ; 10 mL ]**

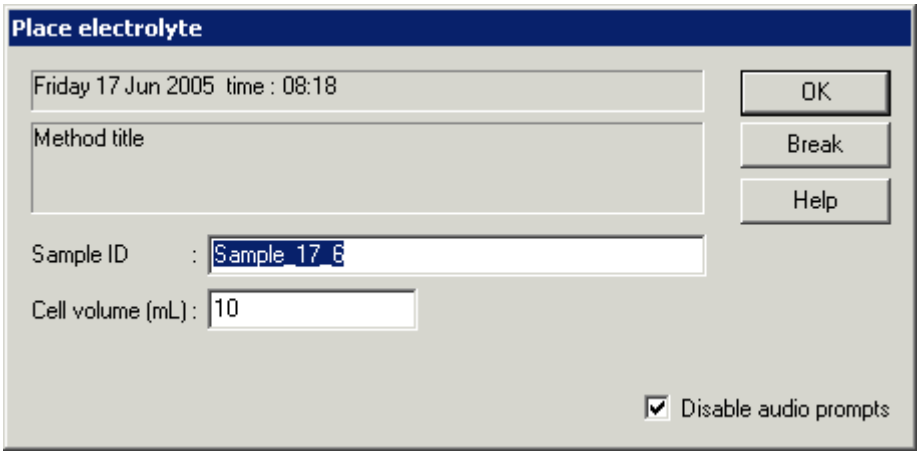
Total volume of solution (sample + auxiliary solution, e.g. buffer (manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination. The calculated sample

concentrations **Conc.** refer to this cell volume. It can be changed for the **Calibration** technique "Standard addition plating bath" if desired.

Add the VMS solution into the measuring vessel and press **<OK>**.

**PLACE ELECTROLYTE**

This window appears in the Electroplating Bath VA with the **Calibration** techniques "RC Sample with response curve" und "RC Record response curve".




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 characters ; "sample" ]**
Identification for sample. The expression defined in the Determination tab is displayed and can be changed if desired.

**Cell volume (mL) [ > 0 mL ; 10 mL ]** (with "RC Sample with response curve" "read only")
With "RC Record response curve": Enter the volume of the added electrolyte solution.
With "RC Sample with response curve": The **Cell volume** defined on the **Determination** tab is displayed.

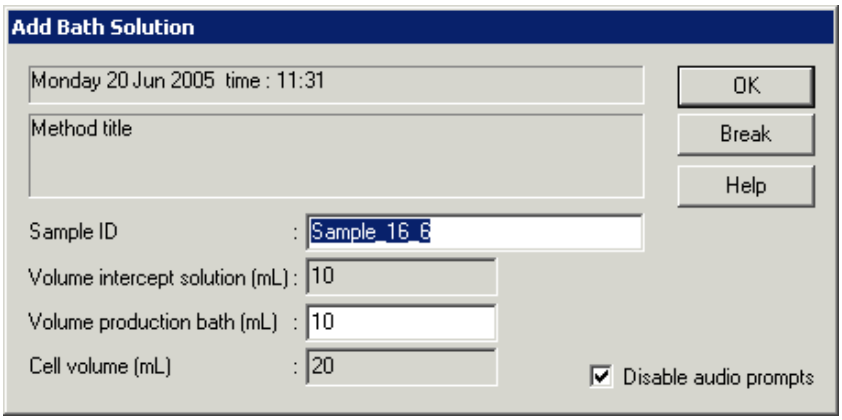
Geben Sie die Electrolyte-Lösung ins Messgefäss und drücken Sie **<OK>**.

Add the Electrolyte solution into the measuring vessel and press <**OK**>.

**ADD BATH SOLUTION**

This window appears in the Electroplating Bath VA

with the **Calibration** technique “MLAT Standard addition for brighteners”.




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 characters ; "sample" ]**
Identification for sample. The expression defined in the **Determination** tab is displayed and can be changed if desired.

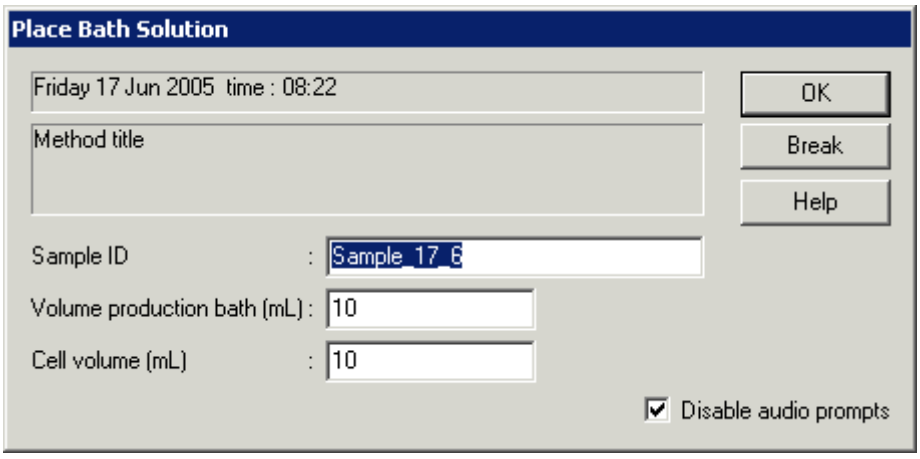
**Volume intercept solution (mL) [> 0 mL ; 10 mL] [nur Anzeige]**
The volume of Intercept solution added is displayed.

**Volume production bath (mL) [ > 0 mL ; 10 mL ]**
The volume of “sample bath solution” added (see *Production bath solution*, *section 6.4*) is displayed and can be changed if desired.

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Total volume of solution (sample + auxiliary solution, e.g. buffer (manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination. The calculated sample concentrations **Conc.** refer to this cell volume. It can be changed if desired.

Add the sample solution into the measuring vessel and press **<OK>**.

**PLACE BATH SOLUTION**
This window appears in the Electroplating Bath VA with the **Calibration** techniques "LAT Standard addition for brighteners" and "RC Sample with response curve".




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 Zeichen ; "sample" ]**

Identification for sample. The expression defined in the **Determination** tab is displayed and can be changed if desired.

**Volume production bath (mL) [ > 0 mL ; 10 mL ]**

The volume of sample bath solution added displayed and can be changed if desired.

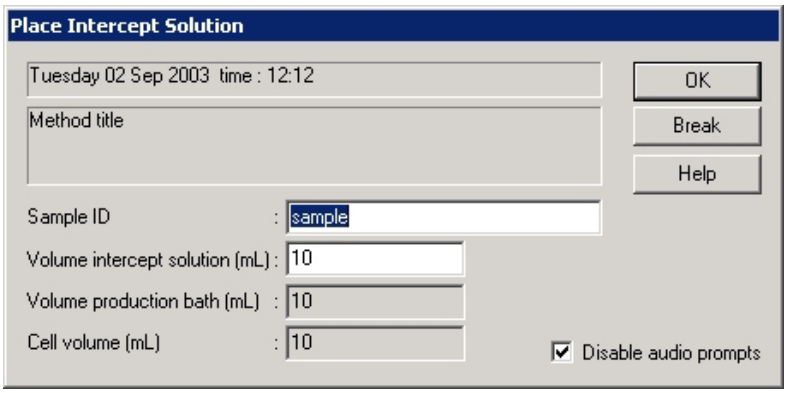
**Cell volume (mL) [ > 0 mL ; 10 mL ]**

Total volume of solution in the measuring vessel at the start of the determination. Is dependent on whether you removed the electrolyte solution before you added the production bath or not.

Add the sample solution into the measuring vessel and press **<OK>**.

**PLACE INTERCEPT SOLUTION**

This window appears in the Electroplating Bath VA with the **Calibration** techniques “MLAT Standard addition for brighteners” and "LAT Record calibration curve".



The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

**Sample ID [ 32 characters ; "sample" ]**
Identification for sample. The expression defined in the **Determination** tab is displayed and can be changed if desired.

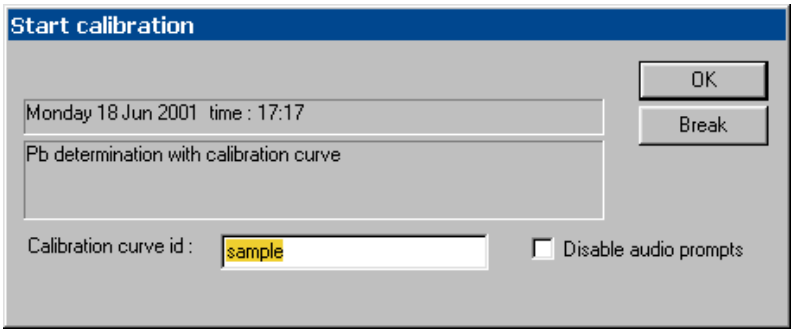
**Volume intercept solution (mL) [> 0 mL ; 10 mL]**
The volume of "Intercept solution" added is displayed and can be changed if desired.

**Volume production bath (mL) [ > 0 mL ; 10 mL ] [read only]**
(only displayed with MLAT)
The volume of "sample bath solution" added (see *Production bath solution*, *section 6.4*) is displayed.

**Cell volume (mL) [ > 0 mL ; 10 mL ] [read only]**
Total volume of solution (sample + auxiliary solution, e.g. buffer (manually or pre-dosed with a Dosing Device)) in the measuring vessel at the start of the determination. The calculated sample concentrations **Conc.** refer to this cell volume.

Add the intercept solution into the measuring vessel and press **<OK>**.

**START CALIBRATION**
This window appears for the recording of calibration curves.




The window displays date and time of the determination start and the title of the method used. Date and time in the format **YYMMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file to be saved automatically (e.g. **0706181712_sample.dth**).

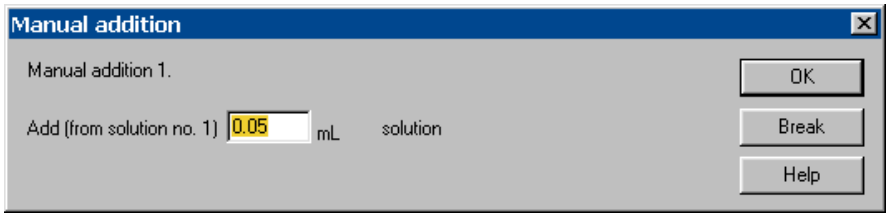
**Calibration curve id [ 32 characters ; "sample" ]**

Identification for calibration curve.

Add the calibration solution into the measuring vessel and press **<OK>**.

**MANUAL ADDITION**

This window appears at the start of each manual addition of standard solutions for standard addition determinations or the recording of calibration curves.




**Add (from solution no. X) (ml) [ > 0.01 ml ; 0 ml ]**

The addition volume for the manual addition defined in the **Substances** tab is displayed and can be changed if desired. Add the addition solution into the measuring vessel and press **<OK>**.

**BATCH SOLUTION EXCHANGE**

This window appears if the **Batch with solution exchange** option is selected for the measurement technique. The number of the solution to be placed and the substances and their concentration defined in the **Substances** tab are displayed. Add this solution into the measuring vessel and press **<OK>**.

**END OF DETERMINATION**

This window appears at the end of the determination. By pressing **<OK>**, the determination is automatically saved if the **Auto save determination and signal** option is enabled in the **General** tab of the **GENERAL SETTINGS** window. The report elements checked in the **Documentation** tab are automatically printed out.

## Graphical properties for monitoring curves

The graphical properties for curves in the **MONITORING** window can be set by selecting the options of the context sensitive menu.

**MONITORING / Page properties**

The page properties of the **MONITORING** window can be set with the **page** tab of the **GRAPHICAL PROPERTIES** window (details see *Page properties*, *section 3.5*).

The properties of the x and y axis can be set with the **x axis** and **y axis** tab of the **GRAPHICAL PROP-**

**ERTIES** window (details see *Axis properties*, *section 3.5*).

**MONITORING / Curve properties**
The properties of the live curve can be set with the **Monitor curve** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

### Copy to clipboard

**MONITORING / Copy to clipboard**
Copy the current live curve in the **MONITORING** window to the clipboard.

## 5.4 Determination curves

### Load/save determinations

Determination files (***.dth**) contain the measurement data and the determination method used. Existing files can be loaded, saved again and exported by the following commands:

**MAIN WINDOW / File / Load determination**
Load an existing determination file into the working memory. The name of the determination loaded is displayed in the status bar of the **MAIN WINDOW**.
The current working method is **not** automatically overwritten by the determination method, but its parameters can be copied to the working method afterwards.

**MAIN WINDOW / File / Save determination**
Save the current determination loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save determination as ...**
Save the current determination loaded in the working memory in a new file. Enter name and directory for storage of the determination file. If the file name already exists, windows asks if you want to overwrite the existing file.

**MAIN WINDOW / File / Save calibration curve**
(only accessible, if "Record calibration curve" is chosen for **Calibration** on the **WORKING METHOD SPECIFICATION** window)
Save the current calibration curve loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save calibration curve as**
(only accessible, if "Record calibration curve" is chosen for **Calibration** on the **WORKING METHOD SPECIFICATION** window)

Save the current calibration curve loaded in the working memory in a new file. Enter name and directory for storage of the calibration curve file. If the file name already exists, windows asks if you want to overwrite the existing file.

**MAIN WINDOW / File / Save response curve**

(only accessible, if "RC Record response curve" is chosen for **Calibration** on the **WORKING METHOD SPECIFICATION** window)

Save the current response curve loaded in the working memory. The old file will be overwritten.

**MAIN WINDOW / File / Save response curve as**

(only accessible, if "RC Record response curve" is chosen for **Calibration** on the **WORKING METHOD SPECIFICATION** window)

Save the current response curve loaded in the working memory in a new file. Enter name and directory for storage of the calibration curve file. If the file name already exists, windows asks if you want to overwrite the existing file.

**MAIN WINDOW / File / Export determination points**

Save the measurement points of all sweeps of the current determination loaded in the working memory into a data file (extension ***.txt**). This data file contains a block of the used method parameters followed by the sweep blocks of X and Y values each preceded by VR number and number of measurement points. The data files can be imported into spreadsheet programs like Microsoft Excel.

**MAIN WINDOW / File / Export extended determination points...**

In the case of **extended determination point export**, this data file contains a block of the used method parameters followed by the voltammetric parameters, a block peak evaluation, a block baseline, a block solutions, a block export options and the sweep blocks of X and Y values each preceded by VR number and number of measurement points.

**MAIN WINDOW / File / Export results / Current Determination...**

Save the results report of the current determination loaded in the working memory into an ASCII file with extension ***.txt**, ***.csv**, or ***.xml**. This file can be imported into spreadsheet programs like Microsoft Excel (*.txt und *.csv) or in a LIMS (*.csv and *.xml).

**MAIN WINDOW / File / Export results / Determinations...**

Save the results report of the selected determination into an ASCII file with extension ***.txt**, ***.csv**, or

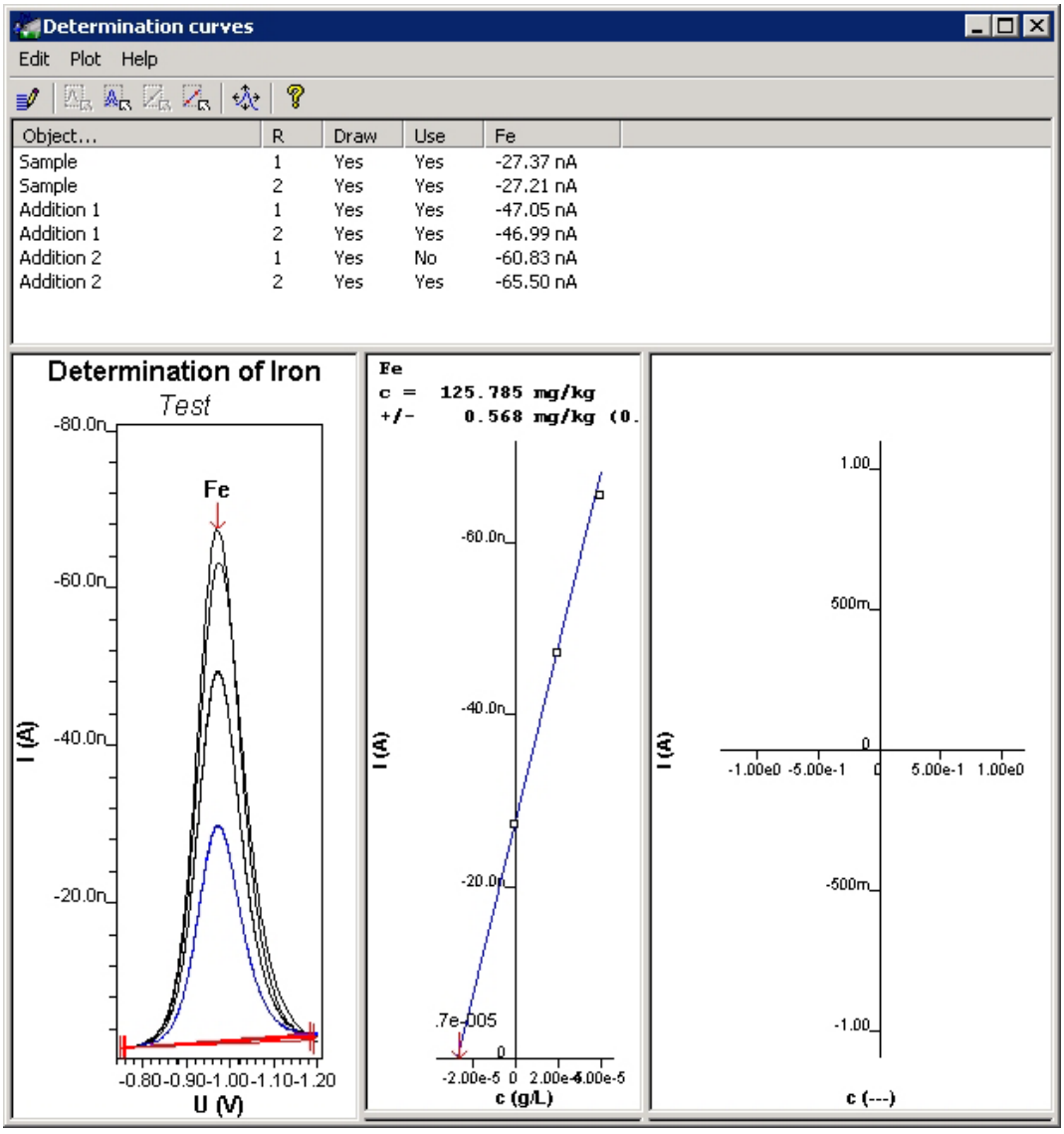
***.xml**. This file can be imported into spreadsheet programs like Microsoft Excel (*.txt und *.csv) or in a LIMS (*.csv and *.xml).

## Copy parameters to working method

**DETERMINATION CURVES / Edit /**
**Copy parameters to working method**
Copy the parameters of the loaded determination method into the **WORKING METHOD SPECIFICATIONS** window (working method).

## Determination curves window

The **DETERMINATION CURVES** window shows the determination and calibration curves of the loaded determination.




The **DETERMINATION CURVES** window contains the following ten subwindows which can be enlarged or reduced inside the **DETERMINATION CURVES** window by moving the frames with the mouse:

### List of curves

The top subwindow lists all available curves of the determination with the evaluated peak heights or peak charges .

### Determination curves

The lower left subwindow shows a single or all determination curves.

### Calibration curves

At the right side of the determination curves, there are eight subwindows for display of each substance calibration curve.

## Edit determination method parameters

**DETERMINATION CURVES / Edit / Determination method parameters**

Open the **EDIT DETERMINATION METHOD PARAMETERS** window for viewing and modifying the parameters of the determination method used to record the determination. This window contains the tabs **Specifications**, **Determination**, **Voltammetric**, **Substances** and **Calculations**. If parameters in the **EDIT DETERMINATION METHOD PARAMETERS** window are changed and **<OK>** is pressed, the determination will be recalculated automatically.

---

**Note**: Irrespective whether fields have been modified or not, the modification date is entered into the **Modified** line if the **EDIT DETERMINATION METHOD PARAMETER** window is closed by clicking <**OK**>. If the determination shall not be marked as "modified", the **EDIT DETERMINATION METHOD PARAMETER** window has to be left with <**Cancel**>.

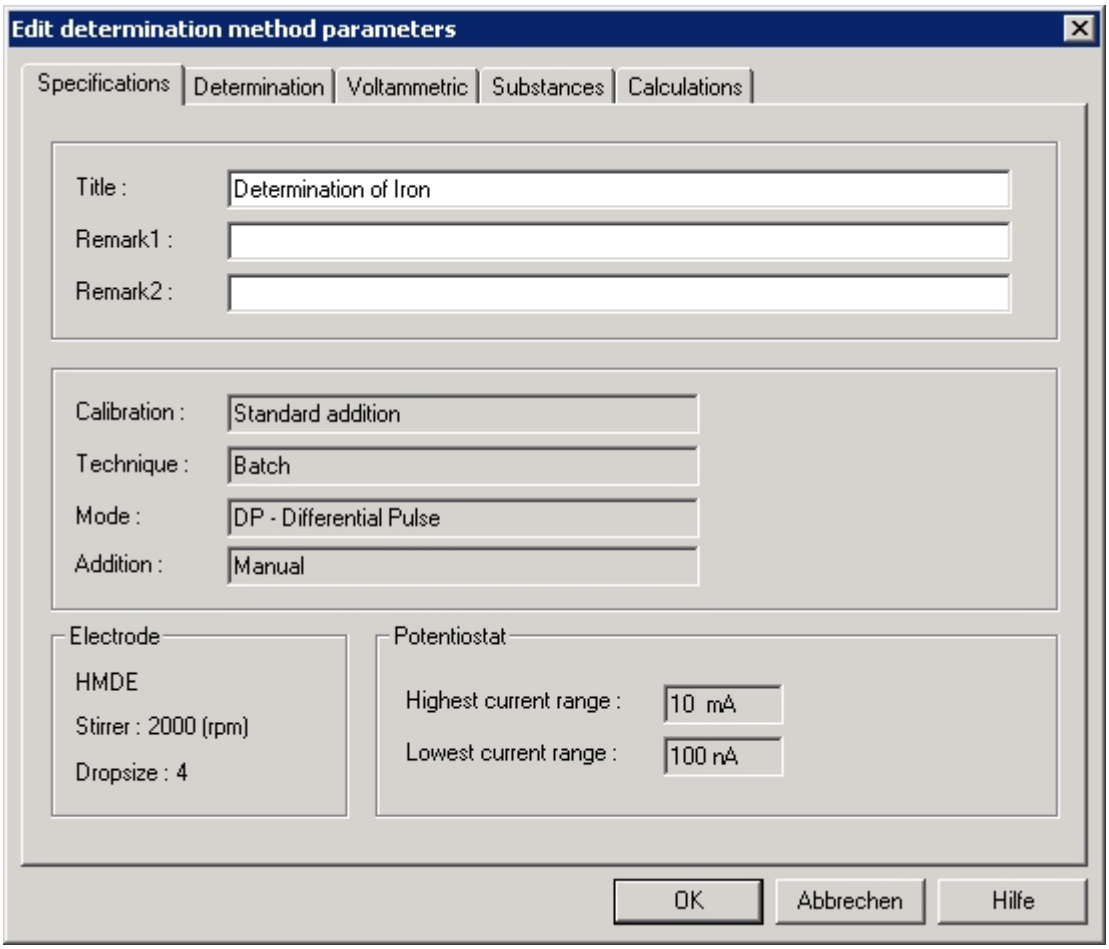
---

**Note**: These parameters will **not** automatically be used for the next measurement. To do this, use the **Copy parameters to working method** command (see *Copy parameters to working method*, *section 5.4*).

---

## Specifications

The **Specifications** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains the main specifications of the determination method. Only **Title**, **Remark1** and **Remark2** can be edited.




**Title [ 0...68 characters ; "Method title" ]**
Method title.

**Remark1 [ 0...68 characters ; ]**
Remark 1 regarding the method.

**Remark2 [ 0...68 characters ; ]**
Remark 2 regarding the method.

**Calibration [ read only ]**
Display of the calibration mode used for the determination (details see *Working method specifications window*, *section 5.2*).

**Technique [ read only ]**
Display of the measurement technique used for the determination (details see *Working method specifications window*, *section 5.2*).

**Mode [ read only ]**
Display of VA measurement mode used (details see *VA measurement modes*, *section 3.2*).

**Addition [ read only ]**
Display of the addition type used (details see *Working method specifications window*, *section 5.2*) .

**Electrode [ read only ]**
Display of electrode used (details see *Electrodes*, *section 3.1*).

**Stirrer [ read only ]**
Display of stirrer settings used (details see *Stirring*, *section 3.4*).

**Drop size [ read only ]**
Display of drop size used (details see *Electrodes*, *section 3.1*).

**Potentiostat [ read only ]**
Display of potentiostat settings used (details see *Potentiostat*, *section 3.3*).

## Determination

The **Determination** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains general specifications used for performing the determination. For details, see the identical **Determination** tab of the **EDIT WORKING METHOD WINDOW**, *section 5.2*. Only **Sample identifier**, **Sample amount**(not with CVS and CPVS mode) and **Cell volume** can be edited.

## Voltammetric

The **Voltammetric** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains the parameters used for preparation procedures and the VA measurement mode selected. For details, see the identical **Voltammetric** tab of the **EDIT WORKING METHOD WINDOW**, *section 5.2*. All parameters are read only.

## Substances

The **Substances** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of addition solutions, for peak evaluation and results calculation. For details, see the identical **Substances** tab of the **EDIT WORKING METHOD WINDOW**, *section 5.2*.

## Calculations

The **Calculations** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains a table with all formulae used for the calculation of the final results for a substance. For details, see the identical **Calculations** tab of the **EDIT WORKING METHOD WINDOW**, *section 5.2*.

## Export

The **Export** tab of the **EDIT DETERMINATION METHOD PARAMETERS** window contains settings for the export of determinations to other file formats. For details, see the identical **Export** tab of the

**EDIT WORKING METHOD WINDOW**.

## Edit addition parameters

**DETERMINATION CURVES / Edit / Addition parameters / Draw**
Enable/disable the drawing of the curve selected in list of curves. The entry in the **Draw** column of the list is changed.

**DETERMINATION CURVES / Edit / Addition parameters / Draw selected**
Draw only the curves selected in the list of curves. The entries in the **Draw** column of the list are set to "No" for all other curves.

**DETERMINATION CURVES / Edit / Addition parameters / Draw all**
Draw all available curves. The entries in the **Draw** column of the list are set to **Yes** for all curves.

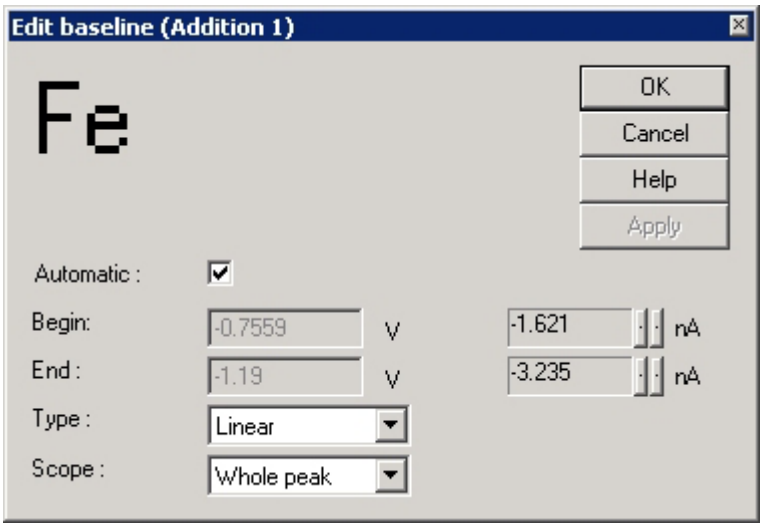
**DETERMINATION CURVES / Edit / Addition parameters / Use**
Enable/disable the use of the object selected in the list of curves for calculation. The entry in the **Use** column of the list is changed and the substance evaluation is recalculated.

**DETERMINATION CURVES / Edit / Addition parameters / Use selected**
Use only the objects selected in the list of curves for calculation. The entries in the **Use** column of the list are set to **No** for all other objects.

**DETERMINATION CURVES / Edit / Addition parameters / Use all**
Use all available objects for calculation. The entries in the **Use** column of the list are set to **Yes** for all objects.

## Edit baseline

**DETERMINATION CURVES / Edit / Baselines / "Substance name"**
Open the **EDIT BASELINE** window for modifying the baseline evaluation for the selected substance peak. The recalculated peak evaluation height is displayed in the **Substance** column of the list of curves.




**Automatic**
Switch on/off the automatic peak baseline evaluation.

**Begin** Manual setting of the start base point for baseline evaluation. The base point can be moved either by manually changing the voltage value (time for CPVS) in the first field or by clicking the buttons of the second field indicating the current value. This field can only be edited if **Automatic** is disabled.

**End** Manual setting of the end base point for baseline evaluation. The base point can be moved either by manually changing the voltage value (time for CPVS) in the first field or by clicking the buttons of the second field indicating the current value. This field can only be edited if **Automatic** is disabled.

**Type [ Linear, Polynomial, Exponential, Horizontal ; Linear ]**
Selection of the baseline type. This field can only be edited if **Automatic** is disabled.

**Scope [ Whole peak, Front end, Rear end ; Whole peak ]**
Selection of the range for baseline evaluation. This field can only be edited if the **Linear** baseline type is selected.

Apply Start baseline evaluation with the current parameters entered in the **EDIT BASELINE** window.

## Zooming

Curve regions in the determination curves subwindow can be enlarged by zooming the desired area while pressing the left mouse button ("drag a box"; reset see *Auto scaling*).

## Auto scaling

**DETERMINATION CURVES / Plot / Auto scale (F4)**
Reset zooming and scale x and y axes so that all measurement points of all determination curves are visible.

## Swap axis

**DETERMINATION CURVES / Plot / Swap axis / abscissa**
Swap x axis for the current determination curve.

**DETERMINATION CURVES / Plot / Swap axis / ordinate**
Swap y axis for the current determination curve.

## Show baselines

**DETERMINATION CURVES / Plot / Show baselines**
If this option is enabled, the calculated baselines are displayed in the determination curves subwindow.

## Show unknown peaks

**DETERMINATION CURVES / Plot / Show Unknown peaks**
If this option is enabled, all peaks found but not assigned to a defined substance are marked in the determination curves subwindow with "**Unk**".

## Show spikes

**DETERMINATION CURVES / Plot / Show Spikes**
If this option is enabled, spikes are shown as red points.

## Graphical properties for determination curves

As default, the axes displayed in the determination curve subwindow have the following orientation:

**x axis** The determination curves are displayed from the left to the right (for anodic sweeps: from - to +; for cathodic sweeps: from + to -). For cyclic sweeps, the forward sweep is displayed from the left to the right.

**y axis** The y axis is always displayed from the bottom to the top with the same direction as the x axis (for anodic sweeps: from - to +; for cathodic sweeps: from + to -).

The following graphical properties for curves in the determination curves subwindow can be set:

**DETERMINATION CURVES / Plot / Properties / Curves window**
The page properties of the determination curves

subwindow can be set with the **page** tab of the **GRAPHICAL PROPERTIES** window (see *Page properties*, *section 3.5*). The properties of the x and y axis can be set with the **x axis** and **y axis** tab of the **GRAPHICAL PROPERTIES** window (see *Axis properties*, *section 3.5*).

**DETERMINATION CURVES / Plot / Properties / Blank**
The properties of the blank curve can be set with the **Blank** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**DETERMINATION CURVES / Properties / Sample**
The properties of the sample curves can be set with the **Sample** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**DETERMINATION CURVES / Plot / Properties / Other**
The properties of all other determination curves can be set with the **Other curves** tab of the **GRAPHICAL PROPERTIES** window (details see *Curve properties*, *section 3.5*).

**DETERMINATION CURVES / Plot / Properties / Baselines**
The properties of the baselines can be set in the **LINE PROPERTIES** window (details see *Line properties*, *section 3.5*).

**Note**: The line properties for determination curve lines can be set in the **LINE PROPERTIES** window (details see *Line properties*, *section 3.5*).

## Graphical properties for calibration curves

The graphical properties for calibration curves in the calibration curves subwindows can be set by selecting the options of the context sensitive menu.

**DETERMINATION CURVES / Page properties**
The page properties of the calibration curves subwindows can be set with the **page** tab of the **GRAPHICAL PROPERTIES** window (see *Page properties*, *section 3.5*). The properties of the x and y axis can be set with the **x axis** and **y axis** tab of the **GRAPHICAL PROPERTIES** window (see *Axis properties*, *section 3.5*).

## Copy/export graphics

The current content of the determination or calibration subwindows can be copied to the clipboard or saved as emf files using the

following options of the context sensitive menu (click right mouse button).

**DETERMINATION CURVES / Copy to clipboard**

Copy the content of the selected subwindow to the clipboard.

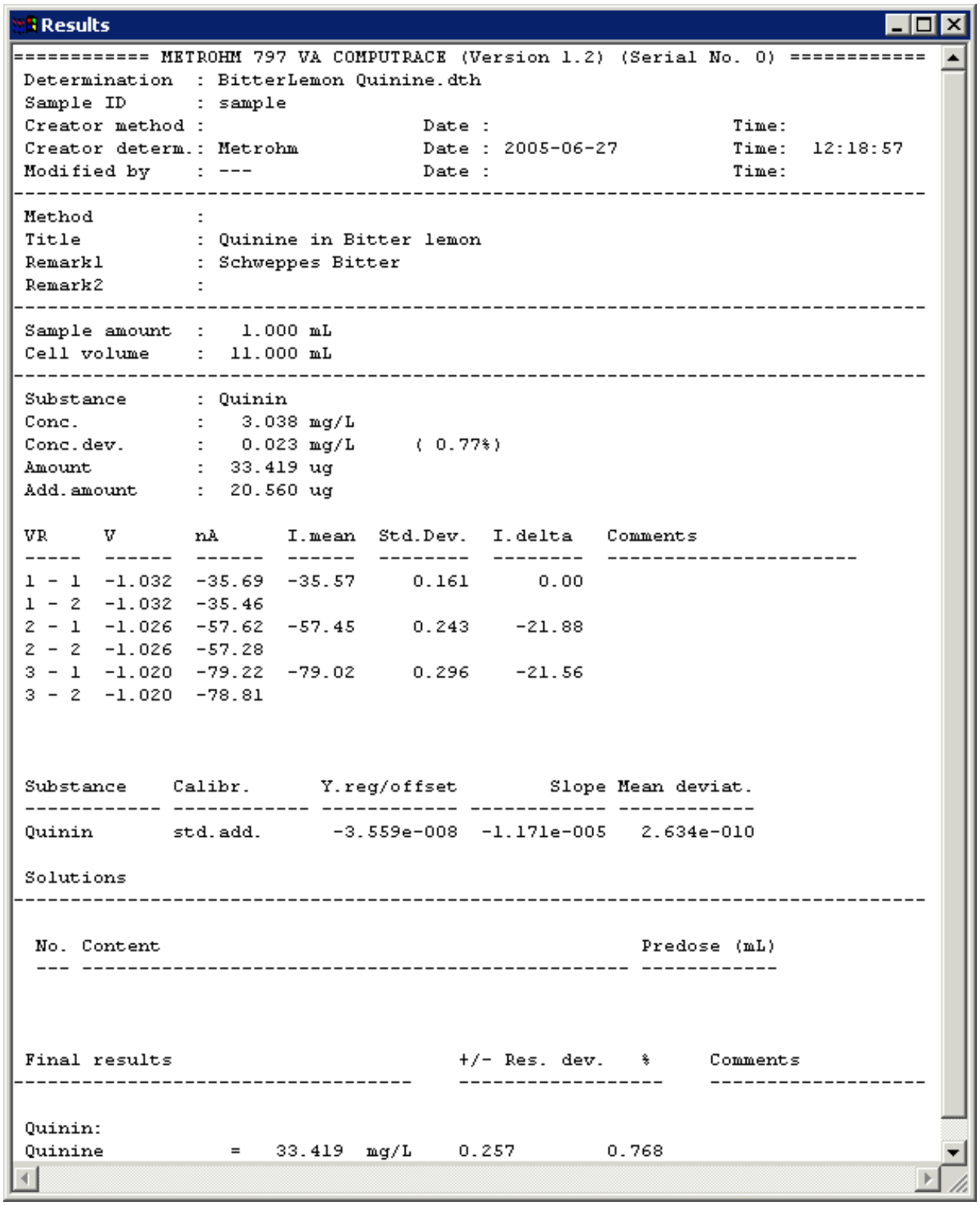
**DETERMINATION CURVES / Save as enhanced metafile**

Copy the content of the selected subwindow as enhanced metafile in the desired directory.

# 5.5 Results

## Results window overview

The **RESULTS** window contains the current full report for the loaded determination. If the determination is recalculated, the **RESULTS** window is automatically renewed.



The **RESULTS** window comprises the following parts:

### Header

`Metrohm 797 VA Computrace`
Name of manufacturer and instrument.

`(Version w1.3.x)`
Version number of PC software.

`(Serial No.)`
Serial number of the instrument.

### Determination data

`Determination`
Name of determination file.

`Sample ID`
Identification for sample (see **Sample identifier** on the **Determination** tab).

`Creator method`
Name of the logged-in user who created the **method** the determination was done with.

`Creator determ.`
Name of the logged-in user who started the determination with `Date` and `Time` of determination start.

`Modified by`
Name of the logged-in user who modified the determination for the last time with `Date` and `Time` of determination modification. The display of `"---"` means that the determination has not been modified for sure.

### Method data

`Method`
File name of the method used for the determination.

`Title`
Method title.

`Remark1`
Remark 1 regarding the method.

`Remark2`
Remark 2 regarding the method.

### Sample data

`Cell volume`
Total volume of solution in the measuring vessel at the start of the determination (see **Cell volume** on the **Determination** tab, *section 5.2*).

`Sample amount`
Amount of sample added to the measuring vessel (see **Sample amount** on the **Determination** tab, *section 5.2*).

**Note:** With the electroplating bath modes CVS and CPVS, and the **Calibration** technique "LAT Record intercept value" **Volume Intercept Solution** is indicated instead of **Sample amount**.

**Note:** With the electroplating bath modes CVS and CPVS, and the **Calibration** techniques "LAT Standard addition for brighteners", "MLAT Standard addition for brighteners" and "RC Sample with response curve" **Volume prod. bath** is displayed instead of **Sample amount**.

## Substance evaluation

**Substance**
Substance name (see **Substance** on the **Substances** tab, *section 5.2*).

**Conc.**
Calculated substance concentration referring to the total volume of solution (**Cell volume**) in the measuring vessel at the start of the first sweep.

**Conc.dev.**
Absolute and relative total deviation of the calculated substance concentration **Conc.**.

**Amount**
Absolute substance amount in the measuring vessel.

**Add.amount**
Substance amount added in every standard addition (only available for constant additions).

**Note**: For CVS and CPVS, additional evaluation values are displayed.

## Peak evaluation

**VR** Number of variation and replication.

**V** Evaluated peak voltage (V).

**A;W;A/V;C {for PSA/CCPSA: s/V;s;s/(V*V)}**
Calculated eval. quantity (height, area, derivative or charge)

**i.mean; P.mean; mean; Q.mean(only with modes CVS and CPVS)**
Mean value of the evaluation quantity for all replications of a variation.

**Std.Dev.**
Standard deviation of the evaluation quantity for all replications of a variation.

`i.delta; P.delta; delta; Q.delta(Only with modes CVS and CPVS)`
Difference of two successive mean values of the evaluation quantities.

`Comments`
Display of comments if any type of error appeared in the sweep (e.g. **Ovl. in scan** = Overload during sweep; **Ovl. in CDE** = Overload during cleaning or deposition; **Ovl. in cond. cycles** = Overload during conditioning cycles; **No peak found** = no peak found for defined substance; **Not used** = peak is not used for calculation).

---

**Note**: For CVS and CPVS, two additional evaluation values are displayed: V(mL) and Q/Q(0).

---

## Calibration data

`Substance`
Substance name (see **Substance** on the **Substances** tab*, section 5.2*).

`Calibr.`
**Calibration** techniques **std.add.**, **rec.cc.** or **smp.cc.** (see **Calibration** on the **Specifications** tab*, section 5.2*).
For electroplating bath analytics: **Calibration** techniques **dt.rec.cc.**, **dt.cc**, **mlat**, **lat rec.rc**, **sam.rc (**see Calibration techniques with CVS and CPVS, *section 6.2***).**

`Y.reg/offset`
Evaluation quantity for the sample calculated from the standard addition curve (for standard addition) or intercept of the calibration curve (for calibration curves).

`Slope`
Slope of the standard addition or calibration curve.

`Nonlin`
Nonlinear factor for nonlinear calibration curves (only displayed, if "Nonlinear Regression" was chosen for parameter **Regression technique**).

`Corr.Coeff`
Corrrelation Coefficient for linear calibration curves (only displayed, if "Linear Regression" was chosen for parameter **Regression technique**).

`Mean deviat.`
Calculated mean deviation of the measured values about the standard addition or calibration curve.

## Solutions

`No.` Number of Dosing Device used for addition or predose.

`Content`
Remarks regarding the solution (see **Content** on the **DOSINOS** window*, section 5.2*).

**predose volume (mL)**
If the Dosing Device is used for solution predose, the message **Predose X.X mL** is displayed in this column.

**Electrode test**
Shows the status of the electrode test before the determination.

**Note**: With the electroplating bath modes CVS and CPVS, and the **Calibration** techniques "MLAT Standard addition for brighteners" and "RC Sample with response curve", **dosed volume after sample transfer (mL)** is displayed additionally.

## Final results

**Final results**
Calculated results for the calculation formulae defined in the **CALCULATION** window.

**Res.dev.**
Absolute and relative deviation of the final results.

## Copy text to clipboard

Text selected in the **RESULTS** window can be copied to the clipboard by selecting the **Copy** option of the context sensitive menu.

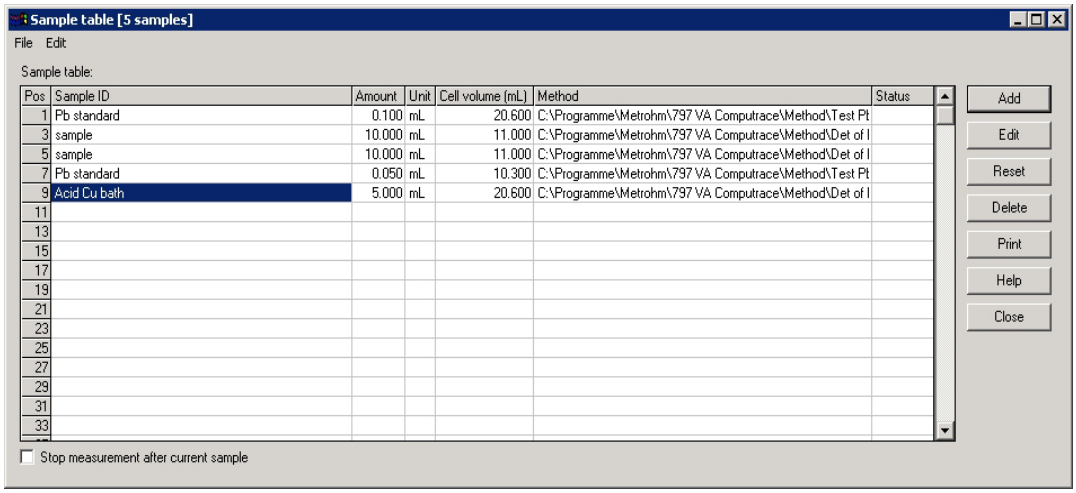
**RESULTS / Select all**
Select the whole text in the **RESULTS** window.

**RESULTS / Copy**
Copy the selected text to the clipboard.

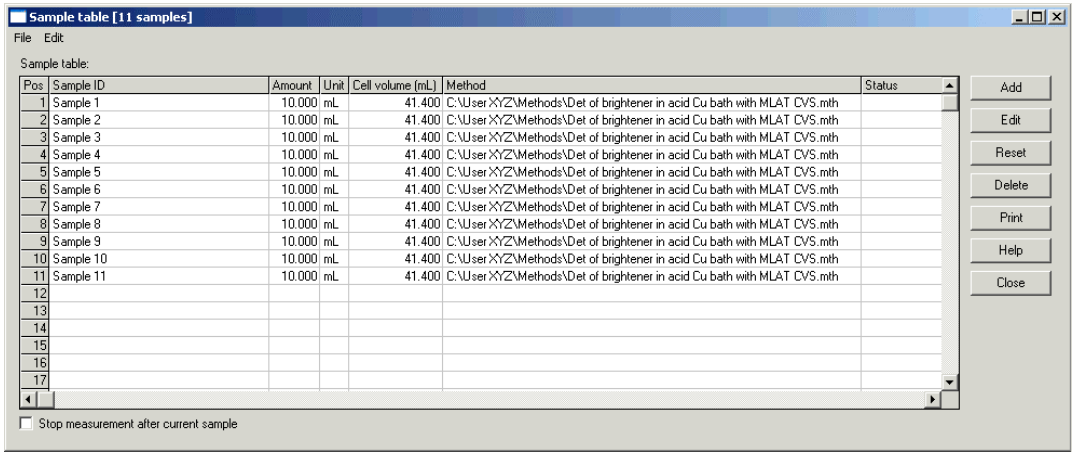
## 5.6 Sample table

The **SAMPLE TABLE** window shows the sample data of the loaded sample table.

With 863 Compact VA Autosampler:




With 838 Advanced Sample Processor:




**Pos.** **[ for 863: 1, 3, 5 ... 127; read only ]**
**[ for 838: 1, 2, 3 ... 112; read only ]**
Position of the sample on the sample rack.

For the **863 Compact VA Autosampler**, only odd numbers are displayed, since for every sample, a vessel containing rinsing solution must be placed at the even sample rack positions.

For the **838** Advanced Sample Processor, all numbers are displayed in the sample table. Starting point on the sample rack is always the last position + 1 (after switching on the 838 it starts with rack position 1). If you want to start with a different position, enter the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

**Sample ID [ 32 characters ; "sample" ]**
Identification for sample.

**Amount [ > 0 ; 10 ]**
Amount of sample added to the measuring vessel.

**Unit [ mL, g ; mL ]**
Selection of unit for sample amount.

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Total volume of solution (sample + auxiliary solution, e.g. buffer) in the measuring vessel at the start of the determination. The sample concentrations **Conc.** refer to this cell volume.

**Method**
Selection of the method used for this sample.

**Status [ read only ]**
Display of sample determination status: **Measuring**, **Done** or "empty" (ready for start).


Add a new sample data row. The **SAMPLE** window for entry of **Method**, **Sample ID**, **Sample amount**, **Sample unit**, and **Cell volume** is opened.


Edit the selected sample data row. The **SAMPLE** window for modification of **Method**, **Sample ID**, **Sample amount**, **Sample unit**, and **Cell volume** is opened.


Reset the **Status** of the sample data rows to "empty" in order to restart the current sample table.


Clear the contents of the selected sample data row.


Print the sample table.

## Load/save sample table

Sample table files (***.spt**) containing sample table data can be created, loaded and saved by the following commands:

**SAMPLE TABLE / File / New**
Load an empty sample table into the working memory.

**SAMPLE TABLE / File / Load**
Load an existing sample table into the working memory. The name of the sample table is displayed in the status bar of the **MAIN WINDOW**.

**SAMPLE TABLE / File / Save**
Save the current sample table loaded in the working memory. If the sample table has been changed since loading, the message **The file already exists. Overwrite?** appears. Click **Yes** to overwrite

the sample table file or **No** to cancel saving.

**SAMPLE TABLE / File / Save As ...**
Save the current sample table loaded in the working memory in a new file. Enter name and directory for storage of the sample table file. If the file name already exists, windows asks if you want to overwrite the existing file.

## Edit sample table

The addition of new rows or the modification of existing rows in the sample table is done in the sample table window using the Add or Edit button. In addition to this commands, the following possibilities for edition are available:

**SAMPLE TABLE / Edit / Cut**
Cut the selected sample data row and copy it to the clipboard.

**SAMPLE TABLE / Edit / Copy**
Copy the selected sample data row to the clipboard.

**SAMPLE TABLE / Edit / Copy previous**
Copy the content of the previous row into the selected sample data row.

**SAMPLE TABLE / Edit / Paste**
Copy the content of the clipboard into the selected sample data row.

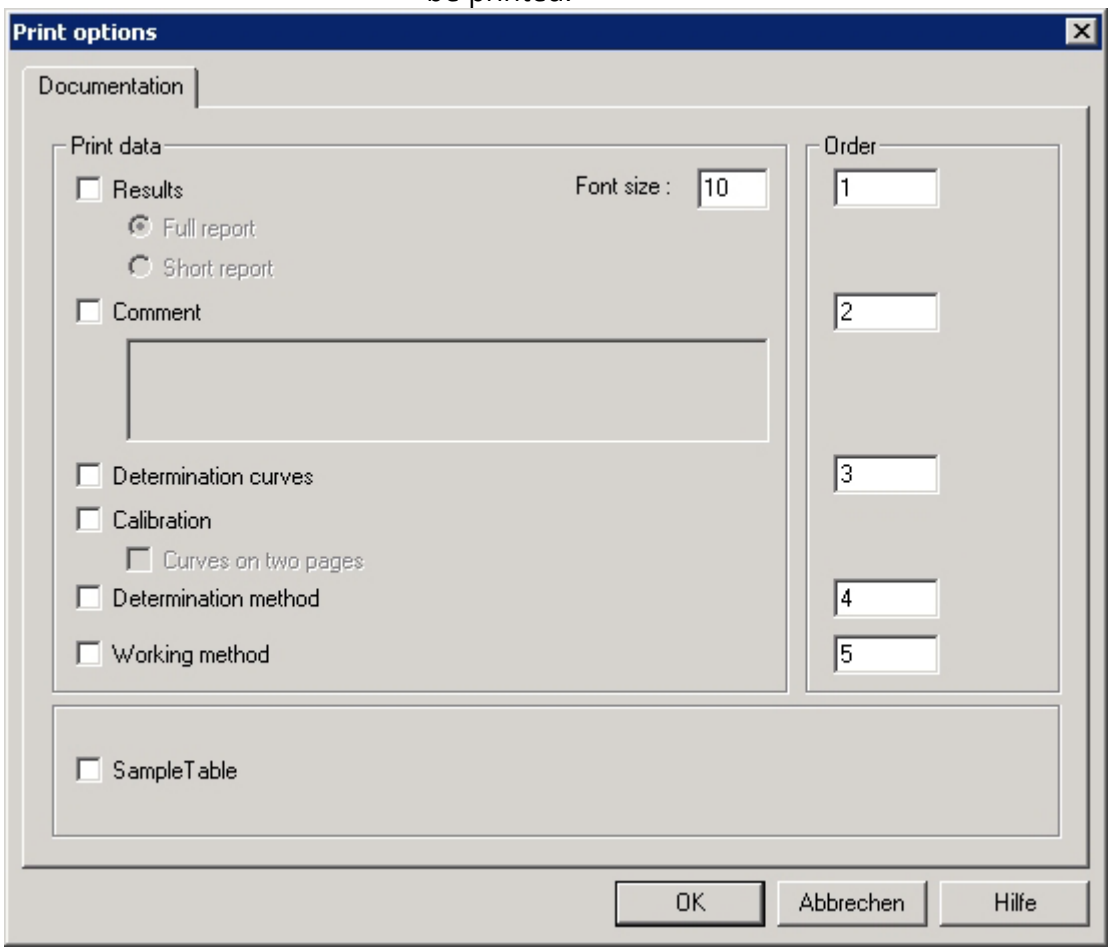
**SAMPLE TABLE / Edit / Delete**
Clear the contents of the selected sample data row.

**SAMPLE TABLE / Edit / Reset**
Reset the **Status** of the sample data rows in order to restart the current sample table.

# 5.7 Printing in determination mode

**MAIN WINDOW / File / Print (Ctrl+P)**

Print reports and/or curves. The **PRINT OPTIONS** window appears for selection of the elements to be printed.




**Results**

Printout of **Full report** or **Short report**.

**Font size**

Font size in points for report printout.

**Comment**

Printout of the method comment defined in the accompanying field.

**Determination curves**

Printout of all determination curves.

**Calibration**

Printout of all calibration curves.

**Curves on two pages**

Printout of the determination and calibration curves on two pages.

**Determination method**

Printout of the method parameters used for the determination.

**Working method**
Printout of the method parameters of the working method in the working memory.

**Order [ 1...6 ; ]**
Order of printout for the element.

**Sample table**
Printout of the sample table.

## 5.8 Data processing and evaluation

### Data transfer

After the start of a determination, the parameters of the current working method are copied into the determination method. The parameters necessary for the VA measurement are then sent from the PC to the VA Computrace via USB connection. The data acquisition at the VA Computrace stand is started and controlled by the internal processor, which receives and stores the measurement data. At the end of each voltammogram, the recorded data are sent back to the PC where they are evaluated and saved in a determination file.

### Data acquisition

The 797 VA Computrace stand operates according the potentiostatic, 3-electrode principle in which the voltage of the working electrode is controlled with the aid of a virtually currentless reference electrode to the preset desired value and the current flows across a separate auxiliary electrode. The voltage drop in the analysis solution is automatically compensated. Measurement of the current with digitalization involves automatic matching of the amplifier sensitivity to the latest measured value so that measurements are always performed with optimum accuracy.

The type of measured value recording, the measurement range and the measurement frequency are defined by the selection of electrode, VA measurement mode and the corresponding sweep parameters. The following combinations of electrode and VA measurement mode are possible:

| | DC | NP | DP | SqW | AC | CV | PSA | CCPSA | CVS | CPVS |
|---|---|---|---|---|---|---|---|---|---|---|
| DME | (•) | (•) | • | | • | | | | | |
| SMDE | (•) | (•) | • | | • | | | | | |
| HMDE | • | (•) | • | • | • | • | • | • | • | |
| RDE | • | (•) | • | • | • | • | • | • | • | • |

(•) This combination can only be used in the exploratory mode.

The measured value pairs recorded per single measurement sweep are stored in data blocks characterized by the VR number (variation

and replication). This identification can be used to select the single sweeps for display.

In connection with the measured value recording, the following rules apply to the sweeps:

- The maximum number of variations (V) is limited to 29 (1 sample + 28 additions), the maximum number of replications (R) to 10.
- The maximum number of measured values is memory limited. If the memory needed for storage of the measured values extends 2 MB, the message **There is not enough memory available to measure the desired points** appears. In this case, reduce the number of data points per sweep.

### Background compensation

In determinations with **background compensation** (**Measure blank** option enabled) the values measured in the recording of the blank sample are subtracted from the values of each subsequent sweep.

### Smoothing and differentiation

Following spike elimination and background compensation, the measured values are smoothed. This is done by weighted moving averaging using the Savitzky/Golay algorithm. The number of points for averaging depends on the **Smooth factor** selected:

| | |
|---|---|
| **1** | 3-point weighed moving average |
| **2** | 5-point weighed moving average |
| **3** | 7-point weighed moving average |
| **4** | 9-point weighed moving average |
| **5** | 11-point weighed moving average |
| **6** | 13-point weighed moving average |

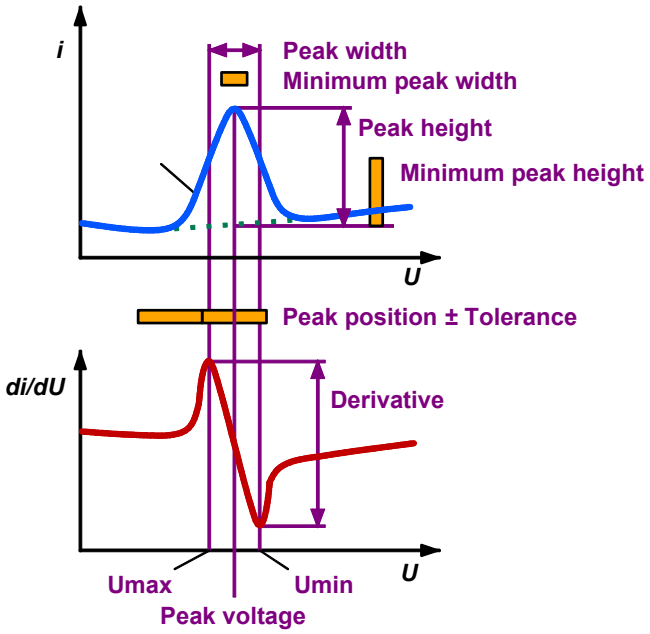
The applicable smooth factor heavily depends on the number of points of the data set. The more points within the curve, the higher the smooth factor can be without modifying the curve too much. Although the smoothed curve itself is not shown, the influence of the smoothing can be seen in the peak recognition and baseline calculation.

In smoothing, the curve is also automatically differentiated to give the derived curve (first derivative) which is used for peak recognition.

### Peak recognition

With the derived curves a search is made for successive minima and maxima. A maximum followed by a minimum indicates a normal peak, a minimum followed by a maximum a reverse peak. With the

aid of these measured maxima and minima values, the **Peak voltage** and **Peak width** values are determined for each peak. After the peak detection a baseline is constructed. The **Peak height** is determined from the value of the peak maximum minus the value of the baseline at the position of the peak voltage.




- **Peak voltage = (Umax + Umin) / 2**
- **Peak width = | Umin - Umax |**
- **Peak height = Peak height at peak voltage**

The peaks found are assigned to defined substances with the aid of these approximate values and the recognition parameters specified for the substances on the **Substances** tab. The following three recognition tests are performed:

**Peak voltage test:** **Peak voltage = Peak position ± Tolerance**

**Peak width test:** **Peak width > Minimum peak width**

**Peak height test:** **Peak height > Minimum peak height**

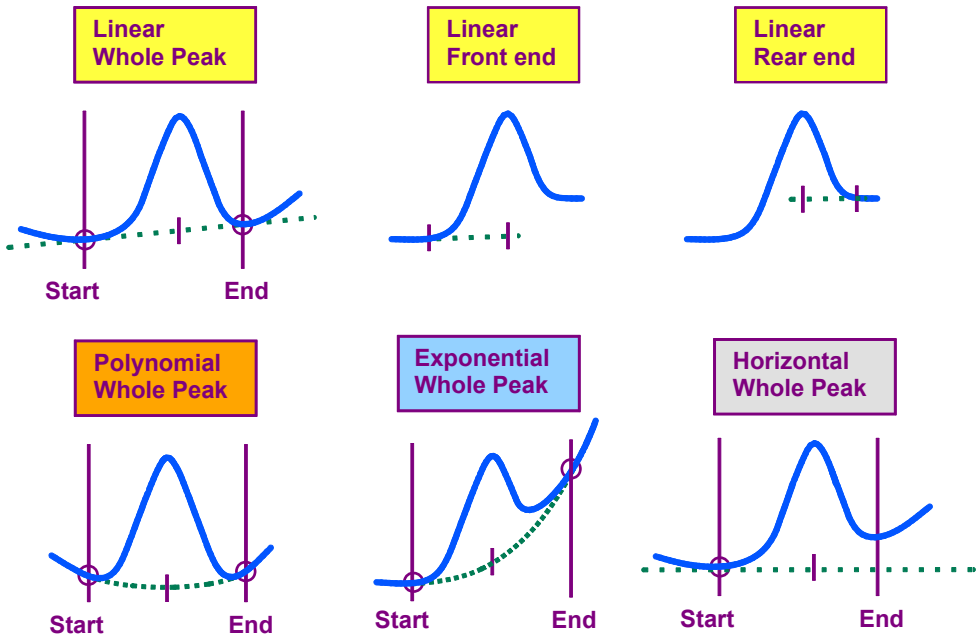
If all three test conditions are met, this peak is assigned to the corresponding substance and thus recognized as a substance peak. In the curve display, this peak is marked with the substance name "**Substance**".

If only the last two test conditions are met, this peak is recognized as an unknown peak but not assigned to a substance. In the curve display, this peak is marked with "**Unk**".

## Baseline calculation

Recognized peaks are evaluated using approximated baselines. The calculation of a baseline for a smoothed substance peak is deter-

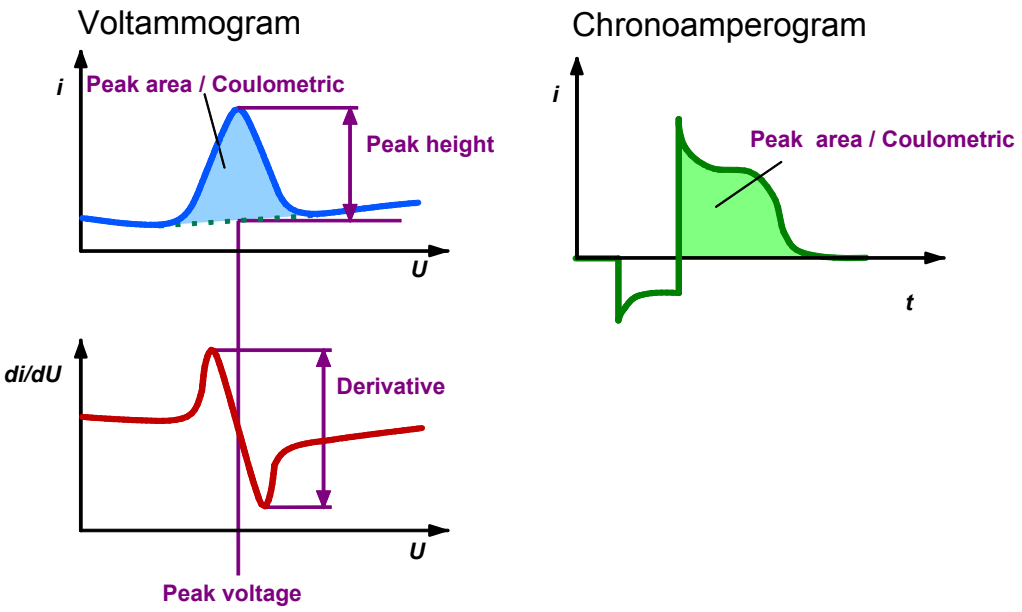
mined by the baseline parameters set for this substance in the **BASELINE** window (see *Baseline*, *section 5.2*). The following possibilities exist for baseline calculation:




As default, the start and end base points of the baselines are calculated automatically. They can be set to fixed voltage values if desired. The baseline scope **Front end** or **Rear end** for linear baselines should be selected for asymmetric or double peaks.

## Evaluation quantity calculation

The peak evaluation quantity is identical for all peaks of a determination and must be set on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (see *Working method specifications window*, *section 5.2*). With the aid of the calculated baselines, the set evaluation quantity **Height**, **Area**, **Derivative** or **Coulometric** is determined for each substance peak and displayed as a result.




Comparing the evaluation quantities **Area** and **Coulometric** you have to consider the differences between voltammograms and chronoamperograms:

**Voltammogram**:

- **Area** is Power (Voltage * Current): V*A = W
- **Coulometric** is Charge (Voltage * Current / Sweep rate): V*A/(V/s) = A*s = C

**Chronoamperogram:**

- **Area** is Charge (Current * time): A*s = C
- **Coulometric** is Charge (Current * time): A*s = C

## Content calculation

With polarographic and voltammetric methods, the measured evaluation quantities (**Height**, **Area**, **Derivative** or **Coulometric**) for a substance are proportional to its mass concentration. The relation between evaluation quantity and mass concentration must be determined by a calibration with reference solutions. The 797 VA Computrace offers the following two techniques for this:

- **Standard addition**
  Content determination using single or multiple addition of a standard solution.
- **Calibration curve**
  Content determination using a calibration curve previously determined with reference solutions.

The goal of these calibration methods is to calculate the sample concentration ***c*(s)** which is defined by the found substance amount **Amount** and the sample amount (mass or volume) in the measuring vessel **Sample amount**:

***c*(s)** = **Amount / Sample amount**

**Note**: With the electroplating modes CVS and CPVS different **Calibration** techniques are used.

## Dilution calculation

In all cases in which the sample volume is diluted in the measuring vessel (e.g. by addition of buffer) before the start of the first sweep, this must be taken into consideration by entering the two parameters **Sample amount** and **Cell volume** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window (see *Determination*, *section 5.2*).

If the sample is additionally diluted after the start of the first sweep (e.g. by standard addition solutions), the dilution is recalculated continuously for every dilution step so that the effective mass concentration of the analyte in the measuring vessel is shown in the calibration curve for each measurement solution.

If an auxiliary solution is added by a Dosing Device using the **Use for predose** or **Use after sample transfer** function, this volume must be taken into consideration by modifying the **Cell volume** manually.

## Standard addition calculation

In the standard addition method, a known amount of the analyte is added once or several times to the sample. The addition may be performed manually or automatically using a Dosing Device. The following procedure is used to calculate the sought mass concentration of the sample:

1. **Measurement of sample solution**
   The sample solution with the unknown mass concentration ***c*(s)** of the sample is measured one or more times (defined by **No. of replications**). This gives:

   | | |
   |---|---|
   | `EV(s)` | Evaluation quantity of a single measurement for the sample |
   | `mean(s)` | Mean value of all evaluation quantities for the sample |
   | `Std.dev.(s)` | Standard deviation of the individual value `EV(s)` = ***s*(s)** |

2. **Measurement of spiked sample solutions**
   The sample solution is spiked **n** times (defined by **No. of additions**) with a standard solution of known mass concentration ***c*(st)**. Each of these spiked solutions is measured one or more times (defined by **No. of replications**). This gives:

   | | |
   |---|---|
   | `EV(n)` | Evaluation quantity of a single measurement for the spiked sample **n** |

| | |
|---|---|
| `mean(n)` | Mean value of all evaluation quantities for spiked sample **n** |
| `Std.dev.(n)` | Standard deviation of the individual value `EV(n)` = ***s*(n)** |
| ***c*(n) – *c*(s)** | Difference in the mass concentrations between the spiked sample **n** and the original sample solution |

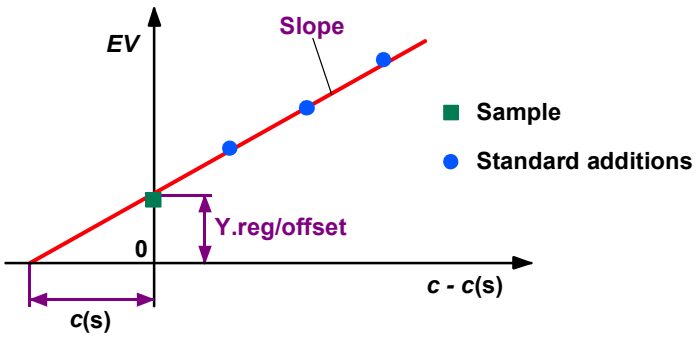
3. **Determination of standard addition curve**
For the calculation of the linear standard addition curve, the parameters ***a*** and ***b*** of the linear regression curve **y** = ***a*** + ***b*****x** are calculated by weighted least square minimization with **y =** `EV` and **x** = ***c*** **–** ***c*(s)**. The weight factor for each point is the standard deviation obtained from the replications. The parameters ***a*** and ***b*** are displayed in the **RESULTS** window and have the following meaning:

| | |
|---|---|
| ***a*** = `Y.reg/offset` | Intercept of std.add. curve |
| ***b*** = `Slope` | Slope of std.add. curve |

4. **Calculation of mass concentration *c*(s)**
A requirement for the use of the standard addition is that when ***c*** = 0 the evaluation quantity `EV` = 0. If 0 is substituted for these two quantities in the calibration function, the sought mass concentration ***c*(s)** can be calculated from the equation:

***c*(s)** = ***a* / *b***

In the graphical representation of the standard addition curve, the sought mass concentration on the x-axis is given by the distance between the zero point and the intersection point with the calibration function.




5. **Calculation of result deviation Conc.dev.**
The total deviation of the calculated substance concentration `Conc.` is determined using a linear error calculation. Independent of the number of measurements, the total deviation `Conc.dev.` is always calculated in a way that `Conc.` ± `Conc.dev.` gives the range in which the mass concentration may be expected with a probability of 68.3%.

## Rules for standard addition

**Standard addition** is the usual **calibration** technique for the majority of the applications possible with the 797 VA Computrace. Its advantage lies in its high dependability as the calibration in the sample takes place under real matrix conditions and all measurement parameters remain unchanged. With regard to optimum accuracy and scatter, several **rules** must be observed in standard addition:

- **Check linearity range**
  In development of the method, the linearity range should be checked for each substance. This involves performing several standard additions over a wide concentration range. Using the calibration curve shown on **DETERMINATION CURVES** window, you can then determine the region in which the standard addition is linear and that in which it is nonlinear.
- **Addition procedure**
  If the substance content lies in the linear range, multiple standard addition is meaningful only if you wish to check the linearity in every determination. To reduce the scatter, it is better to spike the solution once only and to choose as many replications as possible.
- **Standard addition ratio 1:2 to 1:5**
  The optimum standard addition ratio for the entire standard addition is from 1:2 to 1:5, i.e. the sum of all standard addition amounts should be 2 to 5 times the amount of sample in the measuring vessel. This can be easily checked later with the parameters `Amount` and `Add.amount` put out in the **RESULTS** window.
- **Consideration of blank values**
  Any blank values must be determined separately and subtracted by means of the formula in the **CALCULATION** window.

## Calibration curve calculation

The content determination using a calibration curve is performed in two steps:

- First the relation between the mass concentration ***c*** of a substance and the evaluation quantity **EV** is determined by measuring different reference solutions.

**Note:** "Minimum number" as well as "Recommended number" of calibration points which have to be determined for a reliable calibration depend on the chosen **Regression technique** on the tab **Substances** of the window **EDIT WORKING METHOD PARAMETERS**:

| | Minimum number | Recommended number |
|---|---|---|

| | | |
|---|---|---|
| Linear Regression: | 2 | ≥ 3 |
| Nonlinear Regression: | 3 | ≥ 5 |
| Linear Regression (through Zero): | 1 | ≥ 2 |
| Nonlinear Regression (through Zero): | 2 | ≥ 4 |
| Linear Interpolation: | 2 | ≥ 2 |
| Quadratic Interpolation: | 3 | ≥ 5 |

If less than the "Recommended number" of calibration points are used for the calculation, the regression curve might does not fit ideally. Therefore you should always use the "Recommended number" of calibration points.

- Finally, the sample is measured and its mass concentration ***c*(s)** determined using the recorded calibration curve.

In the content determination using a calibration curve, the following procedure is used to calculate the sought mass concentration ***c*(s)** of the sample:

1. **Measurement of calibration solutions**
   The calibration solutions with known mass concentration ***c*(n)** are each measured several times (defined by **No. of replications**). This gives:

   | | |
   |---|---|
   | `EV(n)` | Evaluation quantity of a single measurement for calibration solution **n** |
   | `mean(n)` | Mean value of all evaluation quantities for calibration solution **n** |
   | `Std.dev.(n)` | Standard deviation of the individual value `EV(n)`= ***s*(n)** |
   | ***c*(eff,n)** | Effective mass concentrations of the calibration solutions (calculated from ***c*(n)** taking the dilution into account) |

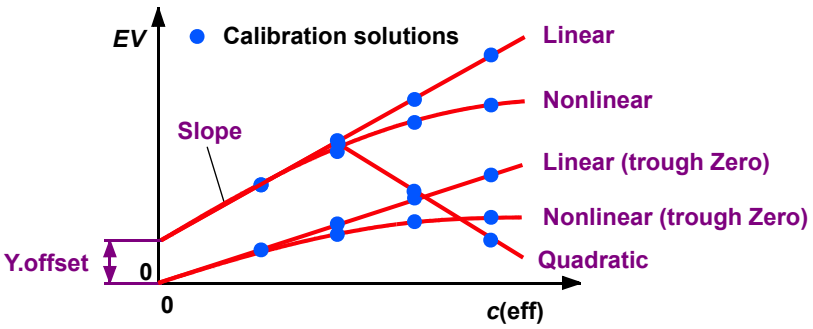
2. **Determination of calibration curve**
   The calculation curve is calculated according to one of the four possible model functions selected under **Regression technique** on the **Substances** tab:

   | | |
   |---|---|
   | $\mathbf{y} = \boldsymbol{a} + \boldsymbol{b}\mathbf{x}$ | Straight line = **Linear Regression / Linear Interpolation** |
   | $\mathbf{y} = \boldsymbol{b}\mathbf{x}$ | Straight line through zero point = **Linear Regression (trough Zero)** |
   | $\mathbf{y} = \boldsymbol{a} + \boldsymbol{b}\,\mathbf{x} + \boldsymbol{d}\,\mathbf{x}^4$ | Nonlinear curve of 4th degree = **Nonlinear Regression** |
   | $\mathbf{y} = \boldsymbol{b}\,\mathbf{x} + \boldsymbol{d}\,\mathbf{x}^4$ | Nonlinear curve of 4th degree through zero point = **Nonlinear Regression (trough Zero)** |

$y = a + b x + c x^2$ Nonlinear curve 2nd degree = **Quadratic Regression**

The parameters ***a***, ***b*** and ***d*** of the regression curves are calculated by weighted least square minimization with **y = EV** and **x = *c*(eff)**. The weight factor for each point is the standard deviation obtained from the replications. The parameters are displayed in the **RESULTS** window and have the following meaning:

| | |
|---|---|
| ***a*** = `Y.reg/offset` | Intercept of calibration curve |
| ***b*** = `Slope` | Slope of calibration curve in the linear region |
| ***d*** = `Nonlin.` | Non-linearity factor |

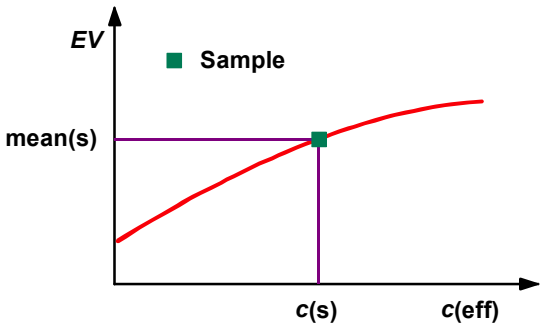



3. **Measurement of sample solution**
The sample solution with the unknown mass concentration ***c*(s)** of the sample is measured one or more times (defined by **No. of replications**). This gives:

| | |
|---|---|
| `EV(s)` | Evaluation quantity of a single measurement for the sample |
| `mean(s)` | Mean value of all evaluation quantities for the sample |
| `Std.dev.(s)` | Standard deviation of the individual value `EV(s)` = ***s*(s)** |

4. **Calculation of mass concentration *c*(s)**
The sought mass concentration ***c*(s)** of the sample is calculated by inserting `mean(s)` in the calibration function determined earlier:

$\text{mean(s)} = d\,c(s)^4 + b\,c(s) - a$




5. **Calculation of result deviation Conc.dev.**
   The total deviation of the calculated substance concentration **Conc.** is determined using a linear error calculation which takes into account both the error contribution from the measurement and that from the calibration. Independent of the number of measurements, the total deviation **Conc.dev.** is always calculated in a way that **Conc.** ± **Conc.dev.** gives the range in which the mass concentration may be expected with a probability of 68.3%.

## Rules for calibration curves

The result determination with the aid of a **calibration curve** saves time compared with standard additions, but is reliable only

- if the matrix of all samples and calibration solutions is identical or has no influence on the measurement.
- if all measurement parameters (capillary, temperature, etc.) remain unchanged during measurements.
- if the accuracy of the results obtained is checked regularly with the standard addition method.

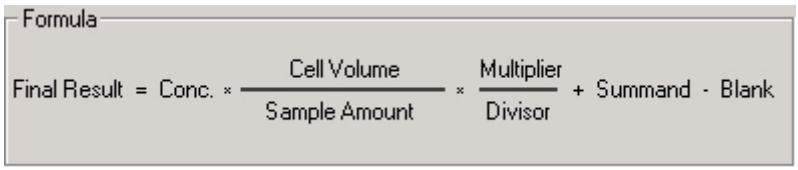
With regard to optimum accuracy and scatter, a number of **rules** must be observed with calibration curves:

- **Check linearity range**
  In development of the method, the linearity range of the calibration curve should be checked for each substance by recording the curve over a wide concentration range. Using the calibration curve shown in the **DETERMINATION CURVES** window, you can then determine the region in which the curve is linear and that in which it is nonlinear.
- **Working in the linear range**
  Performing determinations in the linear range, to keep the scatter as low as possible it is advisable to calibrate above all in the lower and upper part of this range and select as many replications as possible.
- **Checking the offset**
  The size of the offset indicates a possible systematic error or blank value. To convert this error into the effective mass concentration in g/L, **Y.offset** must be divided by **Slope**.

- **Determining the working range**
  The calibration curve is defined only for the range between the calibration solutions with the lowest and highest mass concentrations. Extrapolations outside this range are not allowed.
- **Keep temperature constant**
  Owing to the large temperature dependence of the measured values (≥ 2%/°C), it is advisable to work with the 6.1418.220 thermostatted measuring vessel.
- **Consideration of blank values**
  Any blank values must be determined separately and subtracted by means of the formula in the **CALCULATION** window.

## Formula calculation

The last step in the evaluation is the calculation of the calculation formulae entered in the **CALCULATION** window for the output of the `Final results`:




Without changing the default values for **Multiplier**, **Divisor**, and **Summand**, the **Final Result** is calculated as the **concentration** multiplied by the **Cell volume** and divided by the **Sample amount**. The final result has the **Final unit** selected in the **CALCULATION** window.

# 6 Electroplating Bath VA

## 6.1 Electroplating Bath VA – Introduction

The 797 VA Computrace has two special modes for electroplating bath analysis: **CVS** (Cyclic Voltammetric Stripping) and **CPVS** (Cyclic Pulse Voltammetric Stripping). Working with these two modes, you have to consider that some settings and options differ from working with the other modes.

## 6.2 Calibration techniques with CVS and CPVS

With CVS and CPVS, 8 **Calibration** techniques are available:

- Standard addition plating bath
- LAT Record intercept value
- LAT Standard addition for brighteners
- MLAT Standard addition for brighteners
- DT Suppressors with calibration curve
- DT Record calibration curve
- RC Sample with response curve
- RC Record response curve

### Standard addition plating bath

"Standard addition plating bath" is a **Calibration** technique for CVS and CPVS. It is mainly used to develop methods:

- Optimize addition volumes and concentrations (e.g. to get "Addition ratio" after 5 to 20 additions for "DT Record calibration curve" and "DT Suppressors with calibration curve")
- Optimize dilution with "Intercept solution" for "MLAT"
- Check linear range of standard addition (with "LAT" and "MLAT")

#### Determination tab with Calibration technique "Standard addition plating bath"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the

determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "Standard addition plating bath" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample. The **Sample identifier** is used for the file name.

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Total volume of solution (e.g. Virgin Make-up Solution, see VMS (Virgin Make-up Solution), *section 6.4*) in the measuring vessel at the start of the determination.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Addition mixing time [ 0...80600 s ; 10 s ]**
Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**No. of additions [ 0...28 ; 2 ]**
Number of additions of additive standard solution.

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measure-

ment). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "Standard addition plating bath"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window. With "Standard addition plating bath" following parameters have to be defined:

**Initial mixing time (s) [ 0...80600 s ; 10 s ]** (see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep**
The sweep parameters depend on the mode (see

*CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping section 3.2*)

### Substances tab with Calibration technique "Standard addition plating bath"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "Standard addition plating bath" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**
Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**
Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Additive solution**
Definition of addition solutions for standard addition.

**No. [ 0...8 ; 0 ]**
Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number. If a mixed standard solution is used, the number of this solution must be entered for each substance present in the mixed solution.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**
Value for concentration of addition solution.

**Unit [ fL/L...mL/L ; mL/L ]**
Unit for concentration of addition solution.

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**
Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**
Selection of peak evaluation quantity:

**Height**
Peak height from baseline to peak maximum.

**Area**
Peak area between peak curve and calculated baseline.

**Derivative**
Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**
Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

## LAT Record intercept value

"LAT Record intercept value" is a **Calibration** technique for CVS and CPVS. It is used to determine the "Intercept value". That "Intercept value" is later used automatically for Brightener determination with the **Calibration** technique "LAT Standard addition for brighteners".

**Note**: If possible, "MLAT" should be the preferred **Calibration** technique for Brightener determination. With "MLAT" the "Intercept solution" and "Bath solution" are measured together, what minimizes fluctuations caused by solution exchange and time displacement of the measurements.

**Note**: A determined "Intercept value" can only be adopted automatically, if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

### Determination tab with Calibration technique "LAT Record intercept value"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "LAT Record intercept value" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample.

**Note**: The sample identification is used for the file name. To make sure that always the latest intercept file is taken for the calculation when analyzing Brightener with the 838 Advanced Sample Processor and "LAT", this **Sample identifier** must match with the name of the intercept file defined for the parameter **Intercept determination** on the **Determination** tab with **Calibration** technique "LAT".

Example for **Sample identifier**: Intercept

**Volume intercept solution (mL) [> 0 mL ; 10 mL]**
The volume of intercept solution added (see *Intercept solution*, *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Shows the volume given for **Volume intercept solution**.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "LAT Record intercept value"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window. With "LAT Record intercept value" following parameters have to be defined:

**Initial mixing time (s) [ 0...80600 s ; 10 s ]** (see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep**
The sweep parameters depend on the mode (see *CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping section 3.2*)

## Substances tab with Calibration technique "LAT Record intercept value"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "LAT Record intercept value" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**
Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**
Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**
Selection of peak evaluation quantity:

**Height**
Peak height from baseline to peak maximum.

**Area**
Peak area between peak curve and calculated baseline.

**Derivative**
Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**
Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

## LAT Standard addition for brighteners

**L**inear **A**pproximation **T**echnique ("LAT Standard addition for brighteners") is a **Calibration** technique for CVS and CPVS. It is mainly used to analyze Brighteners in electroplating baths. It is chosen, if the difference between Q("Intercept solution" + "Bath solution") and Q(only "Intercept solution") is too small to use "MLAT Standard addition for brighteners".

The "Intercept value" needed for the calculation can be recorded and adopted automatically with the **Calibration** technique "LAT Record intercept value".

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**Note**: If possible, "MLAT" should be the preferred **Calibration** technique for Brightener determination. With "MLAT", "Intercept solution" and "Bath solution" are measured successively in the same method run, what minimizes fluctuations caused by solution exchange and time displacement of the measurements.

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**Note**: A determined "Intercept value" is only adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

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### Determination tab with Calibration technique "LAT"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "LAT

Standard addition for brighteners" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample. The **Sample identifier** is used for the file name.

**Volume production bath (mL) [> 0 mL ; 10 mL]**
The volume of sample bath solution added (see *Production bath solution*, *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ]**
Total volume of solution ("Production bath solution" + (if necessary) auxiliary solution) in the measuring vessel at the start of the determination. The sample concentrations **Conc**. calculated refers to this cell volume.

The used "Intercept value" can be defined in 2 ways:

**Intercept value (mC) [> 0 ; 0 ] [± ; 0 ]**
Read the previously determined "Intercept value" out of the report and enter it here.

**Intercept determination**
Define the Intercept-file (the file in which the determination of the "Intercept value" was(will be) saved). The method then reads out the value for the calculation automatically. Use the button ... to search for the file.

---

**Note**: To make sure that always the latest intercept file is taken for the calculation when analyzing Brightener with the 838 Advanced Sample Processor and "LAT", the name of the intercept file defined for **Intercept determination**, must match with the parameter **Sample identifier** on the **Determination** tab with **Calibration** technique "LAT Record intercept value".

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Example for **Intercept determination**:
C:\User XYZ\Data\Intercept.dth

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**Note**: To make sure that always the latest intercept file is taken for the calculation when analyzing Brightener with the 838 Advanced Sample Processor and "LAT", the path of the intercept file defined for **Intercept determination**, must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

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**Note**: A determined intercept file curve is only adopted automatically if the checkbox **Save calibration curves additionally without date and time**

on the **General** tab of the **GENERAL SETTINGS** window is checked.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Addition mixing time [ 0...80600 s ; 10 s ]**
Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**No. of additions [ 0...28 ; 2 ]**
Number of additions of additive standard solution.

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "LAT"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and

VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window. With "LAT Standard addition for brighteners" following parameters have to be defined:

**Initial mixing time (s) [ 0...80600 s ; 10 s ]** (see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep**
The sweep parameters depend on the mode (see *CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping section 3.2*).

### Substances tab with Calibration technique "LAT"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD**

**SPECIFICATIONS** window. With "LAT Standard addition for brighteners" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**
Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**
Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Additive solution**
Definition of addition solutions for standard addition.

**No. [ 0...8 ; 0 ]**
Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number. If a mixed standard solution is used, the number of this solution must be entered for each substance present in the mixed solution.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**
Value for concentration of addition solution.

**Unit [ fL/L...mL/L ; mL/L ]**
Unit for concentration of addition solution.

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**
Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Contamination potential [ -5...5 ; 1.125 V ]**

With CVS: If it is activated, the current is readout for the defined potential during the last sweep (in anodic direction) of the bath determination.

With CPVS: One of the defined stripping steps (Voltammetric tab with Calibration technique "LAT") can be selected. If it is activated, the current is readout for the selected potential during the last sweep (in anodic direction) of the bath determination.

The Contamination potential correlates with the concentration of organic degradation products in the electroplating bath.

**Chloride potential [ -5...5 ; 1.475 V ]**

With CVS: If it is activated, the current is readout for the defined potential during the last sweep (in anodic direction) of the bath determination.

With CPVS: One of the defined stripping steps (Voltammetric tab with Calibration technique "LAT") can be selected. If it is activated, the current is readout for the selected potential during the last sweep (in anodic direction) of the bath determination.

The Chloride potential correlates with the concentration of chloride in the electroplating bath.

**Regression technique [ Linear Regression ]**

The regression is calculated with a straight line.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**

Selection of peak evaluation quantity:

**Height**

Peak height from baseline to peak maximum.

**Area**

Peak area between peak curve and calculated baseline.

**Derivative**

Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**

Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**

Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**

Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

## MLAT Standard addition for brighteners

**M**odified **L**inear **A**pproximation **T**echnique ("MLAT Standard addition for brighteners") is a **Calibration** technique for CVS and CPVS. It is the standard technique to analyze Brighteners in electroplating baths. If the difference between Q("Intercept solution" + "Bath solution") and Q(only "Intercept solution") is too small to use "MLAT", try "LAT Standard addition for brighteners".

### Determination tab with Calibration technique "MLAT"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "MLAT Standard addition for brighteners" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample. The **Sample identifier** is used for the file name.

**Volume production bath (mL) [> 0 mL ; 10 mL]**
The volume of sample bath solution added (see *Production bath solution*, *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 20 mL ] [ read only ]**
Total volume of solution ("Intercept solution" + "Production bath solution") in the measuring vessel after addition of "bath solution". The sample concentrations **Conc**. calculated refers to this cell volume.

**Volume intercept solution (mL) [> 0 mL ; 10 mL]**
The volume of "Intercept solution" added.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all

saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Additional conditioning after sample transfer**
If this option is activated, an additional electrode conditioning is started after sample addition. This option can only be activated, if **Initial electrode conditioning** is activated.

**Addition mixing time [ 0...80600 s ; 10 s ]**
Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**No. of additions [ 0...28 ; 2 ]**
Number of additions of additive standard solution.

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

## Voltammetric tab with Calibration technique "MLAT"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window. With "MLAT Standard addition for brighteners" following parameters have to be defined:

**Initial mixing time (s) [ 0...80600 s ; 10 s ]** (see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep**
The sweep parameters depend on the mode (see *CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping section 3.2*)

## Substances tab with Calibration technique "MLAT"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "MLAT Standard addition for brighteners" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**

Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**

Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Additive solution**

Definition of addition solutions for standard addition.

**No. [ 0...8 ; 0 ]**

Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number. If a mixed standard solution is used, the number of this solution must be entered for each substance present in the mixed solution.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**

Value for concentration of addition solution.

**Unit [ fL/L...mL/L ; mL/L ]**

Unit for concentration of addition solution.

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**

Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Contamination potential [ -5...5 ; 1.125 V ]**

With CVS: If it is activated, the current is readout for the defined potential during the last sweep (in anodic direction) of the bath determination.

With CPVS: One of the defined stripping steps (Voltammetric tab with Calibration technique "MLAT") can be selected. If it is activated, the current is readout for the selected potential during the last sweep (in anodic direction) of the bath determination.

The Contamination potential correlates with the concentration of organic degradation products in the electroplating bath.

**Chloride potential [ -5...5 ; 1.475 V ]**

With CVS: If it is activated, the current is readout for the defined potential during the last sweep (in anodic direction) of the bath determination.
With CPVS: One of the defined stripping steps (Voltammetric tab with Calibration technique "MLAT") can be selected. If it is activated, the current is readout for the selected potential during the last sweep (in anodic direction) of the bath determination.
The Chloride potential correlates with the concentration of chloride in the electroplating bath.

**Regression technique [ Linear Regression ]**

The regression is calculated with a straight line.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**

Selection of peak evaluation quantity:

**Height**

Peak height from baseline to peak maximum.

**Area**

Peak area between peak curve and calculated baseline.

**Derivative**

Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**

Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**

Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**

Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**

Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

## DT Suppressors with calibration curve

"DT Suppressors with calibration curve" is a dilution titration **calibration** technique for CVS and CPVS. It is mainly used to analyze Suppressors in electroplating baths.
Choose the calibration curve in the field **Calibration curve** of the **Determination** tab (use "DT Record calibration curve" to record the corresponding calibration curve). The parameters of the **Voltammetric** tab are automatically set to the values used while recording the calibration curve.

**Note**: A determined calibration curve can only be adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

### Determination tab with Calibration technique "DT Suppressors with calibration curve"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "DT Suppressors with calibration curve" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample. The **Sample identifier** is used for the file name.

**Volume VMS (mL) [ > 0 mL ; 10 mL]**
The volume of the Virgin Make-up Solution (see VMS (Virgin Make-up Solution), *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ] [ read only ]**
Total volume of solution (equal to the volume of the VMS (Virgin Make-up Solution)) in the measuring vessel at the start of the determination. The sample concentrations **Conc**. calculated refers to this cell volume.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Addition mixing time [ 0...80600 s ; 10 s ]**

Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**Calibration curve [ path + file name ; ]**

Define the calibration curve file (the file in which the determination of the calibration was(will be) saved). The calibration curve can be recorded with the **Calibration** technique "DT Record calibration curve".

**Note**: To make sure that for Suppressor analysis with 838 Advanced Sample Processor and DT always the latest calibration file is taken for the calculation, the name of the calibration file defined for **Calibration curve**, must match with the parameter **Sample identifier** on the **Determination** tab with **Calibration** technique "DT Record calibration curve".

Example for **Calibration curve**:
C:\User XYZ\Data\Calibration Suppressor.dth

**Note**: To make sure that for Suppressor analysis with 838 Advanced Sample Processor and DT always the latest calibration file is taken for the calculation, the path of the calibration file defined for **Calibration curve**, must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

**Note**: A determined calibration curve is only adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

**No. of replications [ 1...10 ; 2 ]**

Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last ..**

**sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "DT Suppressors with calibration curve"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. With the **Calibration** technique "DT Suppressors with calibration curve" the Voltammetric parameters are not editable. They depend on the parameters defined for recording the calibration curve.

Following parameters have to be defined:

**Initial mixing time (s) [ read only ] [ 0...80600 s ; 10 s ]**(see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles [ read only ]** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ] [ read only ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ] [ read only ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ] [ read only ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep [ read only ]**
The sweep parameters depend on the mode (see CVS - Cyclic Voltammetric Stripping section 3.2,

and CPVS - Cyclic Pulse Voltammetric Stripping section 3.2)

### Substances tab with Calibration technique "DT Suppressors with calibration curve"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "DT Suppressors with calibration curve" following parameters have to be defined:

**Substance [ 24 characters ; ]**

Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**

Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**

Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**

Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Plating bath solution**

Definition of plating bath solutions for standard addition. The concentration of the plating bath is not known (this is the concentration to be determined).

**No. [ 0...8 ; 0 ]**

Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number. Normally, only one plating bath solution is needed (the one which is analyzed).

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**

Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of

a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Regression technique**

Selection of regression technique:

**Linear Regression**

The regression is calculated with a straight line.

**Nonlinear Regression**

The regression is calculated with a nonlinear curve.

**Linear Interpolation**

The regression is calculated with a linear interpolation through 2 points.

**Quadratic Regression**

The regression is calculated with a nonlinear curve.

**Peak evaluation [ Coulometric ] [ read only ]**

Selection of peak evaluation quantity:

**Coulometric**

Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**

Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**

Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**

Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

**Endpoint and evaluation criteria:**

**Addition ratio Q/Q(0) [ 0...1 ; 0.3]**

The „Addition ratio" defines the endpoint criterion. After reaching this point, the standard additions are stopped and the "Calibration factor" is calculated.

**Evaluation ratio Q/Q(0) [ read only ]5]**

The „Evaluation ratio" defines the point of evaluation for the calculation of the "Calibration factor" Z.

**Begin of evaluation Q/Q(0) [ 0...1 ; 1.0]**

Only the measuring points between the „Begin of evaluation" and the „Evaluation ratio" are used for the calculation of the regression (linear, nonlinear and quadratic).

## DT Record calibration curve

"DT Record calibration curve" is used to record calibration curves for the dilution titration calibration technique (with the CVS and CPVS mode). Dilution titration **Calibration** technique is mainly used to analyze Suppressors in electroplating baths. The calibration curves recorded with this **Calibration** technique are used to determine Suppressor concentrations with the **Calibration** technique "DT Suppressors with calibration curve".

**Achtung**: A determined calibration curve can only be adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

### Determination tab with Calibration technique "DT Record calibration curve"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "DT Record calibration curve" following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample.

**Note**: The **Sample identifier** is used for the file name. To make sure that for Suppressor analysis with 838 Advanced Sample Processor and DT always the latest calibration file is taken for the calculation, this **Sample identifier** must match with the name of the calibration file defined for the parameter **Calibration curve** on the **Determination** tab with calibration "DT Suppressors with calibration curve".

Example for **Sample identifier**:
Calibration Suppressor

**Note**: To make sure that for Suppressor analysis with 838 Advanced Sample Processor and DT always the latest calibration file is taken for the calculation, the path of the calibration file defined for the parameter **Calibration curve** on the **Substances** tab with **Calibration** technique "DT Suppressors with calibration curve", must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

**Note**: A determined calibration curve is only adopted automatically if the checkbox **Save cali-**

**bration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

**Volume VMS (mL) [ > 0 mL ; 10 mL]**
The volume of the Virgin Make-up Solution (see VMS (Virgin Make-up Solution), *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ] [ read only ]**
Total volume of solution (equal to the volume of the VMS (Virgin Make-up Solution)) in the measuring vessel at the start of the determination. The sample concentrations **Conc**. calculated refers to this cell volume.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Addition mixing time [ 0...80600 s ; 10 s ]**
Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of repli-**

**cations** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "DT Record calibration curve"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. With the **Calibration** technique "DT Record calibration curve" the Voltammetric parameters are not editable. They depend on the parameters defined for recording the calibration curve.

Following parameters have to be defined:

**Initial mixing time (s) [ read only ] [ 0...80600 s ; 10 s ]**(see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles [ read only ]** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ] [ read only ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ] [ read only ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ] [ read only ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep [ read only ]**
The sweep parameters depend on the mode (see CVS - Cyclic Voltammetric Stripping section 3.2,

and CPVS - Cyclic Pulse Voltammetric Stripping section 3.2)

### Substances tab with Calibration technique "DT Record calibration curve"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "DT Record calibration curve" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**
Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**
Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Suppressor standard solution**
Definition of addition solutions for standard addition.

**No. [ 0...8 ; 0 ]**
Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**
Value for concentration of addition solution.

**Unit [ fL/L...mL/L ; mL/L ]**
Unit for concentration of addition solution.

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**
Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In

this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Regression technique [ see below ; Linear Regression ]**
Selection of regression technique:

**Linear Regression**
The regression is calculated with a straight line.

**Nonlinear Regression**
The regression is calculated with a nonlinear curve.

**Linear Interpolation**
The regression is calculated with a linear interpolation through 2 points.

**Quadratic Regression**
The regression is calculated with a nonlinear curve.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**
Selection of peak evaluation quantity:

**Height**
Peak height from baseline to peak maximum.

**Area**
Peak area between peak curve and calculated baseline.

**Derivative**
Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**
Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

**Endpoint and evaluation criteria:**

**Addition ratio Q/Q(0) [ 0...1 ; 0.3]**
The „Addition ratio" defines the endpoint criterion. After reaching this point, the standard additi-

ons are stopped and the "Calibration factor" is calculated.

**Evaluation ratio Q/Q(0) [ 0...1 ; 0.5]**
The "Evaluation ratio" defines the point of evaluation for the calculation of the "Calibration factor" Z.

**Begin of evaluation Q/Q(0) [ 0...1 ; 1.0]**
Only the measuring points between the „Begin of evaluation" and the „Evaluation ratio" are used for the calculation of the regression (linear, nonlinear and quadratic).

## RC Sample with response curve

"RC Sample with response curve" is a "Response Curve Technique" which can be used with the CVS and CPVS mode). The Response Curve is a normalized calibration curve for electroplating bath additives with suppressing impact. The "Response Curve Technique" is used for the determination of Suppressor in electroplating baths if the "Dilution Titration Technique" can't be applied.

Choose the desired response curve in the field **Response curve** of the **Determination** (Use "RC Record response curve" to record the response curve).

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**Note**: A determined response curve file can only be adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

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### Determination tab with Calibration technique "RC Sample with response curve"

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With "RC Sample with response curve" following parameters have to be defined:

**Sample identifier [ 32 Zeichen ; "sample" ]**
Identification for sample. The **Sample identifier** is used for the file name.

**Volume production bath (mL) [> 0 mL ; 10 mL]**
The volume of sample bath solution added (see *Production bath solution*, *Kap. 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ] [ read only ]**
Zellvolumen; gesamtes Lösungsvolumen (ist gleich gross wie das Volumen der VMS (Virgin Make-up Solution)) im Messgefäss beim Start der Bestimmung. Die berechneten Probekonzentrationen **Conc.** beziehen sich auf dieses Zellvolumen.

**Add production bath to electrolyte [ on, off ; off ]**

If is activated, the Production bath solution is added to the Electrolyte solution. If it is **not** activated, the Electrolyte solution is siphoned off before the Production bath solution is placed into the the measuring vessel.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)

Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**

Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**

Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Additional conditioning after sample transfer**

If this option is activated, an additional electrode conditioning is started after sample addition. This option can only be activated, if **Initial electrode conditioning** is activated.

**Response curve [ path + file name ; ]**

Choose the file which contains the desired response curve (the response curve can be recorded with the **Calibration** technique "RC Record response curve").

**Achtung:** To make sure that for "Suppressor analysis with 838 Advanced Sample Processor and RC" always the latest response curve file is taken for the calculation, the name of the file chosen for **Response curve**, must match with the parameter **Sample identifier** on the Determination tab with **Calibration** technique "RC Record response curve".

Example for **Response curve**:
C:\User XYZ\Data\Response curve.dth

**Achtung**: To make sure that for "Suppressor analysis with 838 Advanced Sample Processor and RC" always the latest response curve file is taken for the calculation, the path of the file chosen for **Response curve**, must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

**Achtung:** A determined response curve file is only adopted automatically if the checkbox S**ave calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

**No. of replications [ 1...10 ; 2 ]**
Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "RC Sample with response curve"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. With the **Calibration** technique "RC Sample with response curve" the Voltammetric parameters are not editable. They depend on the parameters defined for recording the calibration curve.

Following parameters have to be defined:

**Initial mixing time (s) [ read only ] [ 0...80600 s ; 10 s ]**(see *Initial mixing time with CVS and CPVS*, *section 6.3*)
Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles [ read only ]** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ] [ read only ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ] [ read only ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ] [ read only ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep [ read only ]**
The sweep parameters depend on the mode (see CVS - Cyclic Voltammetric Stripping section 3.2, and CPVS - Cyclic Pulse Voltammetric Stripping section 3.2)

## Substances tab with Calibration technique "RC Sample with response curve"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "RC Sample with response curve" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**
Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**
Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Regression technique [ read only ]**
The regression technique is displayed.

**Peak evaluation [ Coulometric ] [ read only ]**
Selection of peak evaluation quantity:

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**
Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

**Endpoint and evaluation criteria**

**Begin of evaluation Q/Q(0) [ read only ]**
Only the measuring points between the „Begin of evaluation“ and the „Evaluation ratio“ are used for the calculation of the regression (linear, nonlinear and quadratic).

## RC Record response curve

"RC Sample with response curve" is a "Response Curve Technique" which can be used with the CVS and CPVS mode). The Response Curve is a normalized calibration curve for electroplating bath additives with suppressing impact. The "Response Curve Technique" is used for the determination of Suppressor in electroplating baths if the "Dilution Titration Technique" can't be applied.

The response curves recorded with this **Calibration** technique are used together with **Calibration** technique "RC Sample with response curve" to determine Suppressor concentrations.

**Note**: A determined response curve file can only be adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

### Determination tab with Calibration technique “RC Record response curve”

The **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window contains general specifications for performing the determination. The parameters displayed depend on the selected **Calibration** technique and measurement **Technique**. With “RC Record response curve” following parameters have to be defined:

**Sample identifier [ 32 characters ; "sample" ]**
Identification for sample.

**Note**: The **Sample identifier** is used for the file name. To make sure that for "Suppressor analysis with 838 Advanced Sample Processor and RC" always the latest response curve file is taken for the calculation, this **Sample identifier** must match with the name of the calibration file defined for the parameter **Response curve** on the **Determination** tab with calibration "RC Record response curve".

Example for **Sample identifier**:
Response Suppressor

**Note**: To make sure that for "Suppressor analysis with 838 Advanced Sample Processor and RC" always the latest response curve file is taken for the calculation, the path of the calibration file defined for the parameter **Response curve** on the **Substances** tab with **Calibration** technique "RC Sample with response curve", must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

**Note**: A determined response curve file is only adopted automatically if the checkbox **Save calibration curves additionally without date and time** on the **General** tab of the **GENERAL SETTINGS** window is checked.

**Volume electrolyte (mL) [ > 0 mL ; 10 mL]**
The volume of the Electrolyte Solution (see *Electrolyte solution*, *section 6.4*).

**Cell volume (mL) [ > 0 mL ; 10 mL ] [ read only ]**
Total volume of solution (equal to the volume of the Electrolyte solution) in the measuring vessel at the start of the determination. The sample concentrations **Conc**. calculated refers to this cell volume.

**Initial electrode conditioning** (see *Initial electrode conditioning*, *section 6.3*)
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**

Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two "conditioning measurements".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Addition mixing time [ 0...80600 s ; 10 s ]**

Time of mixing after Additions (for the first measurement, the **Initial mixing time** is used).

**No. of additions [ 0...28 ; 2 ]**

Number of additions of additive standard solution.

**No. of replications [ 1...10 ; 2 ]**

Number of replications (= total number of measurements) for each variation (sample, standard addition, calibration level, conditioning measurement). For cyclic modes (CV, CVS, CPVS) the "total number of measurements" is the **No. of replications** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of measurements" must not exceed 10.

### Voltammetric tab with Calibration technique "RC Record response curve"

The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. With the **Calibration** technique "RC Record response curve" the Voltammetric parameters are not editable. They depend on the parameters defined for recording the calibration curve.

Following parameters have to be defined:

**Initial mixing time (s) [ read only ] [ 0...80600 s ; 10 s ]**(see *Initial mixing time with CVS and CPVS*, *section 6.3*)

Time of mixing before the first measurement of the sample solution.

**Conditioning Cycles [ read only ]** (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)

**Start potential (V) [ -5...+5 V ; 0.2 V ] [ read only ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ] [ read only ]**
Number of conditioning cycles.

**Pretreatment** (see *Pretreatment with CVS and CPVS*, *section 6.3*)

**Cleaning potential (V) [ -5...+5 V ; 1.625 V ] [ read only ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 0 s ] [ read only ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Equilibration potential (V) [ -5...+5 V ; 1.625 V ]** (This parameter is with CPVS part of the sweep)
Voltage applied to the electrodes during the **Equilibration time**.

**Equilibration time (s) [ 0...80600 s ; 5 s ]** (This parameter is with CPVS part of the sweep)
Waiting time before starting the sweep; with **Equilibration potential** applied to the electrodes. If the checkbox **Hydrodynamic (measurement)** is not checked, the stirrer is switched off during that time.

**Sweep [ read only ]**
The sweep parameters depend on the mode (see CVS - Cyclic Voltammetric Stripping section 3.2, and CPVS - Cyclic Pulse Voltammetric Stripping section 3.2)

## Substances tab with Calibration technique "RC Record response curve"

The **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for the definition and recognition of substances, for the definition of standard solutions, for peak evaluation and results calculation. The parameters displayed depend on the **Calibration** technique selected in the **WORKING METHOD SPECIFICATIONS** window. With "RC Record response curve" following parameters have to be defined:

**Substance [ 24 characters ; ]**
Substance name. For the assignment of a found peak to this substance the checkbox on the left side of the substance name must be checked.

With CVS: **Peak pos. +/- (V) [ -5...+5 V ; 0 V ]**
Position of the peak voltage for the substance and tolerance for this verification voltage.

With CPVS: **Step potential [ read only ; step 1: 0.2 V ]**

Displays the potential values, which are defined in the window **edit stripping steps**.

**Bsln.**

Parameters for baseline evaluation (details see *Baseline*, *section 5.2*). Click the ... button to open the **BASELINE** window for the selected substance.

**Suppressor standard solution**

Definition of addition solutions for standard addition.

**No. [ 0...8 ; 0 ]**

Number of addition solution used for manual or automatic addition. For automatic additions, this number is also the Dosing Device number.

**Achtung:** Dosino 1..3 refer to Dosinos connected to the 797 VA Computrace. Dosino 4...7 refer to Dosinos connected to the 846 Dosing Interface (to MSB 1...4).

**Conc. [ > 0 ; 0 ]**

Value for concentration of addition solution.

**Unit [ fL/L...mL/L ; mL/L ]**

Unit for concentration of addition solution.

**Volume (mL) [ > 0.01 mL / var ; 0 mL ]**

Addition volume. For entering variable addition volumes, click the ... button to open the **EDIT VARIED ADDITION** window for the selected substance (details see *Variable addition*, *section 5.2*). In this case, **var** is entered into the field instead of a fixed value. This field only appears once for solutions with the same number (mixed standards) and it is not displayed if **0** is entered as solution number.

**Regression technique [ see below ; Linear Regression ]**

Selection of regression technique:

**Linear Regression**

The regression is calculated with a straight line.

**Nonlinear Regression**

The regression is calculated with a nonlinear curve.

**Linear Interpolation**

The regression is calculated with a linear interpolation through 2 points.

**Quadratic Regression**

The regression is calculated with a nonlinear curve.

**Peak evaluation [ Height, Area, Derivative, Coulometric ; Coulometric ]**
Selection of peak evaluation quantity:

**Height**
Peak height from baseline to peak maximum.

**Area**
Peak area between peak curve and calculated baseline.

**Derivative**
Difference between positive an negative maximum of the first derivative of the voltammogram.

**Coulometric**
Charge transmitted during the peak.

**Smooth factor [ 1...6 ; 4 ]**
Smoothing power of the Savitzky/Golay smoothing of the baseline (1 = minimum smoothing, 6 = maximum smoothing) (see *Smoothing and differentiation*, *section 5.8*).

**Eliminate spikes**
Eliminates spikes to smooth the signal.

**Reverse sweep [ on, off ; off ]**
Enable peak evaluation of the reverse sweep of cyclic sweeps (not available with CPVS).

**Endpoint and evaluation criteria**

**Begin of evaluation Q/Q(0) [ 0...1 ; 1.0]**
Only the measuring points between the „Begin of evaluation" and the „Evaluation ratio" are used for the calculation of the regression (linear, nonlinear and quadratic).

## 6.3 Different settings and options with CVS and CPVS

- Deposition and Equilibration (see *Pretreatment section 3.4*, and *Pretreatment with CVS and CPVS section 6.3*)
- "Initial mixing time" instead of "Initial purge time" in the voltammetric settings (see *Purging section 3.4*, and *Initial mixing time with CVS and CPVS*, *section 6.3*)
- Different Sweep parameters on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window (see *CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping*, *section 3.2*)
- Different default values for conditioning cycles on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window (see *Conditioning cycles with CVS and CPVS*, *section 6.3*)
- Different **Calibration** techniques are used (see *Working method specifications window section 5.2*, and *Calibration techniques with CVS and CPVS section 6.2*)

- Determination parameters on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window are different (see *Determination* for other modes *section 5.2*, and check the parameters for the **Calibration** technique you are using *Calibration techniques with CVS and CPVS*, *section 6.2*)
- Different **Technique** options (**Batch with solution exchange** is not applicable with CVS and CPVS, see also *Working method specifications window section 5.2*)
- With CVS and CPVS, the RDE/SSE electrodes are used (see *CVS - Cyclic Voltammetric Stripping section 3.2*, and *CPVS - Cyclic Pulse Voltammetric Stripping*, *section 3.2*)
- Substances parameters on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window settings are different (see *Substances* for other modes *section 5.2*, and under the **Calibration** technique you are using *Calibration techniques with CVS and CPVS*, *section 6.2*)
- Some result details are different (see
- *Note: If both No. of* **conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Additional conditioning after sample transfer** (only active with MLAT and RC Sample with response curve , and if Initial electrode conditioning is activated)
If this option is activated, an additional electrode conditioning is started after sample addition. This option can only be activated, if Initial electrode conditioning is activated.

- Result details with CVS and CPVS *section 6.3*, and *Results section 5.5*)

## Pretreatment with CVS and CPVS

There is no deposition possible with CVS and CPVS. For the equilibration you can choose a specific **Equilibration potential**, which is positive enough to prevent metal deposition on the electrode (with the other modes, the **Start potential** is taken as **Equilibration potential**, See *Pretreatment* for other modes *section 3.4*).

## Initial mixing time with CVS and CPVS

With CVS and CPVS, there is no "Initial purge time" (see *Purging section 3.4*), since purging is not necessary (Reasons: solid state electrode is less sensitive against oxygen interferences; measuring at higher current; measuring in the positive voltage range). There is an "Initial mixing time" instead.

In the exploratory mode, you can find this field in the **EXPLORATORY SPECIFICATION** window. In the determination mode, you can

find it on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

## Conditioning cycles with CVS and CPVS

With CVS and CPVS the sweep is mainly in the positive voltage area. Therefore, the default values are positive (compare to *Conditioning of solid state electrodes*, *section 3.4*)

**Start potential (V) [ -5...+5 V ; 0.2V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; 1.575 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

## Initial electrode conditioning

Working with a RDE/SSE electrode, additional conditioning is needed (see *Conditioning of solid state electrodes*, *section 3.4*). With CVS and CPVS initial "conditioning measurements" which include **Conditioning cycles**, **Pretreatment** and **Sweep** should be done. It should be conditioned until the determination value is stable.

**Initial electrode conditioning**
Check the checkbox to use conditioning.

**No. of conditioning measurements [ 1...100 ; 1 ]**
Number of replications of conditioning measurements. The "total number of conditioning measurements" is the **No. of conditioning measurements** multiplied with the number of **Save last .. sweeps** (**Voltammetric** tab). "Total number of conditioning measurements" must not exceed 100.

or **Auto Std.dev (%)[ >0.1 ; 1 ]**
Define until which „Std.dev." the conditioning is continued. The „Std.dev." is calculated from all saved sweeps of the last two replications of the "conditioning measurement".

**Note**: If you set a small value (e.g. < 1%), it can take a long time until reaching the target.

**Note:** If both **No. of conditioning measurements** [ 1...100 ; 1 ] and **Auto Std.dev** (%) [ >0.1 ; 1 ] are activated, the conditioning is finished as soon as the first of the two criterias is reached.

**Additional conditioning after sample transfer** (only active with MLAT and RC Sample with response curve , and if Initial electrode conditioning is activated)
If this option is activated, an additional electrode conditioning is started after sample addition. This option can only be activated, if Initial electrode conditioning is activated.

## Result details with CVS and CPVS

There is some additional information displayed in the **RESULTS** window with CVS and CPVS (compare to *Results* with other modes *section 5.5*):

**Peak evaluation** (see also *Peak evaluation* with other modes, *section 5.5*)

`Q.Mean`
Mean value of the evaluation charge for all replications of a variation.

`Q.delta`
Difference of two successive mean values of the evaluation charge.

`V (mL)`
Volume added.

`Q/Q(0)`
Normalized evaluation charge.

**Calibration data** (see also *Calibration data* with other modes, *section 5.5*)

`Calibr.`
**Calibration** techniques dt.rec.cc., dt.cc, mlat, lat, rec.rc, smp.rc (see *Calibration techniques with CVS and CPVS*, *section 6.2*)

**Sample data** (see also *Sample data* with other modes, *section 5.5*)

`Intercept value`
Measured value of the "Intercept solution" (see *Calibration techniques with CVS and CPVS*, *section 6.2*)

**Substance evaluation** (see also *Substance evaluation* with other modes, *section 5.5*)

`Volume`
With **Calibration** technique "DT Record calibration curve": Volume of added Suppressor standard solution at the "Evaluation ratio".
With **Calibration** technique "DT Suppressors with calibration curve": Volume of added Production bath solution at the "Evaluation ratio".

`V.dev`
: With **Calibration** technique "DT Record calibration curve": Deviation of the volume of added Suppressor standard solution at the "Evaluation ratio". With **Calibration** technique "DT Suppressors with calibration curve": Deviation of the volume of added Production bath solution at the "Evaluation ratio".

`Cal. factor (#L/L)`
: "Calibration factor" used for the determination of Suppressor in the plating bath (displayed with **Calibration** techniques "DT Record calibration curve" and "DT Suppressors with calibration curve").

**Final Results** (see also *Final results*, *section 5.5*)

`Calibration factor`
: "Calibration factor" used for the determination of Suppressor in the plating bath (displayed with **Calibration** techniques "DT Record calibration curve" and "DT Suppressors with calibration curve").

`Intercept value`
: "Intercept value" used for the determination of Brightener in the plating bath (displayed with **Calibration** technique "LAT Record intercept value").

`Contamination current`
: The Contamination potential correlates with the concentration of organic degradation products in the electroplating bath.

`Chloride current`
: The Chloride potential correlates with the concentration of chloride in the electroplating bath.

## 6.4 Some Definitions used with CVS and CPVS

Some definitions used for working with the **Calibration** techniques used with the modes CVS and CPVS:

- VMS (Virgin Make-up Solution)
- Intercept solution
- Intercept value
- Production bath solution
- Addition ratio
- Evaluation ratio
- Begin of evaluation
- Contamination potential

- Chloride potential
- Calibration factor
- Suppressor
- Brightener
- Electrolyte solution

### VMS (Virgin Make-up Solution)

The VMS (Virgin Make-up Solution) is an electroplating bath solution like the one, which is analyzed. But it contains no organic additives and it is made from reagent grade chemicals.

**Note**: The VMS solution should always be adjusted to the bath solution as exactly as possible.

It is used in the Electroplating Bath analysis with the modes CVS and CPVS and the **Calibration** techniques “Standard addition plating bath”, “DT Record calibration curve” and “DT Suppressors with calibration curve”.

**Note**: If you dilute Brightener- or Suppressor standard solution: Always take VMS solution, never water!

### Intercept solution

The “Intercept solution” is VMS(Virgin Make-up Solution) + Suppressor. It is used in the Electroplating Bath analysis with the modes CVS and CPVS and the **Calibration** techniques “MLAT Standard addition for brighteners” and “LAT Record intercept value”.

**Note**: The "Intercept solution" should always be adjusted to the bath solution as exactly as possible.

### Intercept value

The “Intercept value” is the charge generated by the “Intercept solution” during the stripping process in the Electroplating Bath analysis with the modes CVS and CPVS. It is used with the **Calibration** technique “LAT Standard addition for brighteners” and should be redetermined regularly. It can be recorded with the **Calibration** technique "LAT Record intercept value".

### Production bath solution

The "Production bath solution" (or "Plating bath solution") is the sample solution to be analyzed. It is used in the Electroplating Bath analysis with the modes CVS and CPVS.

### Addition ratio

The "Addition ratio" is a certain Q/Q(0) ratio which defines the number of additions with the two "dilution titration technique" **Calibration** techniques "DT Record calibration curve" and "DT Suppressors with calibration curve" (with the modes CVS and CPVS). It should normally be around 0.3 and can be defined on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

The "Addition ratio" defines the criteria for the endpoint. After reaching this point, the standard addition is stopped and the "Calibration factor" is calculated.

**Note**: The following condition must be fulfilled: „Begin of evaluation" > "Evaluation ratio" > „Addition ratio".

### Evaluation ratio

The "Evaluation ratio" is a certain Q/Q(0) ratio and defines the point of evaluation for the calculation of the "Calibration factor" Z. It is used with the two "dilution titration technique" **Calibration** techniques "DT Record calibration curve" and "DT Suppressors with calibration curve" (with the modes CVS and CPVS). It should normally be around 0.5 and can be defined on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

For the regression, all measurement points between 1 and the measurement point after the evaluation ratio are used.

**Note**: The following condition must be fulfilled: „Begin of evaluation" > "Evaluation ratio" > „Addition ratio".

### Begin of evaluation

Only the measuring points between the „Begin of evaluation" and the „Evaluation ratio" are used for the calculation of the regression (linear, nonlinear and quadratic). It is used with the **Calibration** techniques DT Record calibration curve, DT Suppressors with calibration curve , RC Sample with response curve and RC Record response curve (with the modi CVS and CPVS). It should normally be around 1.0 and can be defined on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

**Note**: The following condition must be fulfilled: „Begin of evaluation" > "Evaluation ratio" > „Addition ratio".

### Contamination potential

The Contamination potential correlates with the concentration of organic degradation products in the electroplating bath. It is used with the Calibration techniques LAT Standard addition for brighteners and MLAT Standard addition for brighteners (with the modi CVS and CPVS).

### Chloride potential

The Chloride potential correlates with the concentration of chloride in the electroplating bath. It is used with the Calibration techniques LAT Standard addition for brighteners and MLAT Standard addition for brighteners (with the modi CVS and CPVS).

### Calibration factor Z

The "Calibration factor" Z is determined with the **Calibration** technique "DT Record calibration curve".

It is used for the Suppressor determination with the **Calibration** technique "DT Suppressors with calibration curve".

It is calculated from the following equation:

$$Z = \frac{V_{Std} * c_{Std}}{V_{VMS} + V_{Std}}$$

$V_{Std}$
Is the volume of Suppressor standard solution at the "Evaluation ratio".

$c_{Std}$
Is the concentration of Suppressor standard solution.

$V_{VMS}$
Is the volume of VMS (Virgin Make-up Solution).

Z is equal to the Suppressor concentration in the measurement cell at the "Evaluation ratio".

### Suppressor

Any of various components of electroplating bath solutions that suppresses plating.

### Brightener

Any of various components of electroplating bath solutions that increases the deposition during plating.

## Electrolyte solution

The Electrolyte solution is a mixture of VMS and these additives, which are not to be determined (with "Response Curve Technique").

# 7 Manual control

## 7.1 Computrace control

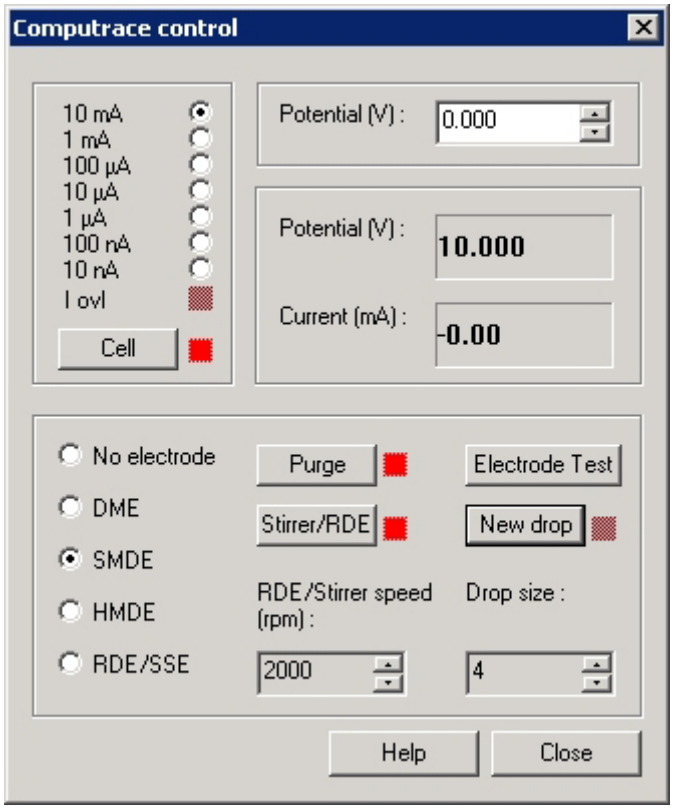
### Computrace control selection

**MAIN WINDOW / Utility / Computrace control**

Start manual control of the 797 VA Computrace stand.

### Computrace control window

The **COMPUTRACE CONTROL** window serves for manual control of the 797 VA Computrace stand.




**10 mA ... 10 nA**

Selection of current range for measurement in the manual control mode.

**I ovl** Indication of current overload by red light.

Cell — Switch on/off current measurement. If switched on, the set **Potential** is applied to the electrodes and the current is measured continuously. This mode is indicated by the red light beside the **<Cell>** button.

**Potential (V) [ -5...+5 V ; 0 V ]**
Voltage to be applied to the electrodes.

**Potential (V) [ read only ]**
Display of current voltage applied to the electrodes.

**Current (xA) [ read only ]**
Display of measured current.

**No electrode** — No electrode connected to the 797 VA Computrace stand. This setting is useful for changing the electrode at the stand.

**DME** — Selection of the Dropping Mercury Electrode (DME).

**SMDE** — Selection of the Static Mercury Drop Electrode (SMDE).

**HMDE** — Selection of the Hanging Mercury Drop Electrode (HMDE).

**RDE/SSE** Selection of the Rotating Disk electrode (RDE).

Purge — Switch on/off inert gas purging.

Electrode Test — Tests the electrodes (see *Check the MME*, *section 8.10*).

**Note**: Occasional electrode tests should be done in this sector and not with the "GLP Wizard" (not to overwrite GLP data).

Stirrer/RDE — Switch on/off stirrer/RDE with the set **RDE/Stirrer speed**.

**RDE/Stirrer speed (rpm) [ 0...3000 rpm ; 2000 rpm ]**
Revolutions per minute of the stirrer/RDE.

New drop
- DME: Switch on free dropping at the MME.
- SMDE: Dropping in intervals of ca. 1 s at the MME.
- HMDE: Formation of a new single mercury drop at the MME .

**Drop size [ 1...9 ; 4 ]**
Size of the mercury drop (surface 0.15 $mm^2$ ... 0.60 $mm^2$).

# 7.2 Dosing Device control

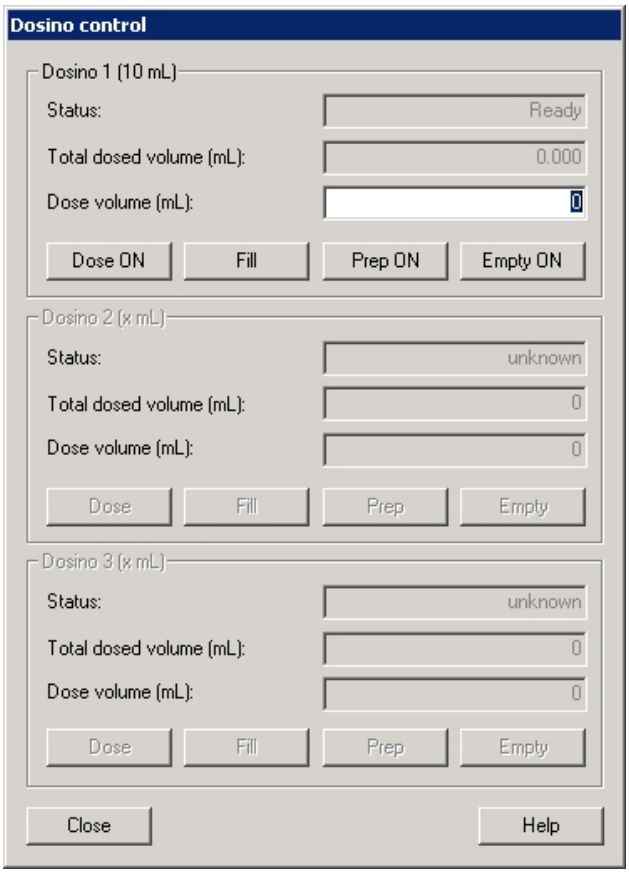
## Dosing Device control selection

**MAIN WINDOW / Utility / Dosino control**

Start manual control of the Dosing Devices (possible: 700/800 Dosino , 685/805 Dosimat) connected to the 797 VA Computrace stand or the 846 Dosing Interface.

## Dosino control window

The **DOSINO CONTROL** window serves for manual control of the Dosing Devices connected to the 797 VA Computrace stand (under **Dosing Processor**) or the 846 Dosing Interface (under **Dosing Interface**).




**Dosino 1..7 (x mL)**

3 Dosing Devices can be connected to the 797 VA Computrace stand, 4 more to a 846 Dosing Interface. Each can be controlled individually.

**Status [ read only ]**

Display of the current Dosing Device status.

**Total dosed volume (mL) [ > 0.01 mL ; 0 mL ]**

Display of current volume dispensed since last filling (first value) and accumulated volume if the display is not reset after filling (value in brackets).

**Dosed volume (mL)**
Dose the set volume.

Dose on
Switch on dosing by Dosing Device. The solution is dispensed until the <**Dose off**> button is pressed or the **Dose volume (mL)** is reached.

Fill
The burette cylinder of the Dosing Device is filled.

Prep ON
Fills burette cylinder and tubes. Used to remove air bubbles, solution exchange and cleaning.

Empty ON
Used to empty the Dosino (not feasible with Dosimats).

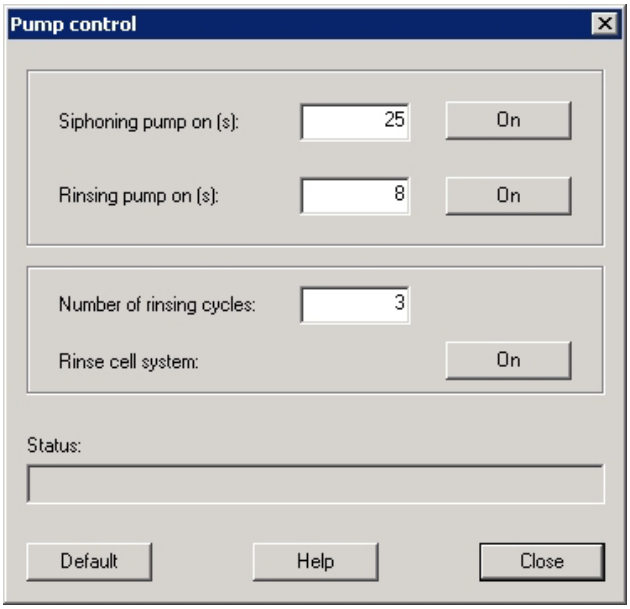
## 7.3 Pump control

### Pump control selection

**MAIN WINDOW / Utility / Pump deposition**
Start manual control of the 772 Pumps Units (or 823 Membrane Pump Units) connected to the 797 VA Computrace stand.

### Pump control window

The **PUMP CONTROL** window serves for manual control of the Pumps connected to the 797 VA Computrace stand.




**Siphoning pump on (s)**
Siphon for so many seconds. Start with clicking On, stop by clicking Off.

**Rinsing pump on (s)**

Rinse for so many seconds. Start with clicking On, stop by clicking Off.

**Number of rinsing cycles**

Number of rinsing/siphoning cycles (after activating **Rinse cell system**). A cycle is siphoning and rinsing once. Length of siphoning and rinsing are defined in **Siphoning pump on (s)** and **Rinsing pump on (s)**.

**Rinse cell system**

Siphon and rinse the cell system. Define settings in **Number of rinsing cycles**, **Siphoning pump on (s)** and **Rinsing pump on (s)**. Start with clicking On, stop with clicking Off.

**Status**

Displays current status of the pumps.

Default

Rinsing/Siphoning - settings of the **GENERAL SETTINGS/Automation** tab (see *Automation*, *section 2.7*) are adopted to the **PUMP CONTROL** window.

# 7.4 Film deposition

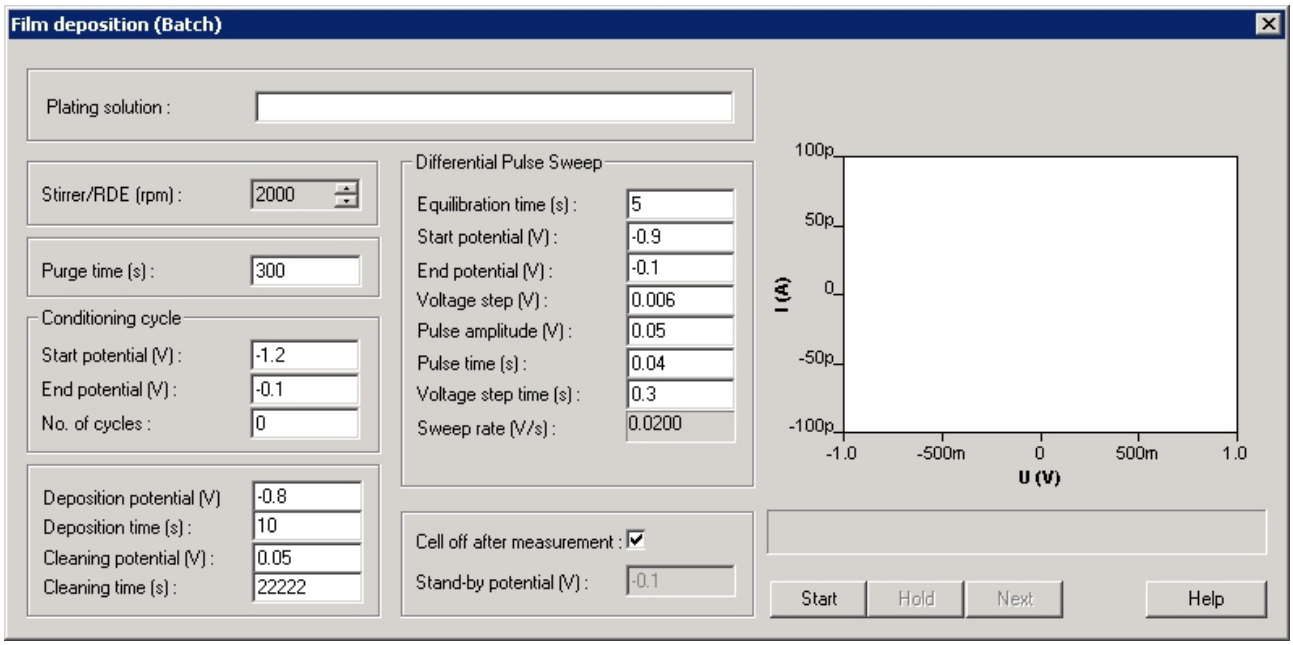
## Film deposition selection

**MAIN WINDOW / Utility / Film deposition**

Start Hg deposition for solid state electrodes in the 797 VA Computrace stand.

## Film deposition window

The **FILM DEPOSITION** window serves for deposition of a mercury or metal film on solid state electrodes at the 797 VA Computrace stand.




**Plating solution [ 48 characters ; ]**

Name of electrolyte solution used for film deposition.

**Stirrer/RDE (rpm) [ 0...3000 rpm ; 2000 rpm ]**

Revolutions per minute of the rotating disk electrode. The stirring of the RDE remains active during all preparation procedure steps until the start of the cleaning sweep.

**Purge time (s) [ 0...80600 s ; 300 s ]**

Time of inert gas purging before the first measurement of the sample solution.

**Conditioning cycles**

Before deposition, the solid state electrode can be electrochemically regenerated by a freely selectable number of conditioning cycles. For every cycle, the voltage is changed at a sweep rate of 1 V/s to the **End potential** and then decreased at the same rate back to the **Start potential**.

**Start potential (V) [ -5...+5 V ; -1.2 V ]**

Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**

Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**

Number of conditioning cycles.

**Deposition potential (V) [ -5...+5 V ; -0.8 V ]**

Voltage applied to the electrodes during the **Deposition time**.

**Deposition time (s) [ 0...80600 s ; 10 s ]**

Time during which the **Deposition potential** is applied to the electrodes.

**Cleaning potential (V) [ -5...+5 V ; -0.05 V ]**

Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 10 s ]**

Time during which the **Cleaning potential** is applied to the electrodes.

**Sweep**
Parameters of DP sweep used at the end of the film deposition for checking the electrode (see *VA measurement modes*, *section 3.2*).

**Cell off after measurement [ on, off ; on ]**
Enable/disable the switching off of the voltage applied to the electrodes after measurement.

**Stand-by potential (V) [ -5...+5 V ; -0.1 V ]**
Voltage to be applied to the electrodes after measurement if the **Cell off after measurement** box is set to **off**.

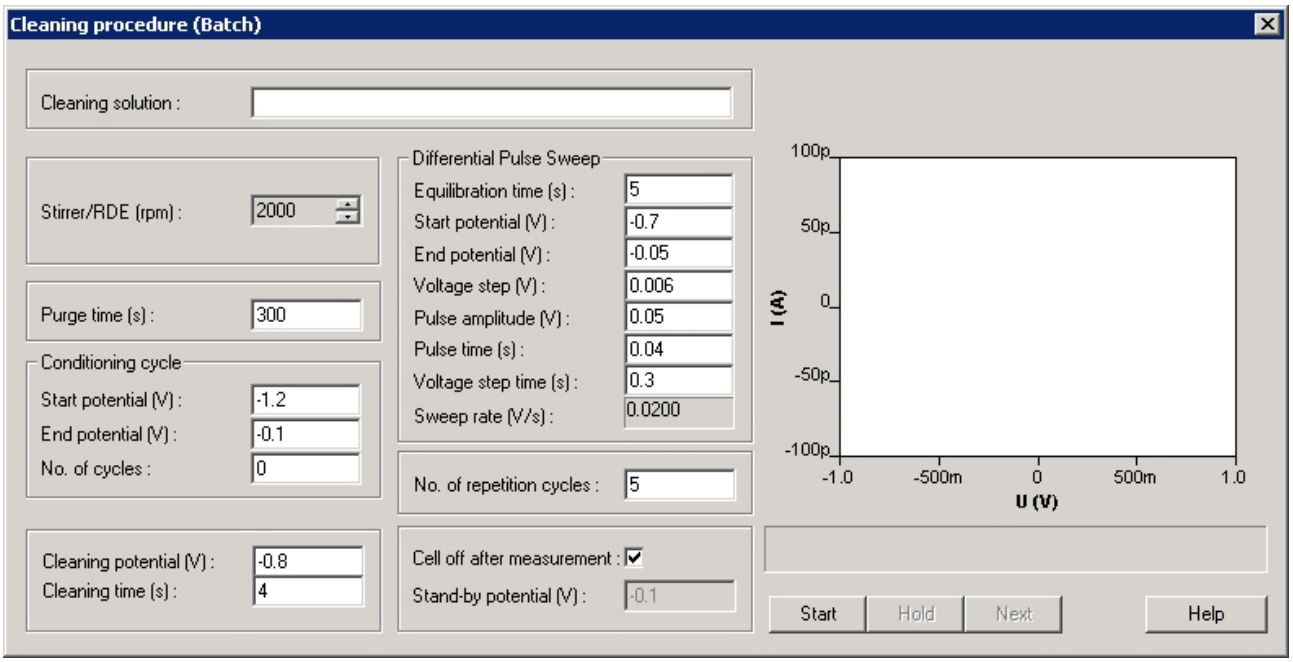
# 7.5 Cleaning procedure

## Cleaning procedure selection

**MAIN WINDOW / Utility / Cleaning procedure**
Start cleaning procedure for solid state electrodes at the 797 VA Computrace stand.

## Cleaning procedure window

The **CLEANING PROCEDURE** window serves for electrochemical cleaning of solid state electrodes at the 797 VA Computrace stand.




**Cleaning solution [ 48 characters ; ]**
Name of cleaning solution used for electrochemical cleaning of solid state electrodes.

**Stirrer/RDE (rpm) [ 0...3000 rpm ; 2000 rpm ]**
Revolutions per minute of the rotating disk electrode. The stirring of the RDE remains active during all preparation procedure steps until the start of the cleaning sweep.

**Purge time (s) [ 0...80600 s ; 300 s ]**
Time of inert gas purging before the first measurement of the sample solution.

**Conditioning cycles**
Electrochemical regeneration of the solid state electrode by a freely selectable number of conditioning cycles. For every cycle, the voltage is changed at a sweep rate of 1 V/s to the **End potential** and then decreased at the same rate back to the **Start potential**.

**Start potential (V) [ -5...+5 V ; -1.2 V ]**
Start voltage for the cyclic conditioning sweep.

**End potential (V) [ -5...+5 V ; -0.1 V ]**
Final voltage for the cyclic conditioning sweep.

**No. of cycles [ 0...X ; 0 ]**
Number of conditioning cycles.

**Cleaning potential (V) [ -5...+5 V ; -0.8 V ]**
Voltage applied to the electrodes during the **Cleaning time**.

**Cleaning time (s) [ 0...80600 s ; 10 s ]**
Time during which the **Cleaning potential** is applied to the electrodes.

**Sweep**
Parameters of DP sweep used at the end of the cleaning cycles for checking the electrode (see *VA measurement modes*, *section 3.2*).

**No. of repetition cycles [ 0...X ; 5 ]**
Number of repetition cycles for applying the conditioning cycles and cleaning potential steps.

**Cell off after measurement [ on, off ; on ]**
Enable/disable the switching off of the voltage applied to the electrodes after measurement.

**Stand-by potential (V) [ -5...+5 V ; -0.1 V ]**
Voltage to be applied to the electrodes after measurement if the **Cell off after measurement** box is set to **off**.

# 8 How to ...?

## 8.1 Installation and program start

### Install Dosing Devices for automatic addition

1. Connect Dosing Devices (possible: 700/800 Dosino , 685/805 Dosimat) to the 797 VA Computrace stand or the 846 Dosing Interface (see *Installation of Dosing Devices*, *section 1.3*).
2. Make hardware settings for Dosing Devices.
3. Select **Automatic** for **Addition** in the **WORKING METHOD SPECIFICATIONS** window.
4. Define the addition or predose solution in the **DOSINOS** window (see *Dosing Devices*, *section 5.2*).
5. The number defined in the **No.** field of the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window should correspond with the number of the Dosing Device used for the addition of this substance.

### Switch on the instruments and start program

1. Switch on PC.
2. Connect Dosing Devices ( see *Installation of Dosing Devices*, *section 1.3*), Sample Changer (see *Installation of 863 Compact VA Autosampler section 1.3*, or *Installation of 838 Advanced Sample Processor section 1.3*) and the 843 Pump Station to the 797 VA Computrace stand.
3. Connect the 797 VA Computrace stand to the PC (via USB).
4. Switch on 797 VA Computrace stand, Sample Changer and 731 Relay Box.
5. Start 797 VA Computrace Software 1.3.x (see *Starting the VA Computrace program*, *section 2.2*).
6. Enter **Name** and **Password** in the **VA COMPUTRACE LOGIN** window (see *Login*, *section 2.6*).
7. Select exploratory or determination mode (see *Mode menu*, section 2.4).
8. Open the desired Exploratory mode windows (Exploratory specifications, Exploratory curves) or Determination mode windows (Working method specifications, Monitor, Determination curves, Results, Sample table).

**Note**: If you switch off the instruments, switch off the 731 Relay Box first.

## 8.2 User rights

### Define a new user

1. Open the **USER RIGHTS** window by clicking on **MAIN WINDOW / User / User rights**.
2. Click the 

button to open the **ADD NEW USER** window.
3. Enter the **Name** and **Password** of the new user.
4. Close the **ADD NEW USER** window by clicking **<OK>**.
5. Select the new user in the list of all users and set his user rights (see *User rights*, *section 2.6*).
6. Close the **USER RIGHTS** window by clicking **<OK>**.

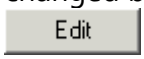
### Change user rights

1. Open the **USER RIGHTS** window by clicking on **MAIN WINDOW / User / User rights**.
2. In the **User rights** tab, select the desired user in the list of all users and change his user rights (see *User rights*, *section 2.6*).
3. In the **User directories** tab you can define where data and methods are saved for each specific user.
4. Close the **USER RIGHTS** window by clicking **<OK>**.

## 8.3 Signals in exploratory mode

### Load a signal curve

1. Click on  or **MAIN WINDOW / Mode / Exploratory**.
2. Click on  or **EXPLORATORY SPECIFICATION / File / Load signal**.
3. Select one or several (Ctrl + Click) signal files ***.sig** in the **OPEN** window and click **<OK>**.

**Note**: As soon as a signal curve is measured or loaded, the voltammetric parameter get read only. Should the parameters be changed before measuring a new signal curve, the button 

needs to be clicked.

### Save a signal curve

1. Select the desired signal curve in the list of the **EXPLORATORY SPECIFICATIONS** window.
2. Click on  or **EXPLORATORY SPECIFICATION / File / Save signal**.
3. Select the desired directory and enter the signal file name ***.sig** in the **SAVE AS** window and click the **<Save>** button. Please note that a user specific data directory can be defined in the **User Directories** tab.

### Save signal curves automatically

1. Click on **MAIN WINDOW / Settings / General settings** and enable the **Auto save determination and signal** option in the **General** tab.
2. Click on **MAIN WINDOW / User / User rights** and choose the **Data folder** in the **User directories** tab (see *User rights*, *section 2.6*), where you want to store your signals. You can search your working space by clicking **Browse**.

### Record a signal curve

1. Click on  or **MAIN WINDOW / Mode / Exploratory**.
2. Select **Electrode** and **Drop size** (for SMDE and HMDE) in the **EXPLORATORY SPECIFICATION** window (see *Electrodes*, *section 3.1*).
3. Set **Stirrer** or **RDE** speed (see *Stirring*, *section 3.4*).
4. If necessary, click 

and limit the **Highest current range** or **Lowest current range** in the **POTENTIOSTAT** window (see *Potentiostat*, *section 3.3*).
5. Select the desired VA measurement mode in the **Mode** field (see *VA measurement modes*, *section 3.2*).
6. Set the **Initial purge time** (see *Purging*, *section 3.4*).
7. Set pretreatment parameters for electrodes (see *Pretreatment*, *section 3.4*).
8. Set **Sweep** parameters of the selected VA measurement mode (see *VA measurement modes*, *section 3.2*).
9. If desired, set **Stand-by potential** to be applied after measurement (see *Stand-by potential*, *section 3.4*).
10. If the recorded signal file should be automatically saved at the end of the measurement, click on **MAIN WINDOW / Settings / General settings** and enable the **Auto save determination and signal** option in the **General** tab.

11. Start the measurement by clicking the  icon or the Start button (see *Performing exploratory measurements*, *section 4.2*).

---

**Note**: As soon as a signal curve is measured or loaded, the voltammetric parameter get read only. Should the parameters be changed before measuring a new signal curve, the button Edit needs to be clicked.

---

## Evaluate signal peaks automatically

1. Select the desired signal file in the **Signal** field of the **EXPLORATORY CURVES** window. The selected signal curve is shown with the **Selected signal properties**.
2. Click on **EXPLORATORY CURVES / Signal / Peak search**. The **PEAK SEARCH** window is opened.
3. Set the parameters **Reverse peak**, **Reverse sweep** (for CV and CVS only), **Minimum peak width**, **Smooth factor**, **Minimum peak height** and **Scope** for peak evaluation (see *Peak search*, *section 4.3*).
4. Click the Search button. The calculated baselines and peak maximum positions are displayed in the **EXPLORATORY CURVES** window. The evaluation results are displayed in the table of results in the **PEAK SEARCH** window.
5. If no peaks are found, try to modify the peak search parameters **Minimum peak width**, **Smooth factor**, and **Minimum peak height** for the automatic signal peak evaluation or switch to the manual signal peak evaluation.

## Evaluate signal peaks manually

1. Select the desired signal file in the **Signal** field of the **EXPLORATORY SPECIFICATION** window. The selected signal curve is shown with the **Selected signal properties**.
2. Click on **EXPLORATORY CURVES / Signal / Peak search**. The **PEAK SEARCH** window is opened.
3. Check the **Manual** option.
4. Set the parameters **Reverse peak**, **Reverse sweep** (for CV and CVS only), **Minimum peak width**, **Smooth factor**, and **Minimum peak height** for peak evaluation (see *Peak search*, *section 4.3*).
5. Set the start and end base points for baseline evaluation by clicking the  buttons of the **Begin** or **End** field.
6. Select **Type** and **Scope** of the baseline.

7. Click the Search button. The calculated baselines and peak maximum positions are displayed in the **EXPLORATORY CURVES** window. The evaluation results are displayed in the table of results in the **PEAK SEARCH** window.

### Evaluate signal waves

1. Select the desired signal file in the **Signal** field of the **EXPLORATORY SPECIFICATION** window. The selected signal curve is shown with the **Selected signal properties**.
2. Click on **EXPLORATORY CURVES / Signal / Wave evaluation**. The **WAVE EVALUATION** window is opened.
3. Set the parameters **Minimum width**, **Minimum peak height** and **Smooth factor** for wave evaluation (see *Wave evaluation*, *section 4.3*).
4. Click the Search button. The calculated tangents and positions of half-wave potentials are displayed in the **EXPLORATORY CURVES** window. The evaluation results are displayed in the table of results in the **WAVE EVALUATION** window.

### Print signal curves and/or voltammetric parameters

1. Click on  or **MAIN WINDOW / File / Print**. The **PRINT EXPLORATORY** window is opened.
2. Check the **Print curves** option if the content of the **EXPLORATORY CURVES** window should be printed.
3. Check the **Print voltammetric parameters** option if the parameters in the **EXPLORATORY SPECIFICATION** window should be printed.
4. Click the **<OK>** button.
5. Select the parameters and properties for printing in the **PRINTER SETUP** window and click the **<OK>** button.

## 8.4 Methods in determination mode

### Load a method

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / File / Load method**.
3. Select the desired method file ***.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.

## Copy parameters from determination methods

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / File / Load determination**.
3. Select the desired determination file ***.dth** in the **OPEN** window and click **<OK>**. The determination is loaded into the **DETERMINATION CURVES** window.
4. Click on **DETERMINATION CURVES / Edit / Copy parameters to working method**.

## Copy parameters from signal files

1. Click on  or **MAIN WINDOW / Mode / Exploratory**.
2. Click on  or **EXPLORATORY SPECIFICATION / File / Load signal**.
3. Select the desired signal file ***.sig** in the **OPEN** window and click **<OK>**.
4. Click on **EXPLORATORY SPECIFICATION / Transfer / Parameters / To working method**.

## Save the working method

1. If you want to save a modified working method under the same name, click on  or **MAIN WINDOW / File / Save method**. The old file will be overwritten.
2. If you want to save the working method under a new name, click on **MAIN WINDOW / File / Save method as**. Select the desired directory, enter the method file name ***.mth** in the **SAVE AS** window, and click the **<Save>** button.

## Edit the working method

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Click on  or **MAIN WINDOW / File / Load method**.
4. Select the desired method file ***.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.
5. Set the parameters in the **WORKING METHOD SPECIFICATIONS** window to the desired values (see *Working method specifications window*, *section 5.2*).

6. If Dosing Devices should be used for addition or predose, click Dosinos and set the parameters to the desired values (see *Dosing Devices*, *section 5.2*).
7. If necessary, click Potentiostat and limit the **Highest current range** or **Lowest current range** in the **POTENTIOSTAT** window (see *Potentiostat*, *section 3.3*).
8. Click Edit parameters and set the parameters on the tabs **Determination**, **Voltammetric**, **Substances**, **Calculations**, **Documentation** und **Export** (see *section 5.2*) in the **EDIT WORKING METHOD PARAMETERS** window.
9. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.

### Modify methods for automatic background compensation

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Click on  or **MAIN WINDOW / File / Load method**.
4. Select the desired method file ***.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.
5. Click the Edit parameters button in the **WORKING METHOD SPECIFICATIONS** window and select the **Determination** tab.
6. Enable the **Measure blank** option, enter the number of measurements **No. of blanks** and the **Blank purge time**.
7. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.

If you start a determination with this modified method, you are first asked to place the specified number of blank solutions into the measuring vessel. The resulting blank curve is then automatically subtracted from all subsequent measured curves.

## 8.5 Determinations with voltammetric trace analysis

### Load a determination

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / File / Load determination**.

3. Select the desired determination file ***.dth** in the **OPEN** window and click **<OK>**. The determination is loaded into the **DETERMINATION CURVES** window.
4. If the method parameters of the loaded determination should be used for a new measurement, copy the determination method parameters to the working method by clicking on **DETERMINATION CURVES / Edit / Copy parameters to working method**.

## Save a determination

1. If you want to save the loaded and modified determination under the same name, click on  or **MAIN WINDOW / File / Save determination**. The old file will be overwritten.
2. If you want to save the loaded determination under a new name, click on **MAIN WINDOW / File / Save determination as**. Select the desired directory, enter the determination file name ***.dth** in the **SAVE AS** window, and click the **<Save>** button.

## Automatically save determinations

1. Click on **MAIN WINDOW / Setting / General settings** and enable the **Auto save determination and signal** option in the **General** tab.
2. Click on **MAIN WINDOW / User / User rights** and choose the **Data folder** in the **User directories** tab (see *User rights*, *section 2.6*), where you want to store your determinations. You can search your working space by clicking **Browse**.

## Perform a determination

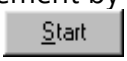
1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. If desired, modify the loaded method (see *How to Edit the working method*, section 8.4).
5. Place the analysis solution in the measuring vessel at the 797 VA Computrace stand.
6. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
7. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.

8. Follow the instructions in the appearing message windows.

### Perform a test determination with the Pb test method

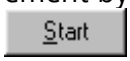
With the aid of this example method for the determination of lead in the ion standard solution supplied using the DME, you can easily check whether the 797 VA Computrace System is functioning properly.

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Click on  or **MAIN WINDOW / File / Load method**.
4. Select the method file **Test Pb in standard solution.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.
5. Add 20 mL ultrapure water to the empty measuring vessel at the 797 VA Computrace stand.
6. Add 0.5 mL potassium chloride *c*(KCl) = 3 mol/L (Metrohm No. 6.2308.020) to the measuring vessel.
7. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
8. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window. The **PLACE SAMPLE** window appears.
9. Use a pipette to add 100 µL Pb ion standard solution β(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
10. The sample solution is measured three times. Then the **MANUAL ADDITION** window appears.
11. Use a pipette to add 100 µL Pb ion standard solution β(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
12. The sample solution spiked with standard addition solution is measured three times. Then the **MANUAL ADDITION** window appears.
13. Use a pipette to add 100 µL Pb ion standard solution β(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
14. The sample solution spiked again with standard addition solution is measured three times. Then the **END OF DETERMINATION** window appears.

15. Click the **<OK>** button. The determination is saved automatically if specified on the **General** tab of the **GENERAL SETTINGS** window and the result report is printed if specified on the **Documentation** tab of the **EDIT WORKING METHOD PARAMETERS** window.

## Perform determinations using the 863 Compact VA Autosampler

1. Install the 863 Compact VA Autosampler (see *Installation of 863 Compact VA Autosampler*, *section 1.3*) and set **method 2**.
2. Click on **MAIN WINDOW / Settings / General settings** and select the **Hardware** tab.
3. Define the **Sample processor** field of the **Hardware** tab.
4. Modify the parameters for Automation in the **Automation** tab of the **GENERAL SETTINGS** window as desired.
5. If desired, test the automation parameters: Click on **MAIN WINDOW / Settings / General settings** and select the **Automation** tab. Fill two sample vessels with water and place them on the sample rack. Click on 

, check the automation parameters and modify them if needed.
6. Click on  or **MAIN WINDOW / Mode / Determination**.
7. Click on  or **MAIN WINDOW** / **Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
8. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, *section 8.4*).
9. If desired, modify and save the loaded method (see *How to Edit the working method*, *section 8.4*).
10. Click on  or **MAIN WINDOW / Window / Sample table** to open the **SAMPLE TABLE** window.
11. Load the desired sample table or edit the current sample table (see *Sample table*, *section 5.6*).
12. Transfer the desired sample amount into the sample vessels. Place the sample vessels at the odd positions on the sample rack of the 863 Compact VA Autosampler. For each sample vessel, place a vessel filled with rinsing solution at the following even position (volume rinsing solution = volume sample solution).
13. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
14. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.

15. Follow the instructions in the appearing message windows.

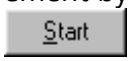
**Note**: If you want to measure all samples with the same working method, you can select **Repeat current method** for Working method source on the **Automation** tab of the **GENERAL SETTINGS** window. The **SAMPLE TABLE** window is not accessible with **Repeat current method**.

## Perform VA determinations using the 838 Advanced Sample Processor

1. Install the 838 Advanced Sample Processor (see *Installation of 838 Advanced Sample Processor section 1.3*) and set a suitable method (depending on the determination, see *section 8.5 "Perform VA determinations using the 838 Advanced Sample Processor"*, *section 8.6 "Brightener Analysis with 838 Advanced Sample Processor and "MLAT"*, *section 8.6 "Brightener Analysis with 838 Advanced Sample Processor and "LAT"*, *section 8.6* "Suppressor Analysis with 838 Advanced Sample Processor and DT", *section 8.6 "Suppressor Analysis with 838 Advanced Sample Processor and RC"*).
2. Click on **MAIN WINDOW / Settings / General settings** and select the **Hardware** tab.
3. Define the **Sample processor** field of the **Hardware** tab.
4. Modify the parameters for Automation in the **Automation** tab of the **GENERAL SETTINGS** window as desired.
5. If desired, test the automation parameters: Click on **MAIN WINDOW / Settings / General settings** and select the **Automation** tab. Fill two sample vessels with water and place them on the sample rack. Click on 

, check the automation parameters and modify them if needed.
6. Click on  or **MAIN WINDOW / Mode / Determination**.
7. Click on  or **MAIN WINDOW** / **Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
8. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
9. If desired, modify and save the loaded method (see *How to Edit the working method*, section 8.4).
10. Click on  or **MAIN WINDOW / Window / Sample table** to open the **SAMPLE TABLE** window.
11. Load the desired sample table or edit the current sample table (see *Sample table*, *section 5.6*).
12. Transfer the desired sample amount into the sample vessels. Place the sample vessels sequential on the sample rack of the

838 Advanced Sample Processor. You can use 50 mL sample vessels (on the two outer rings) or 11 mL sample vessels (on the two inner rings). Place the sample on the outer (e.g. position 1) of the two rings and the rinsing solution on the inner (e.g. position 29) of the two rings. Define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

13. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
14. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window.
15. Follow the instructions in the appearing message windows.

---

**Note**: If you want to measure all samples with the same working method, you can select **Repeat current** method for Working method source on the **Automation** tab of the **GENERAL SETTINGS** window. The **SAMPLE TABLE** window is not accessible with **Repeat current method**.

---

## 838 method for trace analysis

For automated trace analysis with the **838 Advanced Sample Processor** it is recommended to set the method **VA** at the sample changer.

The method **VA** has the following sequence:

### VA

```
parameters
   method                          VA
   number of samples             rack   >  Number of samples to be
                                            processed (entire sample
                                            rack)

>start sequence
   1  CTL:Rm:                     INIT   >  Initialize Remote lines
   2  Move    1    :            sample   >  First Sample on Pos. "SAM-
                                            PLE"
   3  CTL:Rm:           ************1   >  Remote start CT797
   4  CTL:Rm:           ************0

>sample sequence
   1  SCN:Rm:                  *****1**   >  Scan line for incoming signal
                                            from CT797
   2  MOVE    1    :            sample   >  Move needle to sample
   3  LIFT:   1    :          work mm    >  Place needle at working posi-
                                            tion
   4  PERISTALT:   300 s            10   >  Sample transfer
   5  CTL:Rm:           ************1   >  Set line: sample transfer
                                            ready
   6  CTL:Rm:           ************0
```

| | | | | | |
|---|---|---|---|---|---|
| 7 | MOVE | 1 : | +28 | > | Move needle to rinsing position |
| 8 | LIFT: | 1 | work mm | > | Place needle at working position |
| 9 | PERISTALT: | 5 s | 10 | > | Suck rinsing solution in the needle |
| 10 | SCN:Rm: | | *****1** | > | Scan line for incoming signal from CT797 |
| 11 | PERISTALT: | 300 s | 10 | > | Rinse needle |
| 12 | CTL:Rm: | | **********1 | > | Set line: needle cleaning ready |
| 13 | CTL:Rm: | | **********0 | | |

Before starting, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

## Recalculate an existing determination

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / File / Load determination**.
3. Select the desired determination file ***.dth** in the **OPEN** window and click **<OK>**. The determination is loaded into the **DETERMINATION CURVES** window.
4. Click on  or **MAIN WINDOW / Window / Results** to open the **RESULTS** window.
5. Click on  or **MAIN WINDOW / Window / Determination curves** to open the **DETERMINATION CURVES** window.
6. Arrange the subwindows in the **DETERMINATION CURVES** window so that the list of curves, the determination curves and the calibration curves are visible.
7. If desired, select one or several (Ctrl + Click) objects in the list of curves and click on  or **Show selected...** of the context sensitive menu to show only the selected determination curve(s).
8. If desired, zoom the interesting area in the determination curves subwindow.
9. Click on  or **DETERMINATION CURVES / Edit / Determination method parameters** to open the **EDIT DETERMINATION METHOD PARAMETERS** window.
10. Modify the parameters (e.g. **Sample amount**, **Cell volume**, **Peak position**, baseline parameters, standard solution concentrations, calculation parameters) to the desired values on the tabs **Specifications**, **Determination**, **Substances** and **Calculations** (see *section 5.2*).
11. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**. The determination is recalculated and the new results are displayed in the **RESULTS** window.
12. If desired, repeat steps 10 and 11 once or several times.

13. If you want to save the modified determination under the same name, click on  or **MAIN WINDOW / File / Save determination**. The old file will be overwritten.
14. If you want to save the modified determination under a new name, click on **MAIN WINDOW / File / Save determination as**. Select the desired directory, enter the determination file name ***.dth** in the **SAVE AS** window, and click the **<Save>** button.

### Print determination results and curves

1. Click on  or **MAIN WINDOW / File / Print**. The **PRINT OPTIONS** window is opened.
2. Select the elements, which should be printed (see *Printing in determination mode*, *section 5.7*).
3. Select the order of printout for each element checked.
4. Close the **PRINT OPTIONS** window by clicking the **<OK>** button.

## 8.6 Analyze Electroplating Bath Solutions

### Introduction

The 797 VA Computrace can perform electroplating bath analysis. Two modes are especially designed for Electroplating Bath VA: CVS (Cyclic Voltammetric Stripping) and CPVS (Cyclic Pulse Voltammetric Stripping).

With these two modes, 8 different **Calibration** techniques can be chosen:

For method optimization:

"**Standard addition plating bath**" (this **Calibration** technique is used to develop and optimize methods)

For Brightener analyzing:

"**MLAT Standard addition for brighteners**" (Modified Linear Approximation Technique)

"**LAT Standard addition for brighteners**" (Linear Approximation Technique)

"**LAT Record intercept value**" (is used to record the "Intercept value")

For Suppressor analyzing ("Dilution Titration Technique"):

"Dilution Titration Technique"

"**DT Record calibration curve**" (used to record the calibration curve)

"**DT Suppressors with calibration curve**" (used to determine the Sample)

"Response Curve Technique"

"**RC Record response curve**" (Used to record the response curve)

"**RC Sample with response curve**" (Used to determine the sample)

## Choose the mode in Electroplating Bath VA

To run Electroplating Bath VA, you can choose between **2** modes: **CVS** (Cyclic Voltammetric Stripping) and **CPVS** (Cyclic Pulse Voltammetric Stripping).

You can select them in the **Mode** field of the **Determination** tab of the **WORKING METHOD SPECIFICATION** window.

CVS is the standard mode for Electroplating Bath VA. In case your bath solution has a high iron content, and you want to do Brightener analysis, choose CPVS.

## Choose the Calibration technique in Electroplating Bath VA

Working with the CVS or CPVS, 8 different **Calibration** techniques are selectable in the **WORKING METHOD SPECIFICATION** window:

For method optimization:

"**Standard addition plating bath**"
This **Calibration** technique is used to develop and optimize methods. It gives information about the response of a single component of a plating bath.

For Brightener analysis:

**MLAT**
"MLAT Standard addition for brighteners"

This **Calibration** technique is used to analyze Brighteners. It is the standard technique to analyze Brighteners in electroplating baths (Exception: If the difference between Q("Intercept solution" + "Bath solution") and Q(only "Intercept solution") is too small to use "MLAT", try "LAT Standard addition for brighteners").

Typical standard addition scheme for MLAT:

1. Place "Intercept solution" into the sample vessel and press start. The "Intercept value" Q(intercept) is determined in the first measurement after the conditioning of the electrode.
2. Add "Bath solution" and measure the value Q(intercept + bath).

3. Add Brightener standard solution several times and measure Q(addition) for each addition. Usually, two or three standard additions are made for the determination of Brighteners.

### LAT

"LAT Standard addition for brighteners" (and "LAT Record intercept value" to record the "Intercept value").

The second **Calibration** technique (should only be applied if "MLAT" is inapplicable) is "LAT Standard addition for brighteners". It differs from "MLAT" in the fact that the "Intercept solution" with the "Intercept value" Q(intercept) is measured upfront, and then removed for the actual sample measurement.

1. Determination of the "Intercept value". It can be determined in two ways:
   A. Using the **Calibration** technique "LAT Record intercept value". This **Calibration** technique is only used to determine the "Intercept value":
      1. Place "Intercept solution" into the sample vessel.
      2. Measure solution and save the result in a file.
   B. Using the **Calibration** technique "LAT Standard addition for brighteners":
      1. Set **No. of additions** and **Intercept value (mC)** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window to 0. No file needs to be defined for Intercept determination.
      2. Place "Intercept solution" into the sample vessel and click start. After measurement, read "Q.Mean" out of the results sheet: That is the "Intercept value" Q(Intercept) for this solution.
2. The determination of the Bath solution is then done using the **Calibration** technique "LAT Standard addition for brighteners":
      1. Remove the "Intercept solution" from the measuring vessel.
      2. If you determined the "Intercept value" by method **A**:

         Enter path and file name of the (with "LAT Record intercept value") recorded determination into field **Intercept determination** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.

      If you determined the "Intercept value" by method **B**:
      Enter the determined "Intercept value" into field **Intercept value** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.

3. Define the **No. of additions** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.
4. Place the "Bath solution" into the sample vesseland click start. Q(Bath) is determined.
5. Add Brightener standard solution several times and measure Q(addition) for each addition. Normally, two or three standard additions should be done for the brightener determination.

**Note:** If you make several measurements of bath solutions with the same composition, you can do the actual determination of the "Bath solution" several times with the same "Intercept value". However, the "ntercept value" sould be redetermined in regular intervals.

For Suppressor analyses:

### Dilution Titration Technique

"DT Suppressors with calibration curve", and "DT Record calibration curve" to record the calibration curve.

The "Dilution Titration Technique" is used for the determination of Suppressors. It consists of two measurement parts:

A. “DT Record calibration curve”
This **Calibration** technique is used to record the calibration curve and determine the “Calibration factor” with addition of a standard solution containing a known Suppressor concentration.

Typical standard addition scheme for DT Record calibration curve:

1. Define "Addition ratio" and "Evaluation ratio" on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.
2. Place the VMS (Virgin Make-up Solution) into the sample vessel and click on start. Q(0) is determined.
3. Add Suppressor standard solution and measure Q(addition) for each addition, until Q/Q(0) < "Addition ratio". If the "Addition ratio" is reached with less than 5 or more than 20 additions, the concentration of the Suppressor standard solution or the addition volume should be adjusted.

B. "DT Suppressors with calibration curve"
This **Calibration** technique is used to determine the Suppressor concentration. The scheme is similar to "DT Record calibration curve", except that not standard solution, but Production bath solution is added to the VMS.

Typical standard addition scheme for "DT Suppressors with calibration curve":

1. Choose a previously recorded **Calibration curve** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window. Use the Browse... button to search for the Calibration curve file. “Addition ratio” and “Evaluation ratio” are set automatically to the values used for recording the calibration curve.
2. Place the VMS (Virgin Make-up Solution) into the sample vessel and click on start. Q(0) is determined.
3. Add “Production bath solution” and measure Q(addition) for each addition, until Q/Q(0) < “Addition ratio”.

## Response-Curve-Technik

"RC Sample with response curve", and "RC Record response curve" to record the response curve.
The “response curve technique” is used for the determination of suppressor. It should be applied, if the "dilution titration technique" is inapplicable. It consists of two measurement parts:

A. "RC Record response curve”
This **Calibration** technique is used to determine the Suppressor concentration. That is done by addition of a Suppressor standard solution containing a known Suppressor concentration to an Electrolyte solution.

Typical standard addition scheme for "RC Record response curve":

1. Place the Electrolyte sulution into the sample vessel and click on start. Q(0) is determined.
2. Add Suppressor standard solution and measure Q(addition) for each addition.

B. "RC Sample with response curve”
This **Calibration** technique wird zur Bestimmung der Suppressor-Konzentration verwendet.

1. Wählen Sie eine vorher aufgenommene "Response Choose a previously recorded **Response curve** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** Fensters. Use the Browse... button to search for the response curve file.
2. Place the Electrolyte sulution into the sample vessel and click on start. Q(0) is determined.
3. Remove the Electrolyte sulution.

4. Place the Production bath solution into the sample vessel and measure Q.

## Operate a sequence in Electroplating Bath VA

The sequence to measure with the electroplating modes CVS or CPVS includes the following steps:

1. **Initial mixing time**
2. **Initial electrode conditioning**
   a. **Conditioning cycles** (Number of "conditioning cycles" defined in **No. of cycles** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)
   b. **Pretreatment**
   c. **Sweep** (Number of sweeps defined in **No. of sweeps** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)

   **Note**: Define the number of these "Initial electrode conditioning measurements" on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window. You can either set a fixed number, or put a "Std.dev." as stabilizing border.

3. First Measurement:
   a. **Conditioning cycles** (Number of "conditioning cycles" defined in **No. of cycles** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)
   b. **Pretreatment**
   c. **Sweep** (Number of sweeps is defined in **No. of sweeps**, number of saved sweeps in **Save last .. sweeps** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)

   **Note**: Instead of repeating sweeps, you can also repeat the whole Measurement cycle. Define the number of replications in **No. of replications** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window. Metrohm recommends to set the **No. of replications** on 1, the **No. of sweeps** on 4 and **Save last .. sweeps** on 2.

4. First Addition:

   Add standard or bath solution (is depending on the **Calibration** technique). You can do it either manually or automatically using Dosing Devices. The **Volume** should be defined on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

5. **Addition mixing time**:

The "Addition mixing time" can be defined on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window.

6. Second Measurement:
   a. **Conditioning cycles** (Number of "conditioning cycles" defined in **No. of cycles** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)
   b. **Pretreatment**
   c. **Sweep** (Number of sweeps is defined in **No. of sweeps**, number of saved sweeps in **Save last .. sweeps** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window)

   **Note**: Instead of repeating sweeps, you can also repeat the whole Measurement cycle. Define the number of replications in **No. of replications** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window. Metrohm recommends to set the **No. of replications** on 1, the **No. of sweeps** on 4 and **Save last .. sweeps** on 2.

7. Second Addition
8. **Addition mixing time**

Continue with measurement, addition, mixing as long as necessary.

## Brightener Analysis with 838 Advanced Sample Processor and "MLAT"

Following installations and settings are recommended for the automated Brightener determination with the 838 Advanced Sample Processor and **Calibration** technique "MLAT":

### Instruments

Install the **838 Advanced Sample Processor**, three **800 Dosinos** and a **732 Relay Box** with two **823 Membrane Pump Units** (see *Hardware Manual 797* and *Instructions for Use 838*).

Dosinos:

| | | |
|---|---|---|
| Dosino 1: | 50 mL Exchange Unit | VMS solution |
| Dosino 2: | 2 mL Exchange Unit | Brightener standard solution |
| Dosino 3: | 2 mL Exchange Unit | Suppressor concentrate |

### Method at 838

Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

Set method **LAT** at the 838 Advanced Sample Processor.

## LAT

| | | | | | |
|---|---|---|---|---|---|
| parameters | | | | | |
| method | | | LAT | | |
| number of samples | | | rack | > | Number of samples to be processed (entire sample rack) |
| >start sequence | | | | | |
| 1 | CTL:Rm: | | INIT | > | Initialize Remote lines |
| 2 | Move | 1 : | sample | > | First Sample on Pos. "SAMPLE" |
| 3 | CTL:Rm: | | **********1 | > | Remote start CT797 |
| 4 | CTL:Rm: | | **********0 | | |
| >sample sequence | | | | | |
| 1 | SCN:Rm: | | *****1** | > | Scan line for incoming signal from CT797 |
| 2 | MOVE | 1 : | sample | > | Move needle to sample |
| 3 | LIFT: | 1 : | work mm | > | Place needle at working position |
| 4 | PERISTALT: | 300 s | 10 | > | Sample transfer |
| 5 | CTL:Rm: | | **********1 | > | Set line: sample transfer ready |
| 6 | CTL:Rm: | | **********0 | | |
| 7 | MOVE | 1 : | +28 | > | Move needle to rinsing position |
| 8 | LIFT: | 1 | work mm | > | Place needle at working position |
| 9 | PERISTALT: | 5 s | 10 | > | Suck rinsing solution in the needle |
| 10 | SCN:Rm: | | *****1** | > | Scan line for incoming signal from CT797 |
| 11 | PERISTALT: | 300 s | 10 | > | Rinse needle |
| 12 | CTL:Rm: | | **********1 | > | Set line: needle cleaning ready |
| 13 | CTL:Rm: | | **********0 | | |

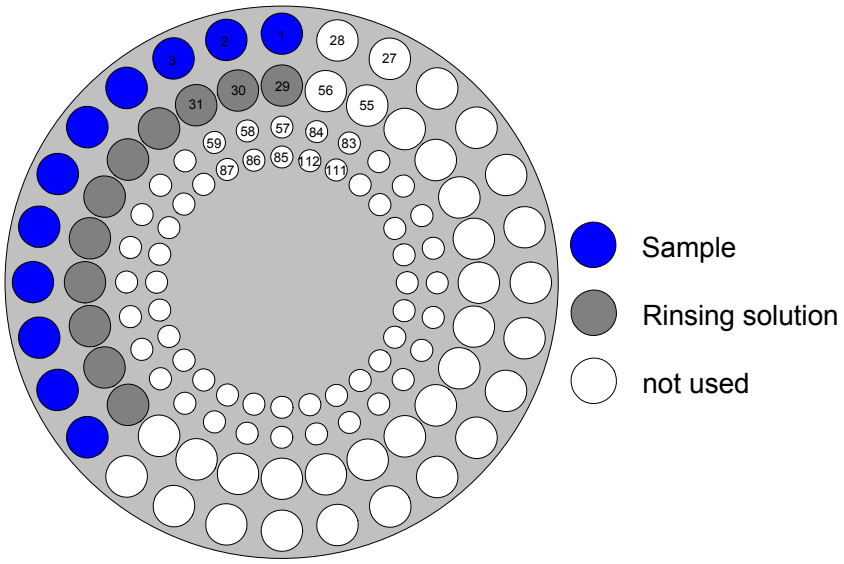
### Samples

With 50 mL sample vessels the two outer rings are used, with 11 mL sample vessels the two inner rings.

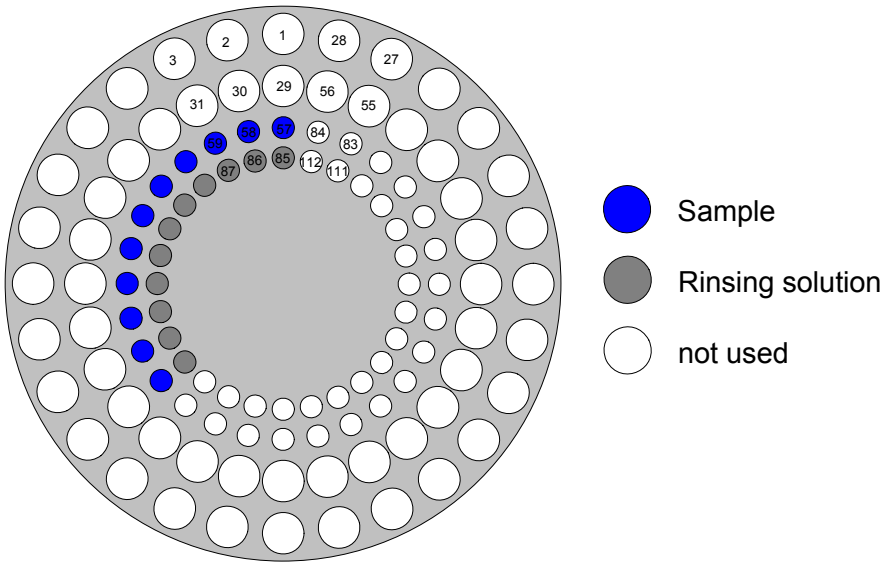
Arrangement: Place samples on the outer of the two rings, place rinsing solutions on the inner of the two rings.

Example for an arrangement with 11 samples:

⇒ With 50 mL sample vessels: first sample on position 1, first rinsing solution on position 29.



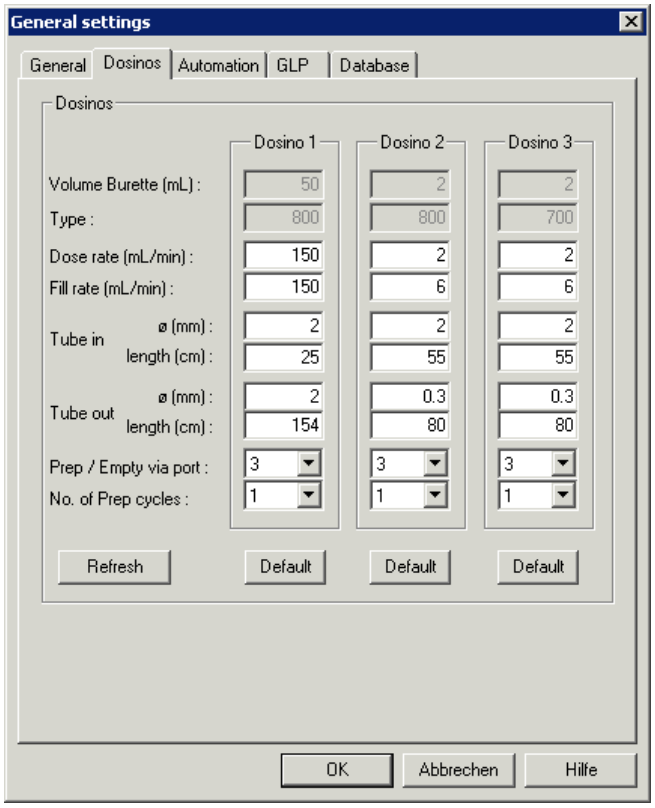

⇒ With 11 mL sample vessels: first sample on position 57, first rinsing solution on position 85.




**Note**: Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

## General Settings in the 797 Software

Settings on the **Dosinos** tab of the **GENERAL SETTINGS** window in the 797 Software:



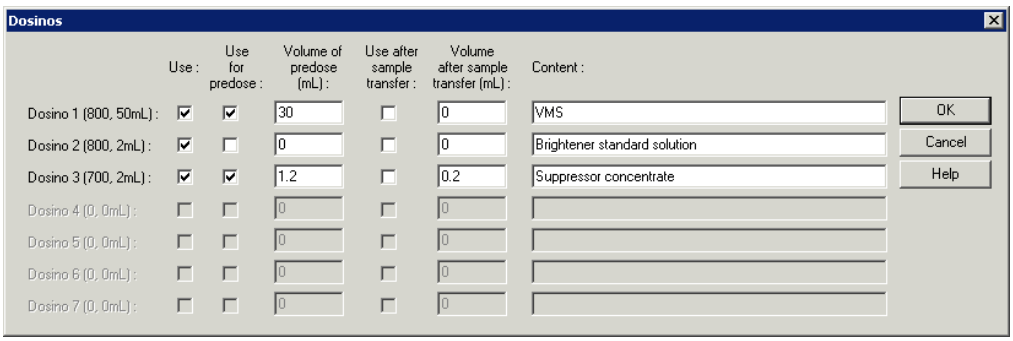

It is recommended to do for all used Dosinos one "Prep cycle".

On the **Automation** tab, select the 838 Advanced Sample Processor. The default settings can be adopted (click button <**Default**>).

## Method Parameters for the 797

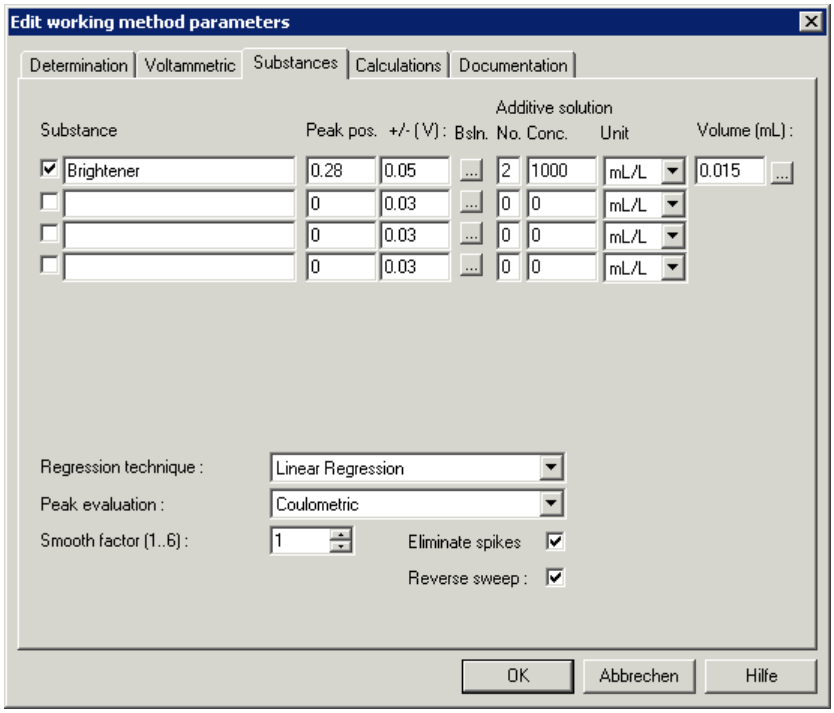
Set CVS or CPVS for **Mode**, and "MLAT" for **Calibration**.

Settings for the **DOSINOS** window:



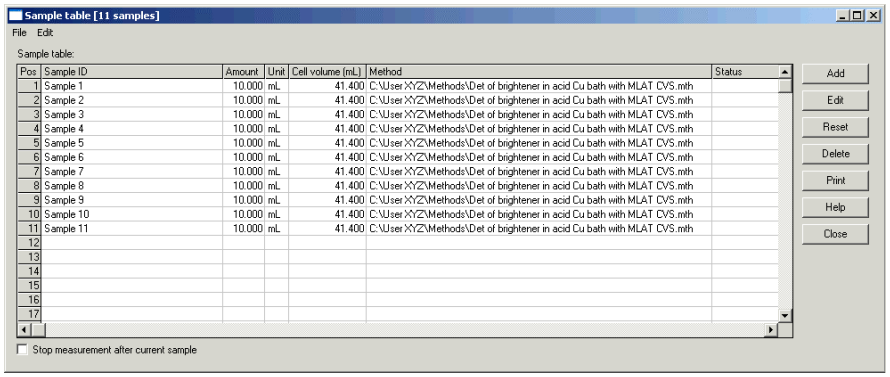

Checking **Use for predose** for Dosino 1, VMS and additional Suppressor concentrate are added to the measuring vessel before the sample transfer. Together, they form the "Intercept solution". To keep the Suppressor concentration stable, additional Suppressor concentrate is added after the sample transfer.

Dosino 2 is used to add Brightener standard solution. That should also be indicated on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (here with CVS):




## Sample table

List the samples in turn on the Sample table, and connect them to the according method (note the method parameters described above):




Start determination.

## Brightener Analysis with 838 Advanced Sample Processor and "LAT"

"LAT" should only be used, if the difference between Q(Intercept solution + Bath solution) and Q(only Intercept solution) is too small for "MLAT".

Following installations and settings are recommended for the automated Brightener determination with the 838 Advanced Sample Processor and **Calibration** technique "LAT":

### Instruments

Install the **838 Advanced Sample Processor**, a **800 Dosino**, a **732 Relay Box** with two **823 Membrane Pump Units** (see *Hardware Manual 797* and *838 Instructions for Use*).

Dosinos:

| | | |
|---|---|---|
| (Dosino 1: | not used) | |
| Dosino 2: | 2 mL Exchange Unit | Brightener standard solution |
| (Dosino 3: | not used) | |

### Method at 838

Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

Set method **LAT** at the 838 Advanced Sample Processor.

**LAT**

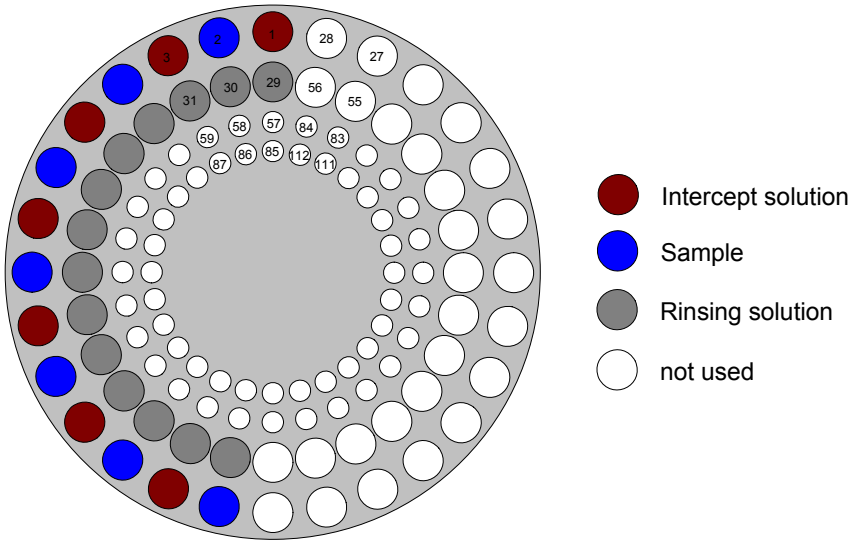
```
parameters
   method                          LAT
   number of samples              rack   >  Number of samples to be
                                             processed (entire sample
                                             rack)

>start sequence
   1  CTL:Rm:                      INIT   >  Initialize Remote lines
   2  Move    1    :             sample   >  First Sample on Pos. "SAM-
                                             PLE"
   3  CTL:Rm:             **********1   >  Remote start CT797
   4  CTL:Rm:             **********0

>sample sequence
   1  SCN:Rm:                   *****1**   >  Scan line for incoming signal
                                             from CT797
   2  MOVE    1    :             sample   >  Move needle to sample
   3  LIFT:   1    :           work mm   >  Place needle at working posi-
                                             tion
   4  PERISTALT:   300 s             10   >  Sample transfer
   5  CTL:Rm:             **********1   >  Set line: sample transfer
                                             ready
   6  CTL:Rm:             **********0
   7  MOVE    1    :               +28   >  Move needle to rinsing posi-
                                             tion
   8  LIFT:   1                 work mm   >  Place needle at working posi-
                                             tion
   9  PERISTALT:   5 s               10   >  Suck rinsing solution in the
                                             needle
  10 SCN:Rm:                   *****1**   >  Scan line for incoming signal
                                             from CT797
  11 PERISTALT:   300 s           10   >  Rinse needle
  12 CTL:Rm:             **********1   >  Set line: needle cleaning
                                             ready
  13 CTL:Rm:             **********0
```

### Samples

50 mL sample vessels can be placed on the two outer rings (11 mL sample vessels on the two inner rings).

Arrangement: Place on the outer of the two rings alternately "Intercept solution" and sample solution, on the inner of the two rings the rinsing solution.

Example for an arrangement with 7 samples:



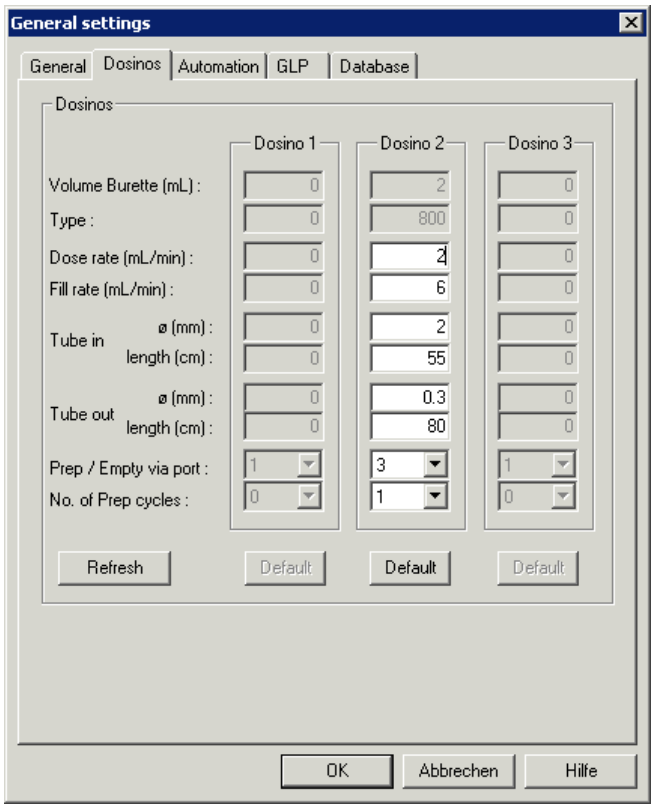

**Note**: Although the first sample is placed on position 2, position 1 remains the starting position in the start sequence of the method at the 838 (recording the "Intercept value").

**Note**: Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

### General Settings in the 797 Software

Activate both options on the **General** tab of the **GENERAL SETTINGS** window, so that a recorded "Intercept value" replaces the old one automatically.

Settings on the **Dosinos** tab of the **GENERAL SETTINGS** window in the 797 Software:




It is recommended to do one "Prep cycle".

On the **Automation** tab, select the 838 Advanced Sample Processor. The default settings can be adopted (click button <**Default**>).

## Method Parameters for the 797

It is recommended to record the "Intercept value" with the **Calibration** technique "LAT Record intercept value" (that way it is stored in a file and can be read out automatically during the sample determination).

Therefore two methods are needed, one for the determination of the "Intercept value", one for the determination of the sample. Set CVS or CPVS for **Mode** for both methods.

Determination of the "Intercept value":

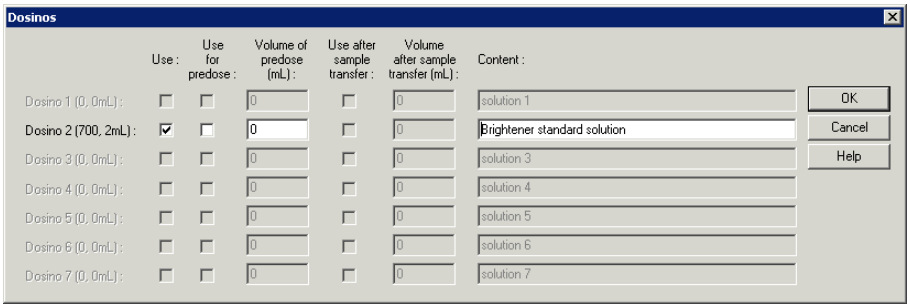
Choose "LAT Standard addition for brighteners" for **Calibration** technique.

In the Dosinos window, the same settings should be made as later for the sample determination with "LAT Standard addition for brighteners" (see below). But for the determination of the "Intercept value" no addition is done.

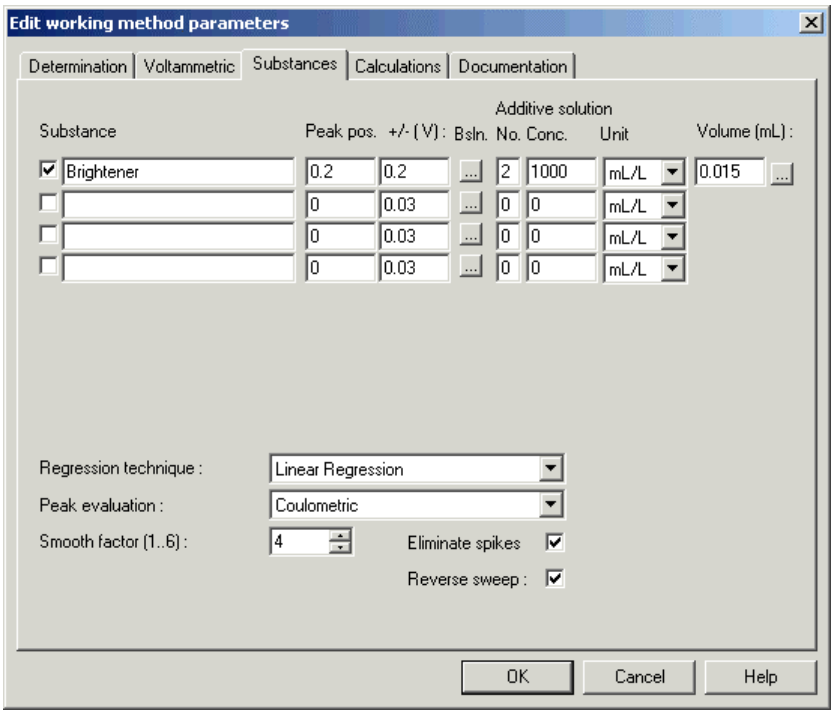
Determination of the sample:

Choose "LAT Standard addition for brighteners" for **Calibration** technique.

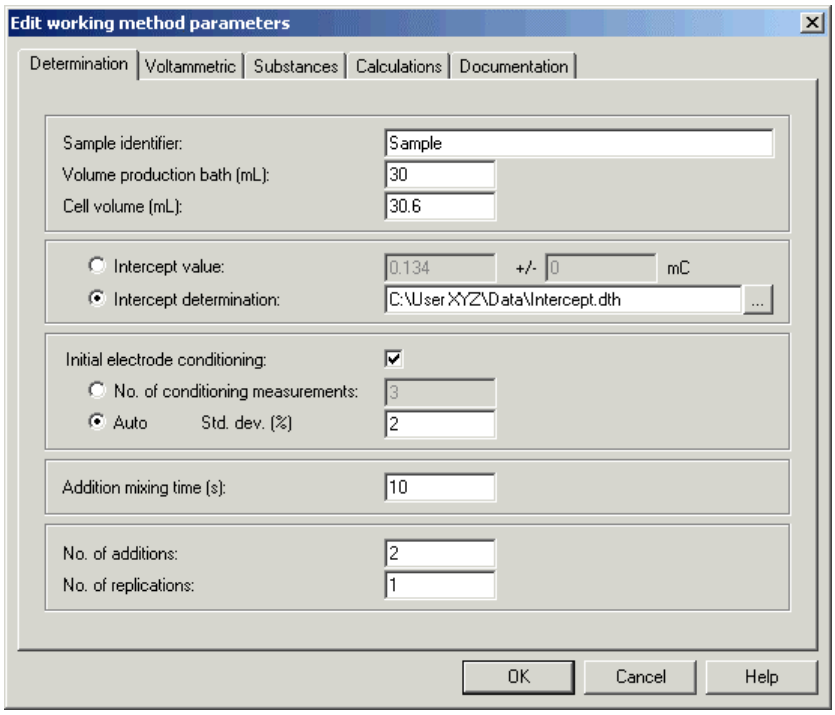
Settings in the **DOSINOS** window:




After the addition of the sample, Brightener standard solution is added via Dosino 2. That should be specified on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (here the window for CVS):




Enter the file name as which the determination of the "Intercept value" was saved into menu item **Intercept determination** on the **Determination** tab of the **EDIT WORKING METHOD PARAMETERS** window (here the window for CVS):

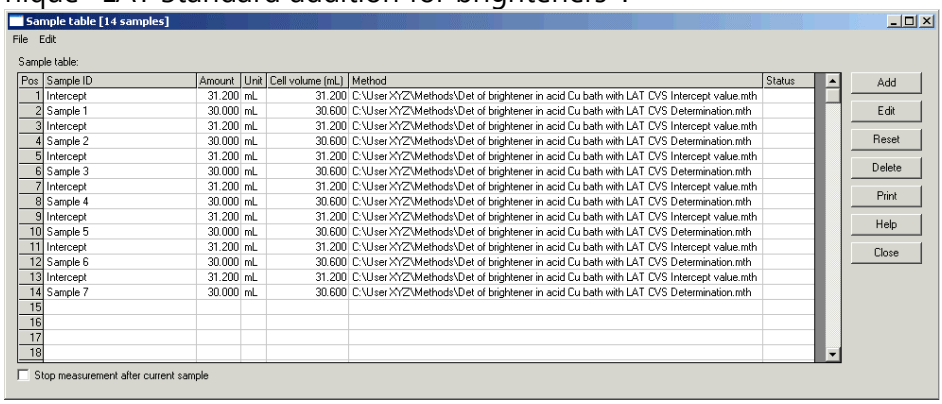



**Note:** To make sure that always the latest intercept file is taken for the calculation, the name of the intercept file defined for the parameter **Intercept determination**, must match with the parameter **Sample identifier** on the **Determination** tab with **Calibration** technique "LAT Record intercept value".

**Note:** To make sure that always the latest intercept file is taken for the calculation, the path of the intercept file defined for the parameter **Intercept determination**, must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

## Sample table

In the Sample table, itemize alternately (based on the arrangement on the sample rack) a method with **Calibration** technique "LAT Record intercept value" (as first) and a method with **Calibration** technique "LAT Standard addition for brighteners":




Start determination.

## Suppressor Analysis with 838 Advanced Sample Processor and DT

Following installations and settings are recommended for the automated Suppressor determination with the **838 Advanced Sample Processor** and the "dilution titration technique":

### Instruments

Install the **838 Advanced Sample Processor**, two **800 Dosinos** and a **732 Relay Box** with two **823 Membrane Pump Units** (see *Hardware Manual 797* and *838 Instructions for Use*).

Dosinos:

| | | |
|---|---|---|
| Dosino 1: | 50 mL Exchange Unit | VMS Solution |
| (Dosino 2: | not used) | |
| Dosino 3: | 2 mL Exchange Unit | Sample / Suppressor standard solution |

Dosino 3 **must** be used to add Suppressor standard solution when recording the calibration curve - and to add sample when determining the sample. It is connected directly to the pipetting needle of the 838 Advanced Sample Processor.

### Method at 838

Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

Set method **DT** at the 838 Advanced Sample Processor.

**Note**: You should enter the exact number of samples for parameter `number of samples`. Otherwise the Dosino won't be rinsed at the end.

**DT**

```
parameters
   method                          DT
   number of samples               16   >  Number of samples to be
                                          processed (entire sample
                                          rack)

>start sequence
   1  CTL:Rm:                     INIT   >  Initialize Remote lines
   2  Move    1    :            sample   >  First Sample on Pos. "SAM-
                                          PLE"
   3  CTL:Rm:            **********1   >  Remote start CT797
   4  CTL:Rm:            **********0   >

>sample sequence
   1  SCN:Rm:                 *****1**   >  Scan line for incoming signal
                                          from CT797
   2  MOVE    1    :            sample   >  Move needle to sample
   3  LIFT:   1    :          work mm   >  Place needle at working posi-
                                          tion
   4  CTL:Rm:            **********1   >  Set line: Needle immersed in
                                          sample vessel
   5  CTL:Rm:            **********0   >
```

```
>final sequence
   1  SCN:Rm:                  *****1**   >  Scan line for incoming signal
                                              from CT797
   2  MOVE    1    :              next   >  Move needle to sample
   3  LIFT:   1    :           work mm   >  Place needle at working posi-
                                              tion
   4  CTL:Rm:              **********1   >  Set line: Needle immersed in
                                              rinsing sol.
   5  CTL:Rm:              **********0   >
```

**Note**: If (as in this example) all used Dosinos are connected to the 797, the originally listed commands 6 – 10 of the **sample sequence** must be deleted.

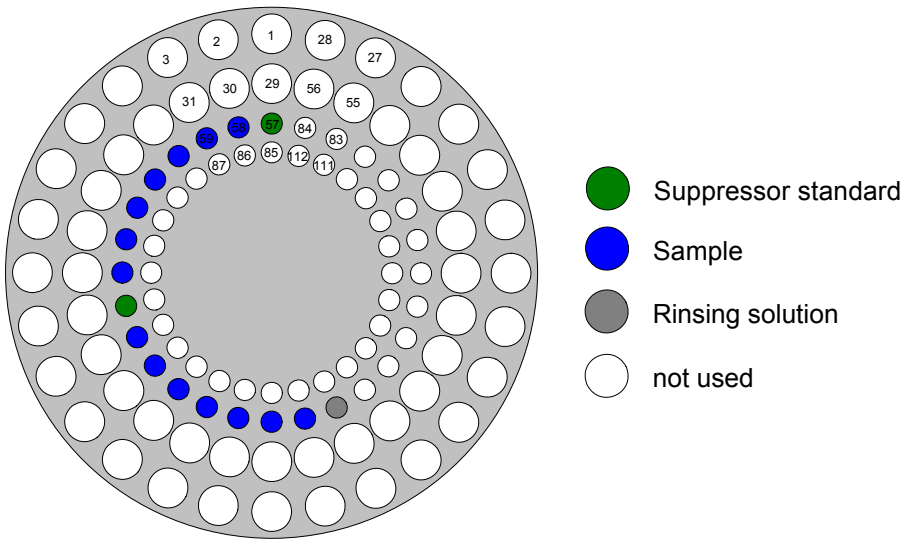
### Samples

Samples and Suppressor standard solutions are placed on the rack. It is recommended to use the two inner rings with 11 ml sample vessels. How frequently the calibration curve needs to be recorded (with **Calibration** technique "DT Record calibration curve") depends on the chemistry of the bath.

**Note**: Place a sample vessel with rinsing solution at the end of the series.

Arrangement: At the first position a Suppressor standard solution to record the calibration curve. Then samples, and, when a recalibration is necessary, another Suppressor standard solution. At the end rinsing solution.

Example for a sample rack with 14 samples, 2 Suppressor standard solutions and one rinsing solution:

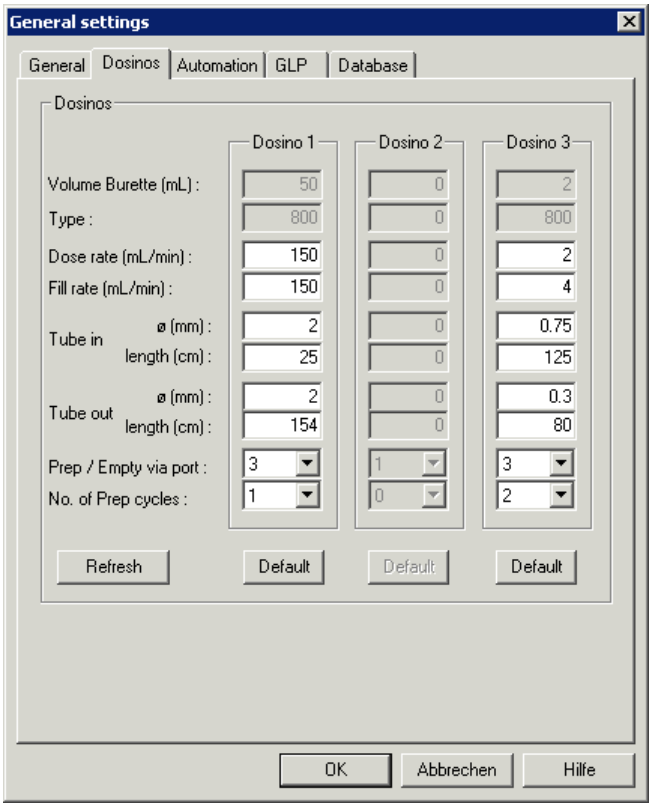



**Note**: Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

### General Settings in the 797 Software

Activate both options on the **General** tab of the **GENERAL SETTINGS** window, so that a recorded calibration curve replaces the old one automatically.

Settings on the **Dosinos** tab of the **GENERAL SETTINGS** window in the 797 Software:




It is recommended to do for Dosino1 one "Prep cycle" and for Dosino3 two "Prep cycles".

On the **Automation** tab, select the 838 Advanced Sample Processor. The default settings can be adopted (click button <Default>).

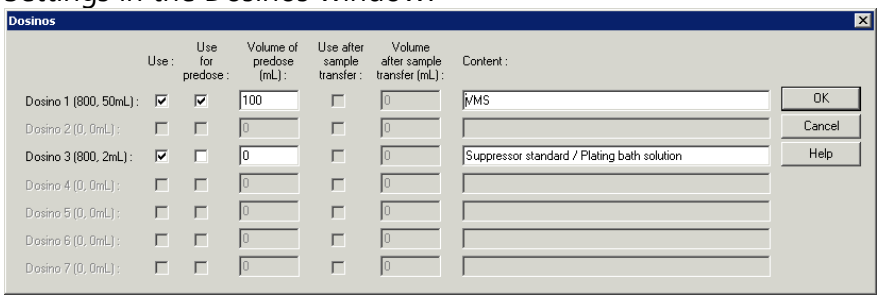
## Method Parameters for the 797

Two steps are required for Suppressor determination. One to record the calibration curve with **Calibration** technique "DT Record calibration curve", another for the actual sample determination with **Calibration** technique "DT Suppressors with calibration curve". Set CVS or CPVS for **Mode** for both methods.

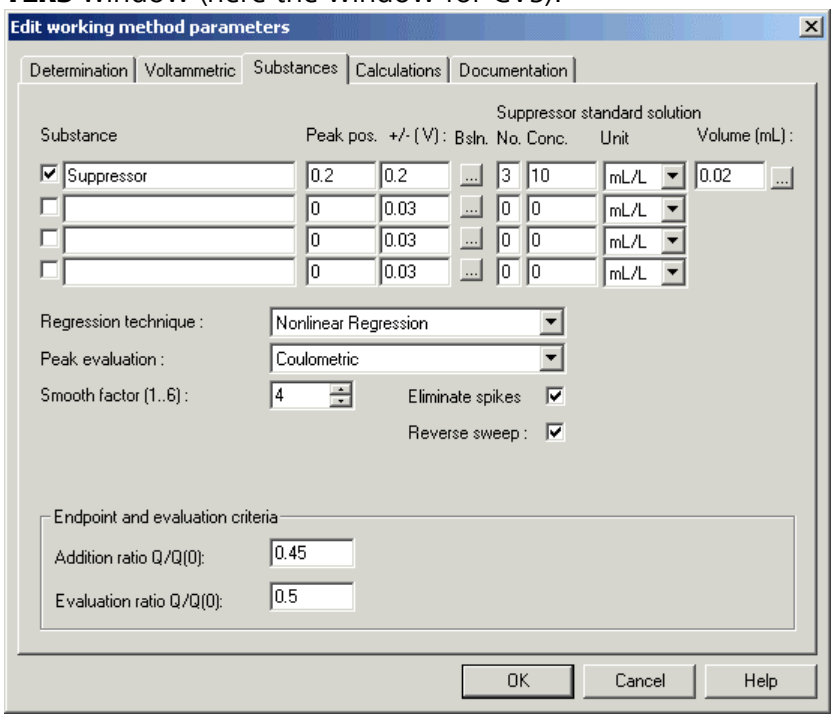
Recording of the calibration curve:

Choose "DT Record calibration curve" for **Calibration**.

Settings in the Dosinos window:



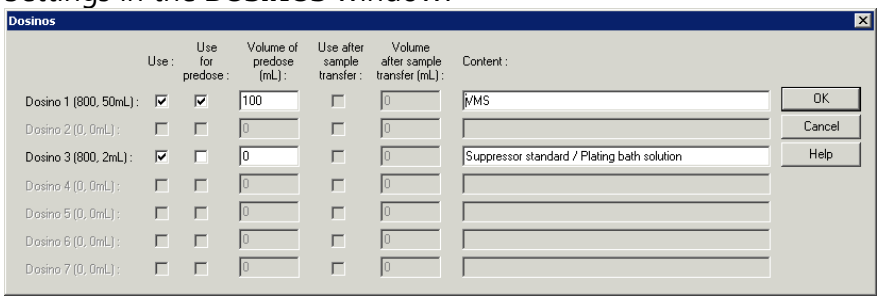
Checking **Use for predose** for Dosino 1, VMS is added to the measuring vessel before the sample transfer. Then Suppressor standard solution is added via Dosino 3. That should be specified on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (here the window for CVS):



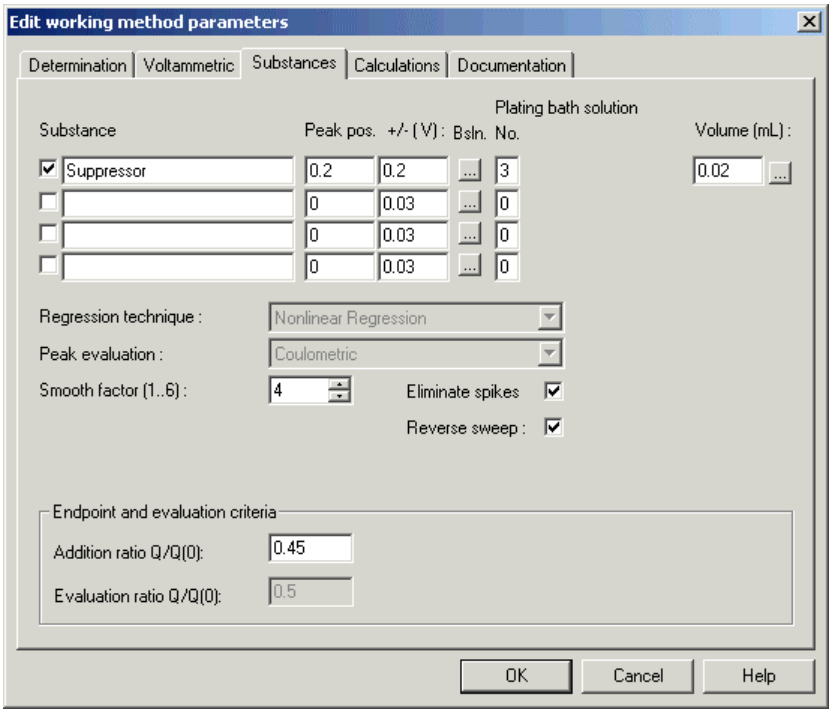

Determination of the sample:

Choose "DT Suppressors with calibration curve" for **Calibration** technique.

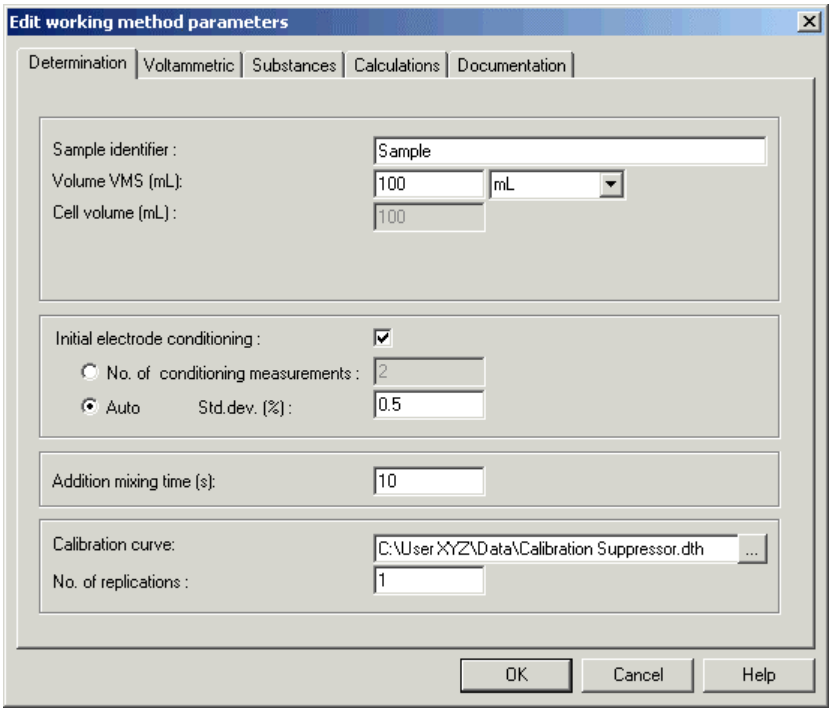
Settings in the **DOSINOS** window:




Checking **Use for predose** for Dosino 1, VMS is added to the measuring vessel before the sample transfer. Then sample is added via Dosino 3. That should be specified on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (here the window for CVS):




The determination tab of the window for CVS:

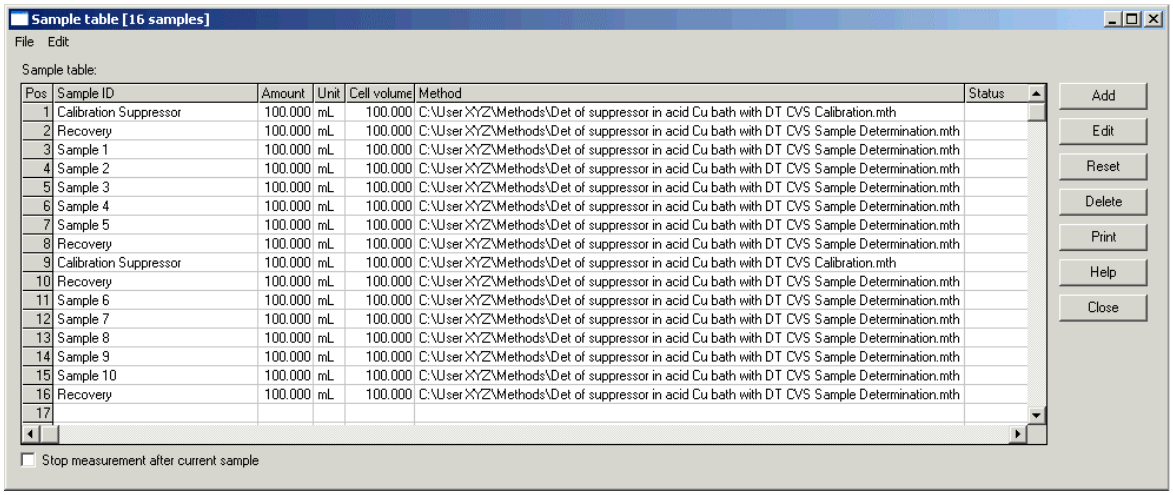



**Note**: To make sure that always the latest calibration file is taken for the calculation, the name of the calibration file defined for the parameter **Calibration curve** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS**) with **calibration** "DT Suppressors with calibration curve", must match with the name defined for the parameter **Sample identifier** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS**) with **Calibration** technique "DT Record calibration curve".

**Note**: To make sure that always the latest calibration file is taken for the calculation, the path of the calibration file defined for the parameter **Calibration curve** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS** with **calibration** "DT Suppressors with calibration curve", must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

### Sample table

In the Sample table, list (according to the arrangement on the sample rack) for every Suppressor standard solution a method with **Calibration** technique "DT Record calibration curve" and for every sample a method with **Calibration** technique "DT Suppressors with calibration curve":




Start determination.

## Suppressor Analysis with 838 Advanced Sample Processor and RC

Following installations and settings are recommended for the automated Suppressor determination with the **838 Advanced Sample Processor** and the "response curve technique":

**Note**: The "response curve technique" is used for Suppressor determination in electroplating baths, if the “dilution titration technique" is inapplicable.

### Instruments

Install the **838 Advanced Sample Processor**, two **800 Dosinos** and a **732 Relay Box** with two **823 Membrane Pump Units** (see *Hardware Manual 797* and *838 Instructions for Use*).

Dosinos:

Dosino 1: 50 mL Exchange Unit Electrolyte solution

| | | |
|---|---|---|
| (Dosino 2: | not used) | |
| Dosino 3: | 2 mL Exchange Unit | Sample / Suppressor standard solution |

### Method at 838

Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

Set method **LAT** at the 838 Advanced Sample Processor.

**LAT**

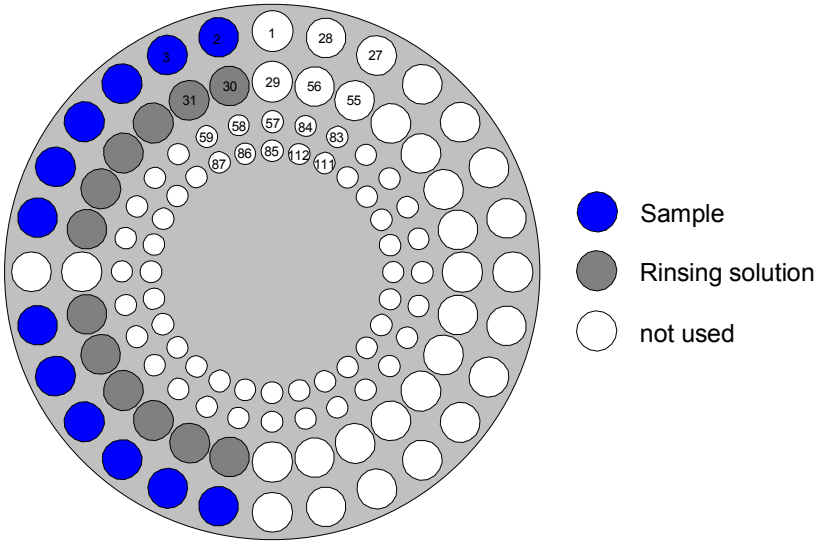
```
parameters
   method                          LAT
   number of samples              rack   >  Number of samples to be
                                             processed (entire sample
                                             rack)

>start sequence
   1  CTL:Rm:                      INIT   >  Initialize Remote lines
   2  Move    1    :             sample   >  First Sample on Pos. "SAM-
                                             PLE"
   3  CTL:Rm:            **********1   >  Remote start CT797
   4  CTL:Rm:            **********0

>sample sequence
   1  SCN:Rm:                  *****1**   >  Scan line for incoming signal
                                             from CT797
   2  MOVE    1    :             sample   >  Move needle to sample
   3  LIFT:   1    :            work mm   >  Place needle at working posi-
                                             tion
   4  PERISTALT:   300 s             10   >  Sample transfer
   5  CTL:Rm:            **********1   >  Set line: sample transfer
                                             ready
   6  CTL:Rm:            **********0
   7  MOVE    1    :               +28   >  Move needle to rinsing posi-
                                             tion
   8  LIFT:   1                work mm   >  Place needle at working posi-
                                             tion
   9  PERISTALT:   5 s               10   >  Suck rinsing solution in the
                                             needle
   10 SCN:Rm:                  *****1**   >  Scan line for incoming signal
                                             from CT797
   11 PERISTALT:   300 s          10   >  Rinse needle
   12 CTL:Rm:            **********1   >  Set line: needle cleaning
                                             ready
   13 CTL:Rm:            **********0
```

### Samples

50 mL sample vessels can be placed on the two outer rings (11 mL sample vessels on the two inner rings).

Arrangement: Place on the outer of the two rings for each method with **Calibration** technique "RC Record response curve" an empty vessel, and for each method with **Calibration** technique "RC Sample with response curve" a vessel with sample (see "Sample table", below).

Example for a sample rack with 12 samples:



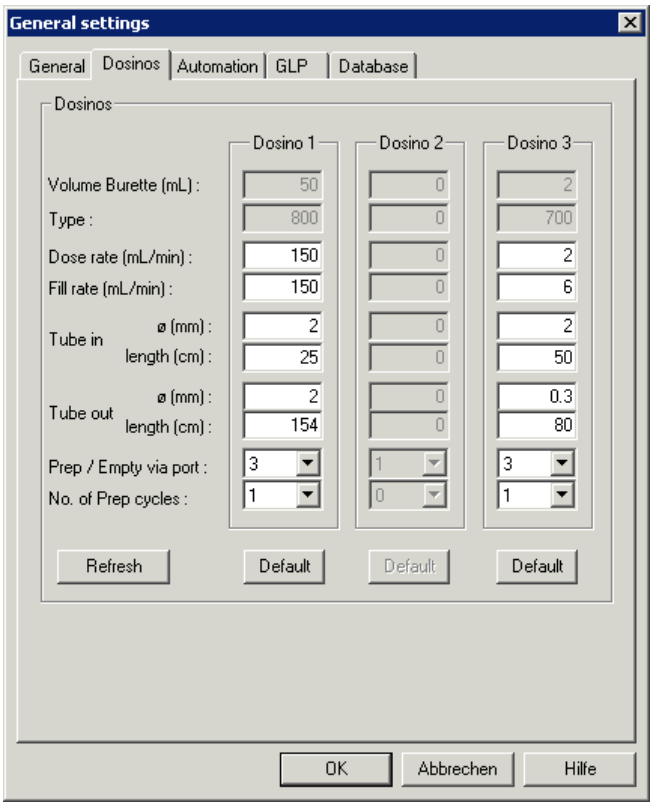

**Note**: Although the first sample is placed on position 2, position 1 remains the starting position in the start sequence of the method at the 838 (recording the **Response curve**).

**Note**: Before each start, define the position of the first sample vessel for the 838 parameter "**SAMPLE**" with the 838 keypad.

### General Settings in the 797 Software

Activate both options on the **General** tab of the **GENERAL SETTINGS** window, so that a recorded calibration curve replaces the old one automatically.

Settings on the **Dosinos** tab of the **GENERAL SETTINGS** window in the 797 Software:




Es wird für beide Dosino ein "Prep-Zyklus" empfohlen.

On the **Automation** tab, select the 838 Advanced Sample Processor. The default settings can be adopted (click button <Default>).

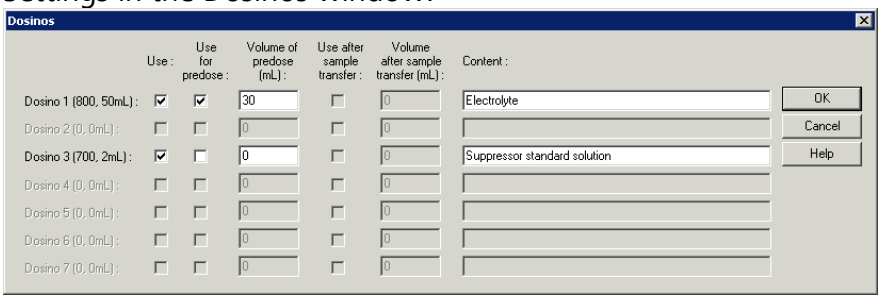
## Method Parameters for the 797

Two steps are required for Suppressor determination. One to record the response curve with **Calibration** technique "RC Record response curve", another for the actual sample determination with **Calibration** technique "RC Sample with response curve". Set CVS or CPVS for **Mode** for both methods.

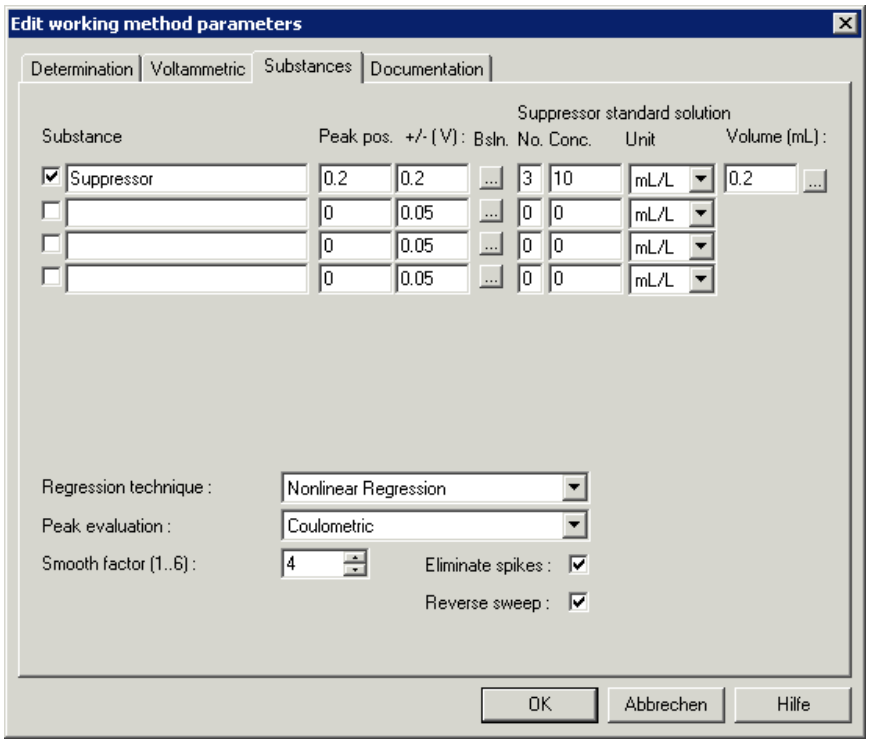
Recording of the Response Curve::

Choose "RC Record response curve" for **Calibration**.

Settings in the Dosinos window:



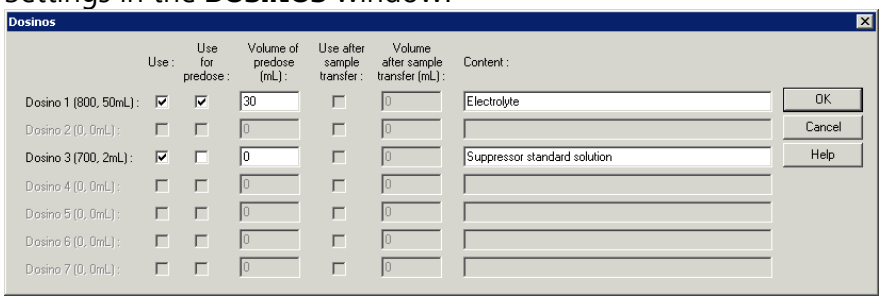

After the addition of Electrolyte solution, Suppressor standard solution is added via Dosino 3. That should be specified on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window (here the window for CVS):




Determination of the sample:

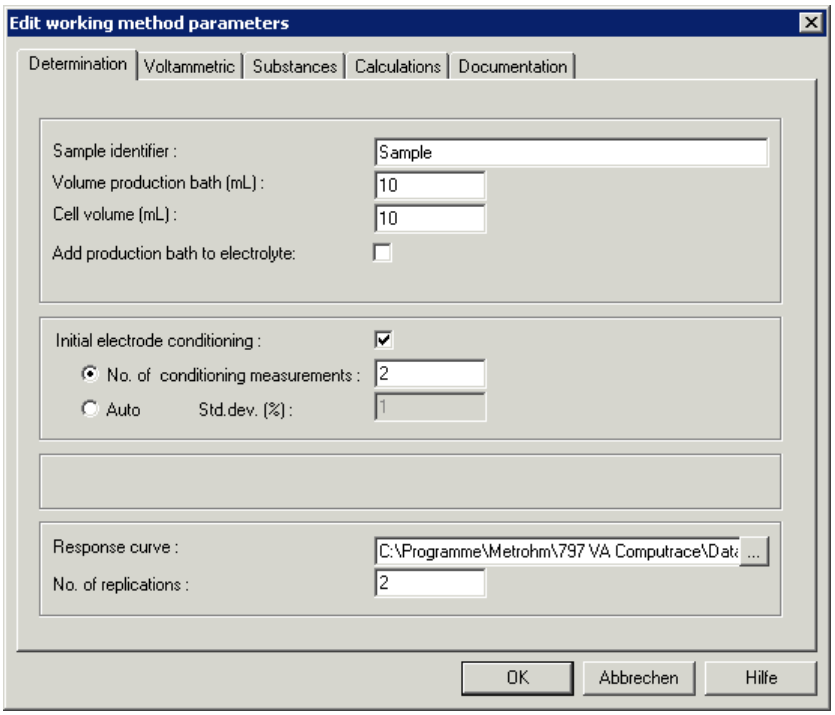
Choose "RC Sample with response curve" for **Calibration** technique.

Settings in the **DOSINOS** window:




Checking **Use for predose** for Dosino 1, Electrolyte solution is placed into the measuring vessel. Then, the measuring vessel is emptied (only if **Add production bath to electrolyte** on the tab **Determination** of the window for CVS is not activated) and the sample is placed.

The **determination** tab of the window for CVS:

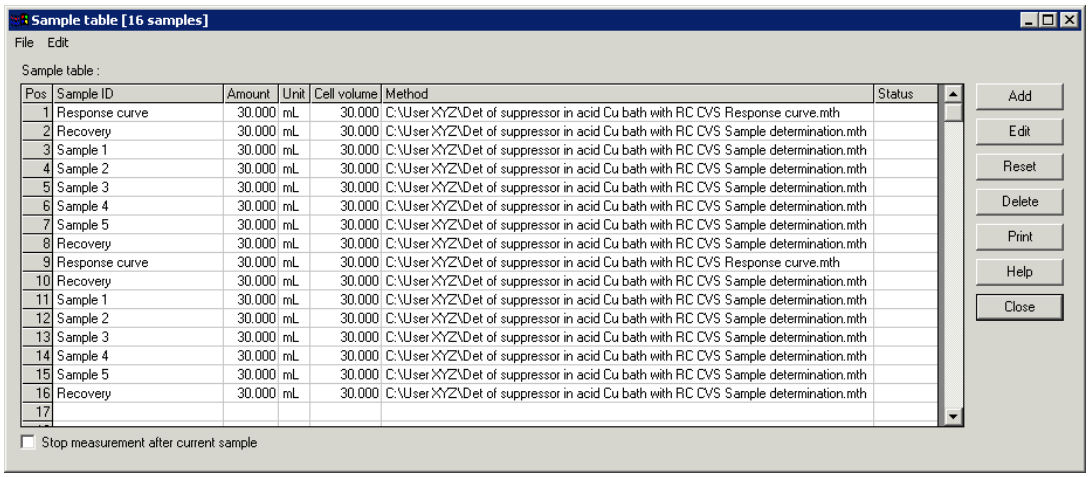



**Note**: To make sure that always the latest "response curve file" is taken for the calculation, the name of the "response curve file" defined for the parameter **Response curve** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS**) with **calibration** "RC Sample with response curve", must match with the name defined for the parameter **Sample identifier** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS**) with **Calibration** technique "RC Record response curve".

**Note**: To make sure that always the latest "response curve file" is taken for the calculation, the path of the calibration file defined for the parameter **Response curve** on the **Determination** tab (of the window **EDIT WORKING METHOD PARAMETERS** with **calibration** "RC Sample with response curve", must match with the path defined for the parameter **Data folder** (for the currently logged-in user) on the tab **User Directories** of the window **USER RIGHTS**.

### Sample table

In the Sample table, list (according to the arrangement on the sample rack) for every empty vessel on the sample rack a method with **Calibration** technique RC Record response curve and for every sample a method with **Calibration** technique RC Sample with response curve:




Start determination.

# 8.7 Standard addition technique

### Use manual standard addition without solution exchange

In the manual standard addition without solution exchange, a known amount of the analyte is added once or several times to the sample using a pipette. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. Select **Standard addition** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
5. Select **Manual** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Batch** in the **Technique** field of the **WORKING METHOD SPECIFICATIONS** window.
7. Click  to open the **EDIT WORKING METHOD PARAMETERS** window.
8. Select the **Determination** tab (see *section 5.2*) and enter **Sample identifier**, **Sample amount** (not with the modes CVS and CPVS), **Cell volume**, and the number of standard additions in the **No. of additions** field. (If you work with the CVS or CPVS mode, see *section 6.2 Calibration techniques with CVS and CPVS* for a description of the parameters on the **Determination** tab).
9. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the number of the sin-

gle or mixed standard addition solution, its concentration and its volume is defined.

10. If the standard addition should be done with variable addition volumes, click the ... button in the **Volume** column to open the **EDIT VARIED ADDITION** window, enter the variable addition volumes in the **Addition** fields, and close this window by clicking **<OK>**.
11. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
12. Place the sample solution in the measuring vessel at the 797 VA Computrace stand.
13. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
14. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the Start button in the **MONITORING** window.
15. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.
16. Each time a standard addition is required in the **MANUAL ADDITION** window, add the standard addition solution using a pipette.

### Use manual standard addition with solution exchange

In the manual standard addition with solution exchange, a new sample solution is used for every standard addition. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. Select **Standard addition** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
5. Select **Manual** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Batch with solution exchange** in the **Technique** field of the **WORKING METHOD SPECIFICATIONS** window (is not selectable with the CVS and CPVS mode).
7. Click Edit parameters to open the **EDIT WORKING METHOD PARAMETERS** window.

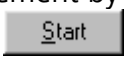
8. Select the **Determination** tab (see *section 5.2*) and enter **Sample identifier**, **Sample amount**, **Cell volume**, and the number of spiked solutions in the **No. of cells** field.
9. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the concentrations of the spiked sample solutions are defined in the **CELL CONCENTRATIONS** window which is opened by clicking on the Cell button.
10. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
11. Place the sample solution in the measuring vessel at the 797 VA Computrace stand.
12. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
13. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the Start button in the **MONITORING** window.
14. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.
15. Each time a solution exchange is required in the **BATCH SOLUTION EXCHANGE** window, replace the measuring solution by the next spiked sample solution.

## Use automatic standard addition

In the automatic standard addition, a known amount of the analyte is added once or several times to the sample using 700/800 Dosinos, or 685/805 Dosimats. Proceed as follows:

1. Install Dosing Devices to the 797 VA Computrace stand (see *How to Install Dosing Devices for automatic addition*, *section 8.1*).
2. Click on  or **MAIN WINDOW / Mode / Determination**.
3. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
4. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
5. Select **Standard addition** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Automatic** for **Addition** in the **WORKING METHOD SPECIFICATIONS** window.
7. Click Dosinos to open the **DOSINOS** window.

8. Check the Dosing Devices, which are used for standard addition in the **Use** field (see *Dosing Devices*, *section 5.2*)
9. Close the **DOSINOS** window by clicking **<OK>**.
10. Click 

to open the **EDIT WORKING METHOD PARAMETERS** window.
11. Select the **Determination** tab (see *section 5.2*) and enter **Sample identifier**, **Sample amount**, **Cell volume**, and the number of standard additions in the **No. of additions** field (If you work with the CVS or CPVS mode, see *section 6.2 Calibration techniques with CVS and CPVS* for a description of the parameters on the **Determination** tab).
12. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the number of the single or mixed standard addition solution, its concentration and its volume is defined. The **No.** of the standard solution must be identical to the number of the Dosing Devices used for automatic addition of this solution.
13. If the standard addition should be done with variable addition volumes, click the  button in the **Volume** column to open the **EDIT VARIED ADDITION** window, enter the variable addition volumes in the **Addition** fields, and close this window by clicking **<OK>**.
14. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
15. Place the sample solution in the measuring vessel at the 797 VA Computrace stand.
16. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
17. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.
18. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.

## 8.8 Calibration curve technique

### Record calibration curve manually by adding standard solution

This method is used for preparing different calibration solutions by adding several times a concentrated standard solution to the measuring solution using a pipette. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.

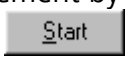
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. Select **Record calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window (is not selectable with the CVS and CPVS mode).
5. Select **Manual** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Batch** in the **Technique** field of the **WORKING METHOD SPECIFICATIONS** window.
7. Click  to open the **EDIT WORKING METHOD PARAMETERS** window.
8. Select the **Determination** tab (see *section 5.2*) and enter the **Cell volume** and the number of additions in the **No. of additions** field.
9. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the number of the single or mixed standard solution, its concentration and its volume is defined.
10. If the addition of the standard solution should be done with variable addition volumes, click the  button in the **Volume** column to open the **EDIT VARIED ADDITION** window, enter the variable addition volumes in the **Addition** fields, and close this window by clicking **<OK>**.
11. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
12. Place the electrolyte solution (e.g. buffer) in the measuring vessel at the 797 VA Computrace stand.
13. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
14. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window.
15. Enter the **Calibration curve id** (used as part of the determination file name) in the **START CALIBRATION** window and click **<OK>**.
16. Each time an addition is required in the **MANUAL ADDITION** window, add the standard solution using a pipette.

### Record calibration curve manually with solution exchange

This method is used for recording a calibration curve using different calibration solutions of known concentration. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. Select **Record calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window (Is not selectable with the CVS and CPVS mode).
5. Select **Manual** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Batch with solution exchange** in the **Technique** field of the **WORKING METHOD SPECIFICATIONS** window.
7. Click 

to open the **EDIT WORKING METHOD PARAMETERS** window.
8. Select the **Determination** tab (see *section 5.2*) and enter the **Cell volume** and the number of calibration solutions in the **No. of cells** field.
9. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the concentrations of the calibration solutions are defined in the **CELL CONCENTRATIONS** window which is opened by clicking on the 

button.
10. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
11. Place the first calibration solution in the measuring vessel at the 797 VA Computrace stand.
12. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
13. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.
14. Enter the **Calibration curve id** (used as part of the determination file name) in the **START CALIBRATION** window and click **<OK>**.
15. Each time a solution exchange is required in the **BATCH SOLUTION EXCHANGE** window, replace the solution measured by the next calibration solution.

### Record calibration curve automatically

This method is used for preparing different calibration solutions by adding automatically several times a concentrated standard solu-

tion to the measuring solution using 700/800 Dosinos or 685/800 Dosimats. Proceed as follows:

1. Install Dosing Devices to the 797 VA Computrace stand (see *How to Install Dosing Devices for automatic addition*, *section 8.1*).
2. Click on  or **MAIN WINDOW / Mode / Determination**.
3. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
4. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
5. Select **Record calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window (Is not selectable with the CVS and CPVS mode).
6. Select **Automatic** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
7. Click 

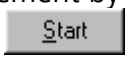
to open the **EDIT WORKING METHOD PARAMETERS** window.
8. Select the **Determination** tab (see *section 5.2*) and enter the **Cell volume** and the number of additions in the **No. of additions** field.
9. Select the **Substances** tab (see *section 5.2*) and make sure that for each substance entered in the table the number of the single or mixed standard solution, its concentration and its volume is defined. The **No.** of the standard solution must be identical to the number of the Dosing Devices used for automatic addition of this solution.
10. If the addition of the standard solution should be done with variable addition volumes, click the  button in the **Volume** column to open the **EDIT VARIED ADDITION** window, enter the variable addition volumes in the **Addition** fields, and close this window by clicking **<OK>**.
11. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
12. Place the electrolyte solution (e.g. buffer) in the measuring vessel at the 797 VA Computrace stand.
13. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
14. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.
15. Enter the **Calibration curve id** (used as part of the determination file name) in the **START CALIBRATION** window and click **<OK>**.

### Measure a sample using a calibration curve

For the determination of a sample using a previously recorded calibration curve, this calibration curve must have been recorded and saved. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Load the desired method into the **WORKING METHOD SPECIFICATIONS** window (see *How to Load a method*, section 8.4).
4. Select **Sample with calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window (Is not selectable with the CVS and CPVS mode).
5. Click 

to open the **EDIT WORKING METHOD PARAMETERS** window.
6. Select the **Determination** tab (see *section 5.2*) and enter **Sample identifier**, **Sample amount**, **Cell volume** and the name and directory of the determination with the recorded calibration curve in the **Calibration curve** field.
7. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
8. Place the sample solution in the measuring vessel at the 797 VA Computrace stand.
9. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
10. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the 

button in the **MONITORING** window.
11. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.

## 8.9 Work with film electrodes

### Deposit a mercury film

You find a suitable method for the determination of heavy metals with mercury film electrodes in Application Bulletins 241 and 254.

1. Polish the glassy carbon (6.1204.110) or Ultra Trace electrode tip (6.1204.100) with alumina powder (6.2802.000) and put the electrode into the 797 VA Computrace stand.
2. Put the electrolyte solution into the measuring vessel, e.g.: Add 10 mL ultrapure water, 200 µL *c*(HCl) = 6 mol/L) and 50 µg

*c*(Hg(II)) = 1 g/L to the empty measuring vessel at the 797 VA Computrace stand.

3. Click on **MAIN WINDOW / Utility / Film deposition** to open the **FILM DEPOSITION** window.
4. Enter suitable parameters in the parameter list.
5. Click on the **<Start>** button.
6. Check the resulting test voltammogram. The voltammogram should show low noise and a low background current (low µA range). No interfering peaks should be visible.

### Remove a mercury film

Mercury films can be easily wiped off manually with a tissue. The cleaning procedure can be used instead to remove the mercury film electrochemically or to clean the electrode surface after having removed the mercury film mechanically.

1. Put the cleaning solution into the measuring vessel, e.g.: Add 10 mL ultrapure water and 1 mL $w(HNO_3) = 0.65$ to the empty measuring vessel at the 797 VA Computrace stand.
2. Click on **MAIN WINDOW / Utility / Cleaning procedure** to open the **CLEANING PROCEDURE** window.
3. Enter suitable parameters in the parameter list.
4. Click on the **<Start>** button.
5. Check the resulting test voltammogram. The resulting voltammogram should show low noise and a low background current (low µA range). If all mercury had been oxidized, no mercury peak remains.

## 8.10 Diagnostic procedures

### Check the purging

1. Connect the inert gas to the 797 VA Computrace stand (see *Hardware Manual*).
2. Make sure that the inert gas pressure is 1 ± 0.2 bar.
3. Add 20 mL ultrapure water to the empty measuring vessel at the 797 VA Computrace stand.
4. Click on  or **MAIN WINDOW / Utility / Computrace control** to open the **COMPUTRACE CONTROL** window.
5. Select **HMDE** and click on 

.
6. Make sure that inert gas bubbles are purging through the solution.

## Check the stirring

1. Click on  or **MAIN WINDOW / Utility / Computrace control** to open the **COMPUTRACE CONTROL** window.
2. Select **HMDE** and click on 

.
3. Change the rotational speed by clicking on the  buttons of the **RDE/stirrer speed** field.

## Check the MME

1. Install the MME at the 797 VA Computrace stand (see *Hardware Manual*).
2. Click on  or **MAIN WINDOW / Utility / Computrace control** to open the **COMPUTRACE CONTROL** window.
3. Select **DME**, **SMDE** or **HMDE** and click on 

.
4. Choose Multi-Mode Electrode (**MME**).
5. Fill the measuring vessel with the specified solution.
6. Press the 

button.

## Check theRDE

1. Install the RDE at the 797 VA Computrace stand (see *Hardware Manual*).
2. Click on  or **MAIN WINDOW / Utility / Computrace control** to open the **COMPUTRACE CONTROL** window.
3. Select **RDE/SSE** and click on 

.
4. Choose **RDE/SSE**.
5. Fill the measuring vessel with the specified solution.
6. Press the 

button.

## Perform a linearity test with the dummy cell

For testing the linearity of current measurement, the dummy cell of the 797 VA Computrace stand is used with the test method **Test797_L.mth**. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Click on  or **MAIN WINDOW / File / Load method**.

4. Select the method file **Test797_L.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.
5. Connect the dummy cell at the 797 VA Computrace stand: Attach electrode cable AE to clamping screw **AE**, attach electrode cable RE to clamping screw **RE**, attach electrode cable WE to clamping screw **WE-L**.
6. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
7. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window.
8. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.
9. At the end of the measurement, a curve is printed out. This curve should satisfy the following conditions:
   - The plotted diagonal must be straight.
   - At -200 mV, the current should be -1.6…-2.4 µA.
   - At +200 mV, the current should be +1.6…+2.4 µA.

## Perform a peak test with the dummy cell

For testing the peak measurement, the dummy cell of the 797 VA Computrace stand is used with the test method **Test797_D.mth**. Proceed as follows:

1. Click on  or **MAIN WINDOW / Mode / Determination**.
2. Click on  or **MAIN WINDOW / Window / Working method specification** to open the **WORKING METHOD SPECIFICATIONS** window.
3. Click on  or **MAIN WINDOW / File / Load method**.
4. Select the method file **Test797_D.mth** in the **OPEN** window and click **<OK>**. The method is loaded into the **WORKING METHOD SPECIFICATIONS** window.
5. Connect the dummy cell at the 797 VA Computrace stand: Attach electrode cable AE to clamping screw **AE**, attach electrode cable RE to clamping screw **RE**, attach electrode cable WE to clamping screw **WE-D**.
6. Click on  or **MAIN WINDOW / Window / Monitor** to open the **MONITOR** window.
7. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window.

8. Enter the **Sample ID** (used as part of the determination file name) in the **PLACE SAMPLE** window and click **<OK>**.
9. At the end of the measurement, a curve is printed out. This curve should satisfy the following conditions:
    - A symmetrical, gaussian-shaped peak should be plotted. The evaluation must provide a result for the peak voltage and the peak current, which are printed out in the full report.
    - The peak voltage *E* should be -450 … -550 mV.

## Perform a GLP Validation

The GLP validation is performed with the **GLP Wizard** (see *section 2.7*, *GLP Wizard*) . To start it, click GLP Wizard on the GLP tab of the **GENERAL SETTINGS** window.

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# 9 Troubleshooting

## 9.1 General procedure for error messages

Error messages and warnings are displayed in the **CT797** window. Read the information about the possible causes and the procedure for their rectification and click the **<OK>** button.

## 9.2 Connection problems

### Error message "Could not start the embedded system"

If this error message appears after starting the VA Computrace program, the USB connection has not established. Possible solutions:

1. Switch on the 797 VA Computrace stand.
2. If the Computrace is on, try to restart the software.
3. If 1.) and 2.) were not successful: Close the software, switch off the 797 VA Computrace stand, wait a moment, then restart 797 VA Computrace stand and software.

## 9.3 Software problems

### Error message "Name or password incorrect"

If the login fails because no password is known any more, proceed as follows:

1. Deinstall the software (see *Deinstallation*, *section 1.3*).
2. Reinstall the software.

### Error message "The file 'ecousb.sys' is needed"

This message indicates problems with the USB connection. Proceed as follows:

1. Insert the installation CD into the CD drive.
2. Click on **<Browse>**. Select the CD drive and click on **<OK>**.

### Wrong language in Help

If you want to change the help language, reinstall the software using the **Modify** option and select the desired language.

### Error message "Please select a new database file"

If you work with the new program version «797 VA Computrace Software 1.3.x» and try to export to a database created with an old program version «797 VA Computrace Software 1.X», following error message appears.

"The selected database file was created with a previous version of CT797. The data cannot be written to this database.

Please select a new database file".

Reason for this error is that the file structure of the Version w1.3.x differs from the file structur of the previous versions 1.X.

Close the autodatabase, and confirm the error message with <OK>. The window **SELECT DETERMINATION DATABASE FILE** opens. Choose a database created with Version w1.3.x, or create a new one by entering a new name and clicking <Open>.

## 9.4 Dosing Device problems

### Dosing Device does not work

1. Check the connecting cable between Dosing Device and 797 VA Computrace stand resp. the 846 Dosing Interface.
2. Click on **MAIN WINDOW / Settings / General settings** and check the entries on the **Dosinos / Dosing Interface** tab of the **GENERAL SETTINGS** window (see *Installation of Dosing Devices*, *section 1.3*).
3. Click the button Refresh.
4. Select **Automatic** for **Addition** in the **WORKING METHOD SPECIFICATIONS** window.
5. Activate the Dosing Device in the **DOSINO** window for every method used (see *Dosing Devices*, *section 5.2*).
6. Check the solution number **No**. on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window. The number defined in the **No.** field of the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window should correspond with the number of the Dosing Device used for the addition of this substance.

### Irreproducible standard additions with a Dosing Device

1. Click on  or **MAIN WINDOW / Utility / Dosino control** to open the **DOSINO CONTROL** window (see Dosino control window, *section 7.2*).
2. Check if there are air bubbles left in the glass cylinder of the dosing unit. If this is the case, press button Prep ON.
3. Close the **DOSINO CONTROL** window.

4. Check the **Dose rate** parameter on the **Dosinos** tab. The default dosing rate for use of the 6.1824.000 4-way microtip is 2 mL/min.

## 9.5 General rules for VA trace analysis

### Chemicals and equipment

1. The purity of the reagents plays an important role in determining the results. Extremely pure chemicals should be used for determining lower concentrations (see *VA Application Note V-49*).
2. Measuring vessel, electrodes and all other equipment in contact with the sample solution must be clean and free of contamination substances.

### Electrolytes

1. The pH during a determination plays an important role (e.g. for Zn, Cd, Pb, Cu it should be approx. 4.5). Acetate, Ammonium acetate or PIPES buffer are often used. For more information see the *Application Bulletins*.
2. The electrolyte must be sufficiently conductive and concentrated.
3. The purity of the electrolytes and the cleanliness of the reagent bottles is very important.
4. The working life of the electrolytes is limited, particularly for organic additives (buffer substances, complex formers). It may be necessary to make up fresh solutions every day.

### Standard solutions

1. The standard solutions should be made acidic (approx. pH = 1…2) and stored in plastic bottles.
2. Diluted standard solutions (ppb range) are very unstable and must be freshly made. They must also be made sufficiently acidic.
3. The concentration of the standard solutions must be arranged so that a volume between 20 and 500 µL has to be added.
4. Standard additions are recommended. The peak height after the last addition should be 2…5 times higher than the sample peak.
5. 1000 ppm solutions (self-made or commercially available) are often used as stock solutions. They are stable over long periods of time. Dilutions have to be made with dilute acids.

## Samples

1. The amount of sample depends on the concentration of the element to be determined.
2. If the sample matrix is known, a better assessment of the analysis can be made (organic components?).
3. A digestion must be carried out on contaminated samples and on samples where contamination is suspected (see Metrohm Monograph «Sample preparation for techniques in voltammetric trace analysis»).
4. A lot of errors are made during sampling and when storing the sample. Caution and a critical approach are required.
5. The sample should have a good solubility in the electrolyte and be mixable with it.

## Blank values, contamination

The following points should be checked if the **results are too high**:

1. Have the dilutions been made correctly?
2. Have contamination risks been excluded?
3. Contamination risks are very high at low concentrations: measuring vessels should be conditioned with dilute $HNO_3$ solution.
4. Are the chemicals pure enough?
   "Suprapure" grade reagents should be used at low concentrations.
5. Very high concentrations were measured in the previous analysis:
   electrodes and measuring vessels must be carefully cleaned and conditioned (memory effects).
6. Has the standard addition been carried out properly?
   Was the volume set correctly on the pipetting unit?

The following points should be checked if the **results are too low**:

1. Concentration too high?
   HMDE overloaded, use DME/SMDE instead?
2. Buffer not correct?
   Make up new one if necessary.
3. Addition ratio too low?
4. Addition ratio too high?

## Selection of VA Measurement mode

The following points should be considered by selecting the VA measurement mode:

1. **DP** (Differential Pulse) should always be the first choice. It is the most universal and frequently used voltammetric determination method and is equally well suited for reversible and irreversible systems. It offers a high sensitivity down to $10^{-8}$ mol/L and a separation ability of 1:50'000.
2. **DC** (Direct Current) is the classic, simplest VA method with limited sensitivity (down to $10^{-5}$ mol/L) and a separation ability of only 1:10. It is mainly used in teaching labs, for the clarification of reduction/oxidation processes and for stripping voltammetry. In determination mode DC can only be used with stationary electrodes (HMDE, RDE).
3. **NP** (Normal Pulse) is the classic pulse voltammetric VA method with direct recording of the current. It is equally well suited for irreversible and reversible systems and offers a higher sensitivity than the DC voltammetry. The NP mode can only be used in the exploratory mode.
4. **AC1** (Alternating Current, 1st harmonic) is primarily suitable for determinations based on reversible redox reactions and is virtually completely insensitive to irreversible reactions.
5. **AC2** (Alternating Current, $2^{nd}$ harmonic) also primarily suitable for determinations based on reversible redox reactions. Compared with the AC1 measurements, an increase in sensitivity, resolution and separation efficiency is often obtained.

   **Note**: To measure in the **AC2** mode, choose **AC – Alternating Current Voltammetry** as **Mode** in the **WORKING METHOD SPECIFICATION** window, click Edit parameters and check the checkbox **2nd harmonic** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

6. **SqW** (Square Wave) is primarily suitable for investigations of reversible electrode processes and kinetic studies. It is used particularly for sensitive stripping voltammetric determinations at the HMDE or RDE.
7. **PSA** (Potentiometric Stripping Analysis) is mainly used to determine metal traces in aqueous solutions contaminated with organic matter by means of mercury film electrodes without prior digestion. Only analytes that form an amalgam can be analyzed.
8. **CCPSA** (Constant Current Potentiometric Stripping Analysis) is mainly used to determine substances in aqueous solutions contaminated with organic matter using mercury film electrodes or rotating precious metal electrodes without prior digestion.
9. **CV** (Cyclic Voltammetry) is mainly used to investigate electrode processes and for kinetic studies.
10. **CVS** (Cyclic Voltammetric Stripping) is mainly used for the determination of organic additives in electroplating electrolytes.

11. **CPVS** (Cyclic Pulse Voltammetric Stripping) is mainly used for the determination of organic additives in electroplating electrolytes. CPVS is a chronoamperometric mode, current is measured against time.

## 9.6 Voltammetric problems

### Low background current or unstable baseline

With **all types of electrodes**:

1. Check electrolyte concentration and pH of the solution.
2. Check **Start potential** and **End potential** of the sweep.
3. If the ion concentration in the solution is too high: dilute the electrolyte.
4. Has the sample been degassed? Degassing with nitrogen for at least 5 min is recommended, for alkaline solutions approx. 10 min is recommended.
5. Is the reference electrode sufficiently full (inside and outside, see *Hardware Manual*)?
6. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

With **DME/SMDE**:

1. If the electrode drops irregularly: check the MME.
   Adjust sealing needle. If necessary, change capillary and replace sealing needle (see *Hardware Manual*).
2. Check tapping mechanism on VA Stand. If tapping strength is too weak, turn corresponding slotted screw on the valve block during operation in an anticlockwise direction until a drop falls each time the tapper is triggered (see *Hardware Manual*).
3. Is the gas pressure correctly set (1 bar)?
4. If the concentration to be determined is considerably lower than expected: increase sample volume or change the electrode mode (e.g. HMDE).

With **HMDE**:

1. If the electrode drops or the drops do not remain hanging: check the MME. Change capillary and replace sealing needle (see *Hardware Manual*).
2. If the concentration to be determined is considerably higher than expected: reduce sample volume or change the electrode mode (e.g. from HMDE to SMDE or DME).

With **RDE/SSE**:

1. The electrode surface must be repolished.
2. Has the correct RDE type been used?

3. Exchange the RDE.
4. Has the electrode been conditioned (e.g. by using **Conditioning cycles** and **Cleaning potential**) ?
5. If the concentration to be determined is considerably higher than expected: reduce sample volume.
6. The background current is normally higher if RDE is used in place of MME; a background current of several 100 nA is possible.

## Curves with high noise

Did you work in the SqW mode (if yes, see *SqW Problems*, *section 9.6*)? If not:

With **all MME types**:

1. Adjust sealing needle.
2. Change capillary and replace sealing needle (see *Hardware Manual*). If necessary, clean the MME (see *Hardware Manual*).
3. Check tapping mechanism on stand. If tapping strength is too weak, turn corresponding slotted screw on the valve block during operation in an anticlockwise direction until a drop falls each time the tapper is triggered (see *Hardware Manual*).
4. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

With **DME/SMDE**:

1. If the electrode drops irregularly: check the MME.
   Adjust sealing needle. If necessary, change capillary and replace sealing needle (see *Hardware Manual*).
2. If the electrode drops much too quickly: increase the **Voltage step time** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

With **HMDE**:

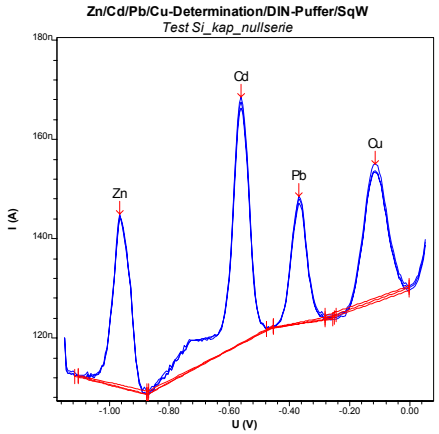
1. If the electrode surface is overloaded: check deposition potential and time.
2. If no drops are at the capillary: change the capillary and replace sealing needle (see *Hardware Manual*).

## SqW Problems

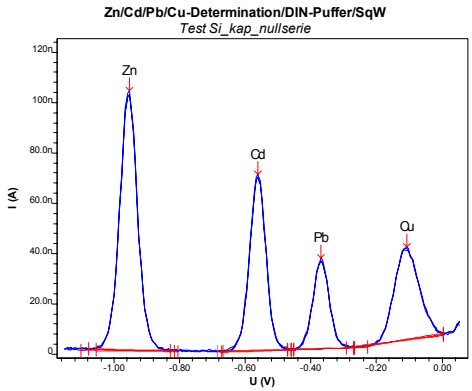
In order to get good results for measurements in the "Square wave" mode, the auto current range feature of the potentiostat should not be used. The potentiostat parameters **Highest current range** and **Lowest current range** should be set on the same level. Finding the optimal current level needs trying. It should be as small as possible, but larger than the expected maximum peak (to minimize noise and not disturb the peak shape).

**Example:**
(For all measurements: Amplitude: 0.02 V , Frequency: 50 Hz)

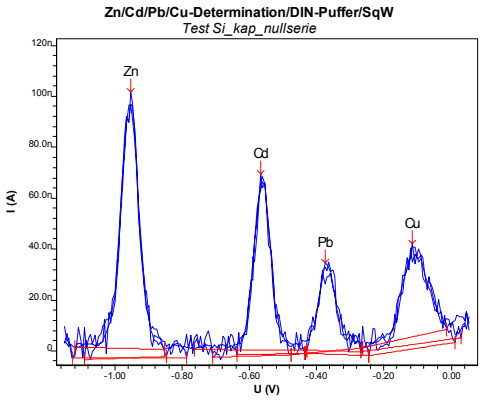
**Highest current range**: 10 nA
**Lowest current range**: 10 nA




**Highest current range**: 1 µA
**Lowest current range**: 1 µA




**Highest current range**: 10 µA
**Lowest current range**: 10 µA




## Standard addition curves are not reproducible

With **all types of electrodes**:

1. Check method parameters (stirring time, etc.).

2. Check and test the pipetting process: Pipetting the standard solutions must be carried out by one and the same person or with the same instrument or the same pipette. Was the pipetting unit used properly? When were the pipettes last calibrated (GLP)?
3. Organic components interfere with the analysis: carry out a UV digestion or other suitable sample preparation.
4. Are the calibration solutions too old?
5. Would a calibration curve be more suitable?

With **MME**:

1. Check the MME, change capillary if necessary and replace sealing needle (see *Hardware Manual*).
2. The linearity at the HMDE is naturally not as good as with the DME. The linear range is in general no larger than 1 - 2 decades.

With **RDE/SSE**:

1. Check the RDE (see *Hardware Manual*).

## Peak displacement

1. Check and adjust the pH of the solution.
2. Check electrolyte composition and correct if necessary. Use a buffer solution instead of an acid.
3. Carry out a standard addition to check whether the correct peak has been evaluated.
4. Organic components interfere with the analysis: carry out a UV digestion or other suitable sample preparation.
5. Enter a new half-wave potential in the instrument and recalculate the results.
6. Check reference electrode (see *Hardware Manual*).
7. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

## No peak found

With **all types of electrodes**:

1. The peak is only displaced: adjust the half-wave potential and recalculate the results.
2. The sample concentration is too low: increase the sample volume or the amount of sample.
3. Are the **Start potential** and **End potential** correct?
4. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

5. Are organic components present? Carry out a UV digestion or other suitable sample preparation.

With **DME/SMDE**:

1. The concentration of the ion to be determined is too low: use HMDE (stripping voltammetry) instead of DME or SMDE.

With **HMDE**:

1. Has the complexing agent been forgotten? (adsorptive stripping voltammetry).
2. The **Deposition time** in the inverse voltammetry is too short: increase the time on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.
3. No Hg drops at the capillary: check MME. Adjust sealing needle. If necessary, change capillary and replace sealing needle (see *Hardware Manual*).

With **RDE/SSE**:

1. The background current is too high: try to improve the background current by electrochemical conditioning. If, necessary, repolish the electrode. Polishing is only recommended, if electrochemical treatment does not improve the performance of the electrode
2. The **Deposition time** in the inverse voltammetry is too short: increase the time on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

### Peak is in the highest µA range

With **all types of electrodes**:

1. The concentration of the ion to be determined is too high: reduce the sample volume and carry out the analysis again.

With **HMDE**:

1. The **Deposition time** is too long: Reduce the time.
2. If necessary use a SMDE or DME electrode instead of HMDE.

With **RDE/SSE**:

1. The background current is too high: repolish the electrode.
2. The **Deposition time** is too long: reduce the time.
3. Is the **Deposition potential** correct?

### Double peak

With **all types of electrodes**:

1. Organic components interfere with the analysis: carry out a UV digestion or other suitable sample preparation.
2. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

3. If a second element is present at the same potential: add this element to the sample and carry out the analysis again. If the second peak has become higher then the second element is present. Might it be possible to selectively mask this second element with a complexing agent?
4. For Cu: work without chlorides in the electrolyte or increase the chloride concentration massively.
5. Has any substance formed a precipitate in the measuring vessel (e.g. lead perchlorate standard with KCl as electrolyte)?
6. Try out eluents with different compositions (addition of complexing agents).
7. Check method parameters.
8. Try another measurement mode like AC1. If one substance is reversible and the second one irreversible, only the reversible substance is detected by AC1.

With **MME**:

1. Check MME. If necessary, change capillary and replace sealing needle (see *Hardware Manual*).

With **RDE/SSE**:

1. Check RDE and polish if necessary (see *Hardware Manual*).

### Standard addition peaks displaced

With **all types of electrodes**:

1. Standard solutions have been made too acidic.
2. Buffering capacity of the electrolyte is not sufficient: increase electrolyte volume.
3. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

With **HMDE**:

1. If HMDE is used potential displacements of more than 20…30 mV are often normal and have to be accepted; particularly in adsorptive stripping voltammetry.

With **RDE/SSE**:

1. Electrode surface overloaded: reduce sample volume.

### No addition

With **all types of electrodes**:

1. Has the correct standard solution been used or is the concentration of the solution too low: increase the volume of the standard addition solution or use a higher concentration or reduce the sample amount accordingly.

2. If organic components are present: carry out a UV digestion or other suitable sample preparation.
3. Concentration of the analyte is too high: dilute.
4. Electrolyte solution too old: make up a new one. Its working life with organic additives may be as short as 1 day or less.

With **HMDE**:

1. Standard addition solution containing metal complexing agents need time to form the metal complex.

### Spikes / signal jump in voltammogram

1. For MME: check the electrode.
2. Reduce the dynamic range of the potentiostat (see *Potentiostat*, *section 3.3*).

### Oxygen interference

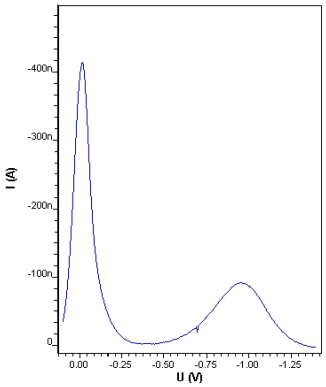
Oxygen can be electrochemically reduced and produces two waves in the voltammogram, one of which is characterized by the appearance of a pronounced maximum. The oxygen reduction can interfere for two reasons:

- The signals of the analytes are masked by the oxygen waves. This becomes noticeable primarily in trace analysis as the oxygen is present in a relatively high concentration in solutions saturated with air (ca. 8 mg/L at room temperature).
- The hydrogen peroxide formed in the first step of the oxygen reduction can react further with certain substances.

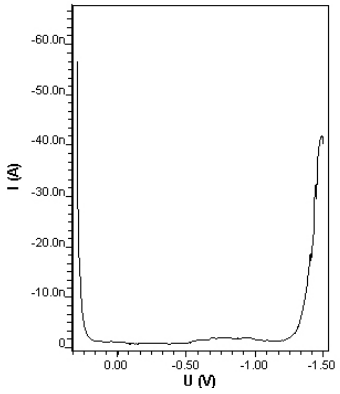
For these reasons, oxygen must be removed from the analysis solution before the polarographic analysis by saturation with inert gas (usually nitrogen). With the inert gas flow rate of ca. 20 L/h set on the 797 VA Computrace stand in the factory, a purging time of 3...5 min usually suffices.

Compare the curves (0.1 mol/L KNO3) before and after purging:

Before purging (Still oxygen in the solution):



After Purging (oxygen removed from solution):




## Unsuitable bridging electrolyte in the reference electrode

When choosing the bridging electrolyte in the reference electrode, possible complications with the substances present in the analysis solution must be taken into account.

With regard to the bridging electrolyte solution **KCl 3 mol/L** used in many cases, the following are examples of disturbances which can appear:

- **Precipitation of $KClO_4$ in the ceramic diaphragm with supporting electrolytes containing $HClO_4$**
  With partial blockage, inexplicable side peaks can appear. To avoid such precipitations, with analysis solutions containing $HClO_4$ a bridging electrolyte solution free from potassium (e.g. NaCl 3 mol/L) must be used.
- **Introduction of chloride through KCl outflow from the reference electrode**
  The outflow of bridging electrolyte from the ceramic diaphragm of the 6.1245.010 Electrolyte vessel (part of the reference electrode) is 2...5 µL/h. The chloride $Cl^-$ flowing into the analysis solution can interfere with the determination of vitamin C or the determination of Cu (see also *Complex formation*, *section 9.6*). The use of chloride $Cl^-$ free bridging electrolyte solutions (e.g. $KNO_3$ sat.) is recommended as a countermeasure.

## Overloading of the working electrode

Under unfavorable conditions (high concentrations and/or long deposition times), the deposition of species at polarized electrodes leads to overloading phenomena such as non-linear standard addition curves or splitting into multiple peaks which are caused by saturation and different deposition forms.

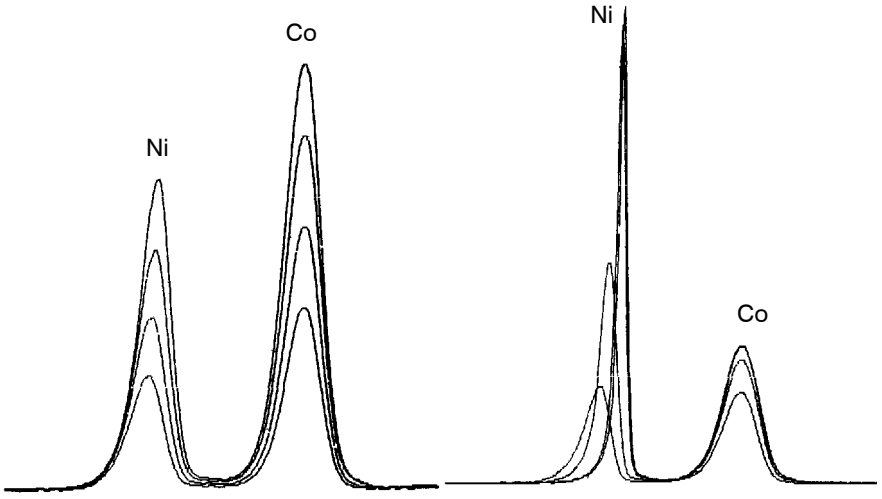
A **shorter deposition time** usually solves the problem. The following rule of thumb holds: In general, deposition should not be carried out except in solutions with a mass concentration $\rho < 0.5$ mg/L (= 0.5 ppm). In several cases work can be carried out without

deposition even with concentrations $\rho > 100$ µg/L (e.g. DP voltammetry at the HMDE or also at the DME).

The effects of a deposition time which is too long are shown by the following two examples:

- **Nickel and cobalt determination in the trace region by cathodic adsorption stripping voltammetry (with dimethylglyoxime complexes)**
  Prolongation of the deposition time from 30 s to 120 s (keeping all other measurement parameters constant) leads to non-linear standard additions and in the case of nickel also to shifts in the peak maximum:

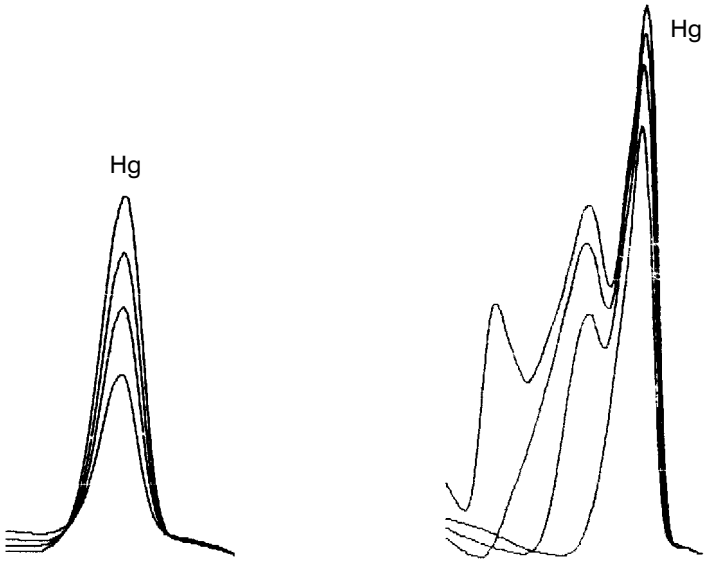
**Deposition time: 30 s** **Deposition time: 120 s**




| | |
|---|---|
| Analysis solution: | 20 µg/L Ni; 20 µg/L Co |
| Supporting electrolyte: | 0.1 mol/L $NH_4Cl/NH_3$; pH = 9.3 |
| | $5 \cdot 10^{-4}$ mol/L dimethylglyoxime (DMG) |
| Standard addition: | with 200 ng Ni / 200 ng Co |
| Electrode: | HMDE |

- **Mercury determination at the gold electrode**
  On prolongation of the enrichment time from 30 s to 240 s, side peaks appear during standard addition:

**Enrichment time: 30 s** **Enrichment time: 240 s**




| | |
|---|---|
| Analysis solution: | 100 µg/L Hg |
| Supporting electrolyte: | HClO4/HCl |
| Standard addition: | with 1 µg Hg |
| Electrode: | Au-RDE |

## Disturbances at the HMDE through gas formation

Gas formation at the HMDE during the deposition phase can lead to drop fall or to a contact break in the Hg capillary. The following example illustrates such a case:

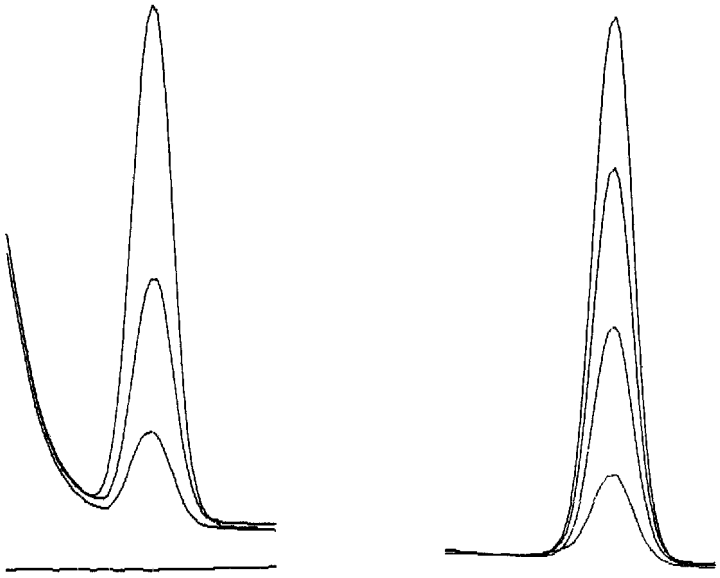
- **Determination of zinc in deionised water**
  If the zinc sample is acidified to pH 2 with $HClO_4$ or another acid, hydrogen is also formed at the voltage selected for enrichment. In the present example this leads to premature release of an Hg drop in the 2nd standard addition thus making an evaluation impossible. If acetate buffer (pH = 4.64) is used, no such difficulties arise. However, a requirement for this is that chemicals of the highest purity are used to keep the zinc blank value as low as possible (it is advisable to prepare the acetate buffer using ultrapure ammonia and ultrapure acetic acid).

**Supporting electrolyte: 0.01 mol/L HClO4; pH = 2**

Zn

**Supporting electrolyte: acetate buffer pH = 4.64**

Zn



Analysis solution: deionised water
Standard addition: with 50 ng Zn
Electrode: HMDE (enrichment 60 s at –1.2 V)

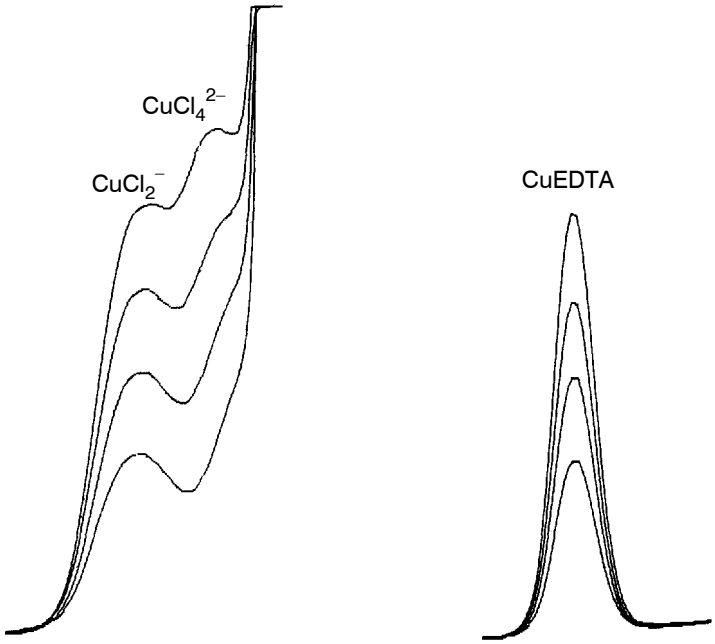
## Complex formation

Substances determined polarographically can occur in various complexed forms, depending on the composition of the analysis solution. As complexing is always associated with a shift in the half-wave potential and the limiting current, difficulties can arise in the peak evaluation. Such difficulties must be eliminated by appropriate changes in the composition of the supporting electrolyte.

If it is not possible to remove the interfering complexing agents from the analysis solutions or to mask them by suitable substances, it is often helpful to change the pH of the supporting electrolyte. Another measure that is often used involves the addition of a ligand of high complexing power (e.g. EDTA) to bring about 100% change of the analyte to a definitive form. The latter possibility is also used in the following example:

- **Copper determination in chloride-containing solutions**
  Copper can occur in chloride-containing solutions as both a $CuCl_4^{2-}$ and a $CuCl_2^-$ complex. The two associated current peaks are near each other. In unfavourable cases, the determination of copper is not possible. The difficulties disappear after addition of the complexing agent EDTA as now all copper is completely in the form of a Cu-EDTA complex. (Increasing the chloride concentration [e.g. by addition of 1 mL of a 1.5 mol/L KCl solution of the greatest possible purity per 10 mL analysis solution] would also give a clearly defined current peak for $CuCl_2^-$.)

**Supporting electrolyte: without EDTA** | **Supporting electrolyte: with EDTA (0.001 mol/L)**




| | |
|---|---|
| Analysis solution: | 25 µg/L Cu; 10 µL HCl 30% |
| Standard addition: | with 250 ng Cu |
| Electrode: | HMDE (enrichment 90 s at –600 mV) |

## Peak on highly curved baseline

If peaks lie on a highly curved baseline, the first attempts at rectification should involve chemical or measurement technique countermeasures to eliminate the adverse effect on the peak evaluation due to the highly curved baseline. Such measures include longer purging times (see *Oxygen interference*, *section 9.6*), changing the pH value, changing the supporting electrolyte concentration, modifying or changing the supporting electrolyte, use of complexing agents (see *Complex formation*, *section 9.6*), longer deposition times and changing the measurement technique.

If the curvature of the baseline can not or only partially be eliminated by the above measures, the 797 VA Computrace offers the possibility to approximate a curved baseline by selecting **Polynomial** or **Exponential** for the baseline **Type** (see *Baseline, section 5.2*).

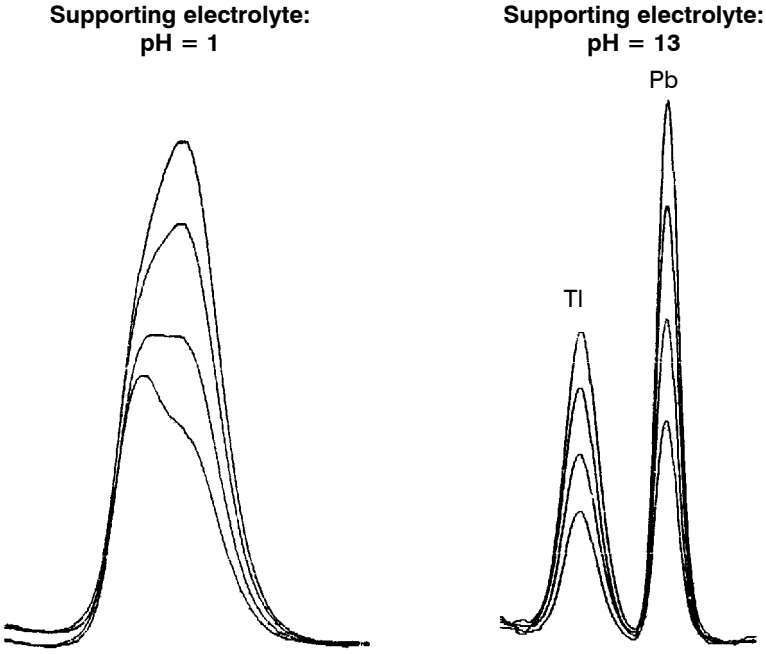
A further possibility to evaluate peaks on curved baselines involves the background subtraction after measuring a blank solution, in particular when the curved baseline can be clearly attributed to the supporting electrolytes (see *Determination, section 5.2*).

## Peak overlapping

If the peak overlapping has reached a critical level at which the calculated peak height or peak area is falsified by the neighboring peak, it is advisable to take the overlapping into account by a change in the baseline calculation. For this, select the **Front end** or **Rear end** option for the baseline **Scope** (see *Baseline, section 5.2*).

If the overlapping is too large, the peak can no longer be evaluated. In this case chemical or measurement technique countermeasures must be used to attempt to separate these peaks better. Possible measures include changing the pH value, changing the supporting electrolyte concentration, changing the supporting electrolyte, use of complexing agents (see *Complex formation*, *section 9.6*), longer deposition times and modifying or changing the measurement technique.

- **Determination of lead and thallium**
  With a supporting electrolyte of pH = 1, Pb and Tl peaks overlap greatly. Changing the pH to 13 separates the two peaks. (The separation of lead and thallium can also be achieved by subsequent electrolysis or in acetate buffer with EDTA).




| | |
|---|---|
| Analysis solution: | 0.5 mg/L Pb; 1 mg/L Tl |
| Standard addition: | with 10 µg Pb and 10 µg Tl |
| Electrode: | SMDE |

## Calibration with chemically non-isoformal standards

With all possible **Calibration** techniques, it must be ensured that the standards used for calibration are chemically isoformal with the analytes. The standard substances must therefore have the same valency (e.g. with Fe, Al) or complex formation form (e.g. with As, Cr, Se) as the substances already present in the analysis solution. If this is not the case the calibration can produce completely wrong results owing to the different peak voltages and sensitivities.

## Results not reproducible

Voltammetric measurements (including CVS and CPVS!) strongly depend on the temperature.

To get reproducible results, the following points have to be considered:

- Avoid strong temperature fluctuations in the laboratory.
- Do not place the instrument directly below an air conditioning outlet.
- If required, use a thermostatic measuring cell with connection to a thermostat/cryostat.

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# Declaration of conformity – Software validation

The software "797 VA Computrace" was developed in accordance with the requirements of the ISO 9001 quality system regarding the design, testing and servicing of Metrodata software. The relevant procedures are described in the document "Project procedure for creating Metrodata software" which is available at your Metrohm agency on request.

The software was validated with respect to functionality, analytical performance and accuracy of results. The technical specifications and software functions are described in the Instructions for Use.

Herisau, 08. June 2007

D. Strohm

Vice President
Head of R&D

Ch. Buchmann

Production and
Quality Assurance Manager

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