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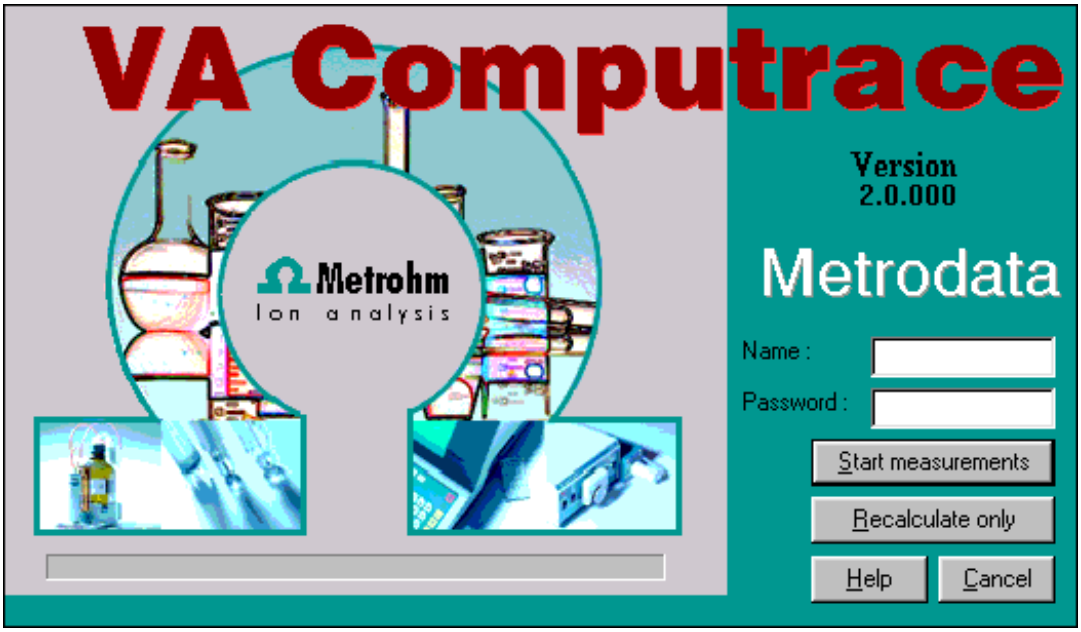
2.757.01X0

757 VA Computrace



8.757.8023 Software Manual

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Table of contents

1 Introduction

1.1 Purpose of program

«VA Computrace 2.0» is the name of the control software for the PC-controlled 757 VA Computrace System for voltammetric analysis. This system consists of the following parts:

1.757.0010 **VA Computrace Stand** with accessories

3.757.1300 **Add-on Board for PC** or
6.5326.000 **VA Computrace Interface**

6.2135.010 **Connecting Cable**

6.6032.100 **VA Computrace Software 2.0**

For a detailed description of the hardware components of the 757 VA Computrace System see the **757 Hardware Manual**.

This **757 Software Manual** describes the features and operation procedures of the 757 VA Computrace Software 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 757 VA Computrace Software 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 seven 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. 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 II with 233 MHz or higher
Operating system	Windows™ 98 or Windows™ 2000 for operation with add-on board; Windows™ 2000 for operation with VA Computrace Interface (USB)
Free space on hard disk	10 MB for program files 100 MB recommended for data files
Working memory RAM	64 MB for Windows™ 98 128 MB for Windows™ 2000
Graphics resolution	1024×768 or more
Interface	1 free ISA slot for add-on board or 1 free USB connection for VA Computrace Interface
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 6.6032.100 VA Computrace Software 2.0 is installed on a PC without installation of VA Computrace Stand and Add-on board or VA Computrace Interface, 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 **8.757.1027 Registration card** as soon as possible. Only registered users will get updated program versions at a special price.

1.3 Installation

Installation of software and VA Computrace Interface

1. Switch on PC and start operating system (Windows™ 2000) without connection of the VA Computrace Interface 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 "**757**" and follow the instructions given in the setup program. Select the **VA Computrace Interface (USB)** option for the interface type.
5. The software package will be installed in the desired directory (the default directory is **Programs/Metrohm/757 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**).

   Demo data
   Folder containing signal and determination file examples. The subfolder **Practical Voltammetry** contains all examples of the **8.757.5003 Metrohm Monograph "Practical Voltammetry"**, which is available from Metrohm on request.

   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 **Hardware Test**.

   Hardware
   Folder for hardware control files and drivers.
6. Restart the PC.
7. Connect VA Computrace Interface to the 757 VA Computrace using the **6.2135.010 cable** and switch on 757 VA Computrace Stand.
8. Connect VA Computrace Interface to the **6.2158.000 Mains Adapter** connected to the mains.
9. Connect VA Computrace Interface 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.
10. Start the VA Computrace software.

Installation of software and add-on board

1. Switch off PC and disconnect power cable from the power socket.
2. Disconnect all other cables to computer peripherals (keyboard, display, printer, etc.).
3. Disassemble PC and install **3.757.1300 Add-on Board** in a free ISA slot (see instruction manual of the PC).
4. Reassemble PC.
5. Switch off 757 VA Computrace Stand.
6. Connect the built-in add-on board to the "PC Interface" socket of the 757 VA Computrace Stand with the **6.2135.010 cable**.
7. Switch on 757 VA Computrace Stand and PC and start operating system (Windows™ 98 or Windows™ 2000).
8. Insert installation CD into CD drive.
9. 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>**.
10. Click on "**757**" and follow the instructions given in the setup program. Select the **Add-on Board (3.757.1300)** option for the interface type.
11. The software package will be installed in the desired directory (the default directory is **Programs/Metrohm/757 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**).

    Demo data
    Folder containing signal and determination file examples. The subfolder **Practical Voltammetry** contains all examples of the **8.757.5003 Metrohm Monograph "Practical Voltammetry"**, which is available from Metrohm on request.

    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 **Hardware Test**.

    Hardware
    Folder for hardware control files and drivers.
12. Restart the PC.
13. Start the VA Computrace software.

Software upgrade with add-on board

If you want to upgrade from the 757 VA Computrace 1.0 software to the 757 VA Computrace 2.0 software on a PC with add-on board installed, proceed as follows:

1. Switch off 757 VA Computrace Stand.
2. Switch on PC and start operating system (Windows™ 98 or Windows™ 2000).
3. Select **<Start>** / **Settings** / **Control** panel and double-click the **Software** icon.
4. Select 757 VA Computrace in the list and click on **<Add/remove>** to remove the VA Computrace 1.0 program. All program files and icons are removed, all user-created method and data files are retained in the **Data** and **Method** folder of the program directory.
5. Restart the PC.
6. Insert installation CD into CD drive.
7. 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>**.
8. Click on "**757**" and follow the instructions given in the setup program. Select the **Add-on Board (3.757.1300)** option for the interface type.
9. The software package will be installed in the desired directory (the default directory is **Programs/Metrohm/757 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**).

   Demo data
   Folder containing signal and determination file examples. The subfolder **Practical Voltammetry** contains all examples of the **8.757.5003 Metrohm Monograph "Practical Voltammetry"**, which is available from Metrohm on request.

   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 **Hardware Test**.

   Hardware
   Folder for hardware control files and drivers.
10. If desired, copy all user-created method and data files of the old program directory into the **Method** and **Data** folders of the new program directory.

11. Restart the PC.
12. Connect the built-in add-on board to the "PC Interface" socket of the 757 VA Computrace Stand with the **6.2135.010 cable** and switch on 757 VA Computrace Stand.
13. Start the VA Computrace 2.0 software.

Installation of Dosimats

Up to five **665** or **765 Dosimats** can be connected to the 757 VA Computrace Stand. For the connection of 1 or 2 Dosimats, the 6.2141.080 Cable is used. Other cables for the connection of more than 2 Dosimats are available from Metrohm on request (e.g. 6.9921.170 for 5 Dosimats). For the connection of two Dosimats, proceed as follows:

1. Switch off the 757 VA Computrace Stand.
2. Switch off the Dosimats.
3. Connect the "**A**" socket of the first Dosimat to the "**Remote**" socket of the 757 VA Computrace Stand with the **6.2141.080 cable** by using the cable end "**665-1**".
4. Connect the "**A**" socket of the second Dosimat to the "**Remote**" socket of the 757 VA Computrace Stand with the **6.2141.080 cable** by using the cable end "**665-2**".

Note: If Dosimats are connected to the 757 VA Computrace Stand, the instruments must always be switched on in the sequence Dosimats → 757 → PC.

Installation of 813 Compact Autosampler

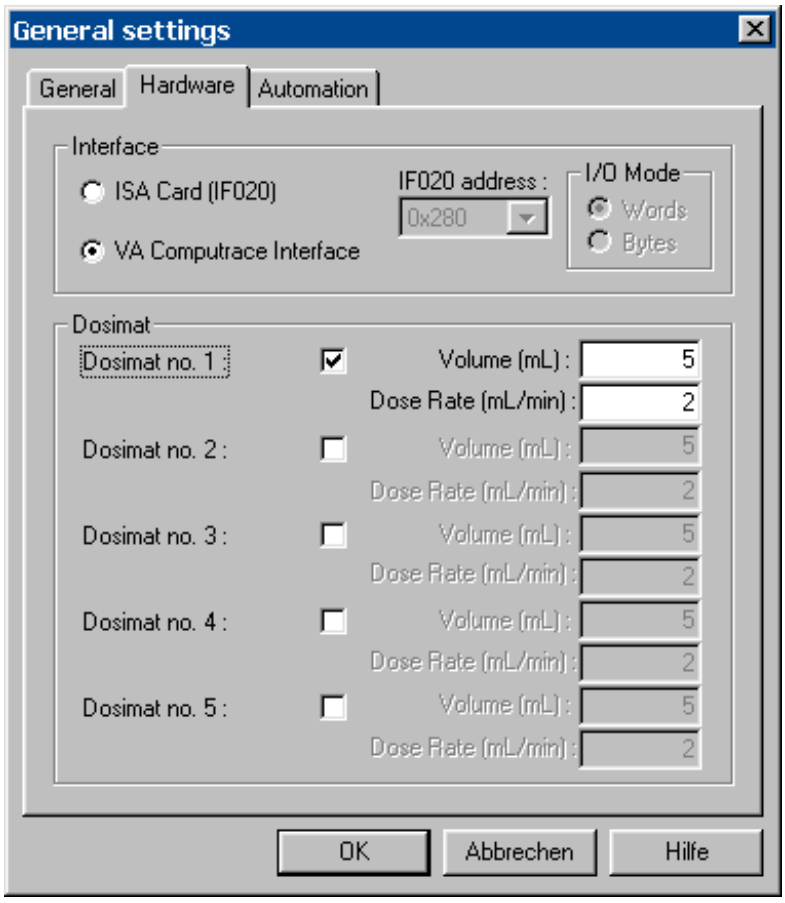
It is possible to connect a **813 Compact Autosampler** and a **731 Relay Box** (for the operation of two **772 Pump Units**) to the 757 VA Computrace Stand. Proceed as follows:

1. Connect 813 Compact Autosampler, 731 Relay Box and two 772 Pump Units to the 757 VA Computrace Stand using the 6.2141.150 cable (see *813 Instructions for Use*).
2. Install the accessories on the 813 Compact Autosampler (see *813 Instructions for Use*).
3. Connect 665 or 765 Dosimats to the 757 VA Computrace Stand (see *813 Instructions for Use*).
4. Set **Method 2** at the 813 Compact Autosampler (see *813 Instructions for Use*).

5. Make hardware settings for the 813 Compact Autosampler (see *Automation*, *section 2.7*).
6. Make hardware settings for Dosimats (see *Hardware settings for Dosimats*).
7. Define the addition or predose solution in the **DOSIMATS** window (see *Dosimats*, *section 5.2*).

Hardware settings for Dosimats

1. Switch on PC and start operating system 95.
2. Start the VA Computrace software by double-clicking the program icon or starting the **ct757.exe** file.
3. Login without entering **Name** and **Password**. Click on **Recalculate only**.
4. Select **MAIN WINDOW** / **Settings** / **General Settings.** Open the **Hardware** tab in the **GENERAL SETTINGS** window:



5. For each 665 or 765 Dosimat connected to the remote interface of the 757 VA Computrace Stand, check the **Dosimat no.** checkbox and enter the **Volume** of the exchange unit installed on the Dosimat and the **Dose rate** of the Dosimat.

6. Close the VA Computrace software by clicking on  or selecting **File** / **Exit**.
7. Switch on the Dosimats connected to the 757 VA Computrace Stand.
8. Switch on 757 VA Computrace stand.
9. Restart the VA Computrace software.

Note: If Dosimats are connected to the 757 VA Computrace Stand, the instruments must always be switched on in the sequence Dosimat → 757 → PC.

Deinstallation

1. Select **<Start>** / **Settings** / **Control panel.**
2. Double-click the **Software** icon.
3. Select **757 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

VA Computrace 2.0 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 and curve evaluation

EXPLORATORY CURVES Display of exploratory mode curves

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 the **Use Autosampler** option is checked on the **Automation** tab of the **GENERAL SETTINGS** window).

COMPUTRACE CONTROL Manual control of 757 VA Computrace Stand

DOSIMAT CONTROL Manual control of 665 or 765 Dosimats connected to the remote interface

FILM DEPOSITION Manual control of Hg film deposition on solid state electrodes

CLEANING PROCEDURE Manual control of cleaning procedures for solid state electrodes

1.5 Overview of file types

The following file types are produced by the 757 VA Computrace software:

***.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 tabe file** (binary file)
Contains sample tabel data.

***.txt** **Text file** (ASCII file) for data export
A ***.txt** file is produced if measurement points of determination files or signal files are exported.
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 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.

1.6 Context sensitive menus

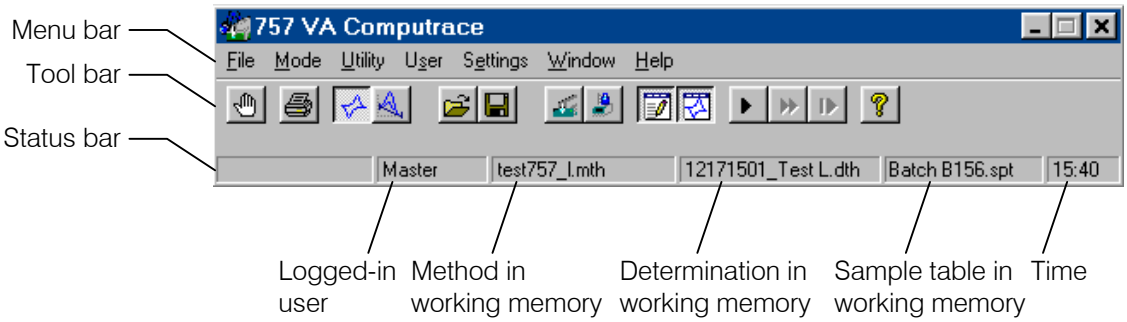
Most of the menu functions of the program windows are also accessible by clicking on the desired window or item and pressing the **right mouse button**. The pop up windows have different contents and functions depending on the selected active window or item type.

2 Main window

2.1 Main window overview

Main window elements

The **MAIN WINDOW** is the center of the VA Computrace software. 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
Mode	Switching between exploratory and determination mode
Utility	VA Computrace Stand control; Dosimat control; film deposition and cleaning procedure for solid state electrodes
User	Login, user rights entry and overview
Settings	General settings for saving, default directories, add-on board, VA Computrace Interface and Dosimats
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 2.0 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 757 VA Computrace Stand.


Manual control of Dosimats connected to the 757 VA Computrace Stand.


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.

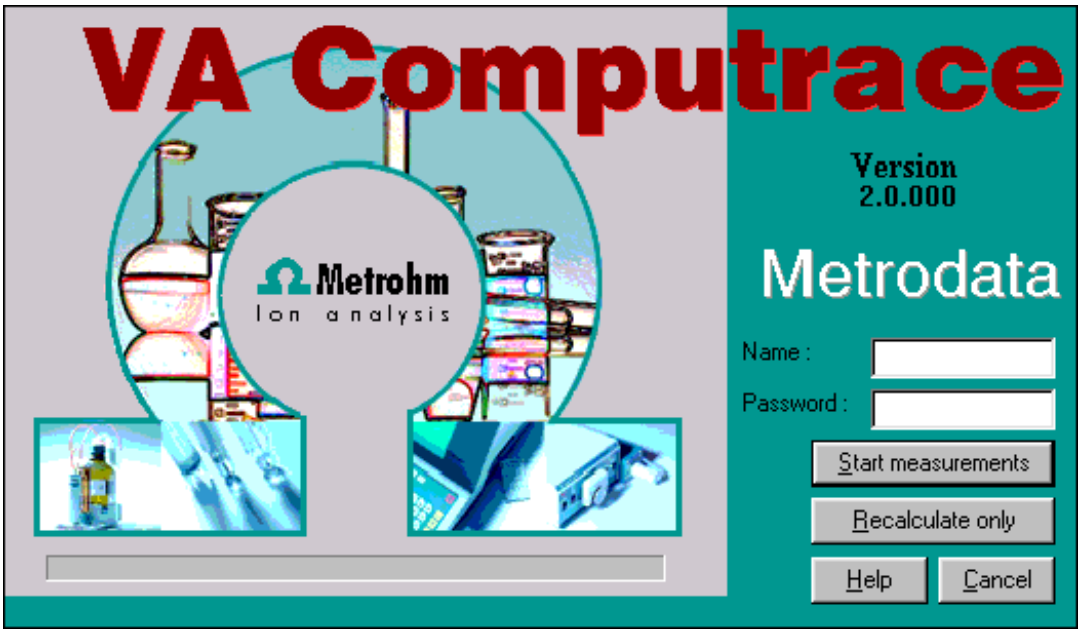

Go to next step in operation sequence.

2.2 Starting/closing the program

Starting the VA Computrace program

Start the Program

Double-click the **757 VA Computrace** icon or the **Ct757.exe** file to start the VA Computrace 2.0 program. The **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*.

Closing the VA Computrace program

MAIN WINDOW / File / Exit

Exit the VA Computrace 2.0 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 DP 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. If the method has been changed since loading, the message **The file already exists. Overwrite?** appears. Click **Yes** to overwrite the method file or **No** to cancel saving.

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.

757 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. If the determination has been changed since loading, the message **The file already exists. Overwrite?** appears. Click **Yes** to overwrite the determination file or **No** to cancel saving.

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.

757 VA COMPUTRACE / File / Export results ...

Save the results report of the current determination loaded in the working memory into an ASCII file (extension ***.txt**). This file can be imported into spreadsheet programs like Microsoft Excel.

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* for exploratory mode and *section 5.7* for determination mode).

MAIN WINDOW / File / Printer setup

Selection of a printer and definition of paper size and format.

Program exit

MAIN WINDOW / File / Exit

Quit the VA Computrace 2.0 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 recording and displaying of determinations (see *section 5*).

2.5 Utility menu

Computrace control selection

MAIN WINDOW / Utility / Computrace control

Start manual control of 757 VA Computrace Stand (details see *section 6.1*).

Dosimat control selection

MAIN WINDOW / Utility / Dosimat control

Start manual control of 665 or 765 Dosimats connected to the 757 VA Computrace Stand (details see *section 6.2*).

Film deposition selection

MAIN WINDOW / Utility / Film deposition

Start Hg film deposition for solid state electrodes in the 757 VA Computrace Stand (details see *section 6.3*).

Cleaning procedure selection

MAIN WINDOW / Utility / Cleaning procedure

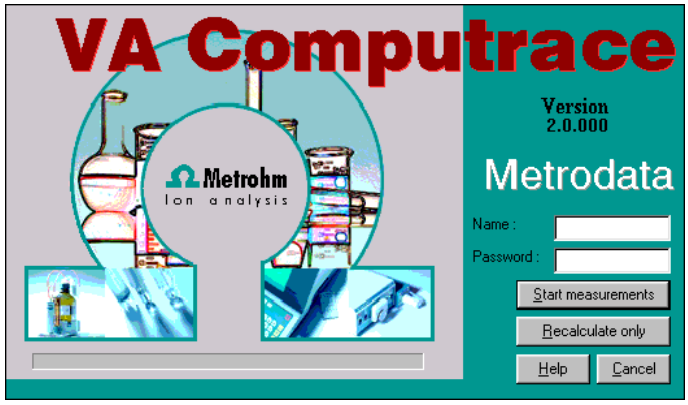
Start cleaning procedure for solid state electrodes in the 757 VA Computrace Stand (details see *section 6.4*).

2.6 User menu

Login

MAIN WINDOW / User / Login

The **VA COMPUTRACE LOGIN** window appears.



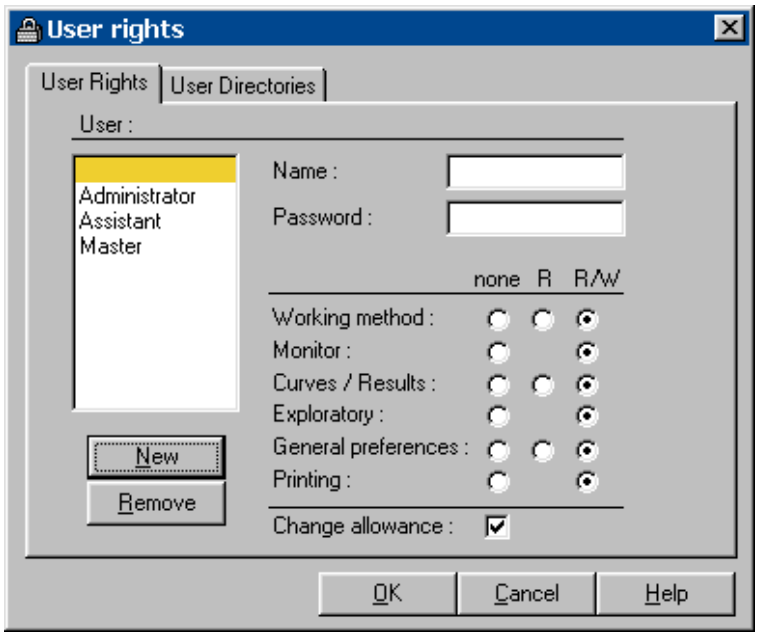
Enter the desired **Name** and **Password** to login as a new user and click **OK**.

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.



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.

Master

Access to all program parts, but no allowance to change the user rights.

Assistant

Limited access for loading and running existing determination methods.

" " (empty)

same as **Administrator**

Name

Display of user name (read only). This name is inserted in the **User** field of all reports and results windows. For addition of a new user name click the **<New>** button.

Password

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.

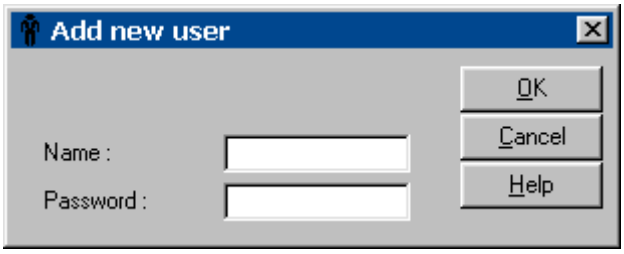
R/W Permission to read/write in this program part.

Change allowance

Permission to edit the user rights.

New

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



Name [13 characters;]

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

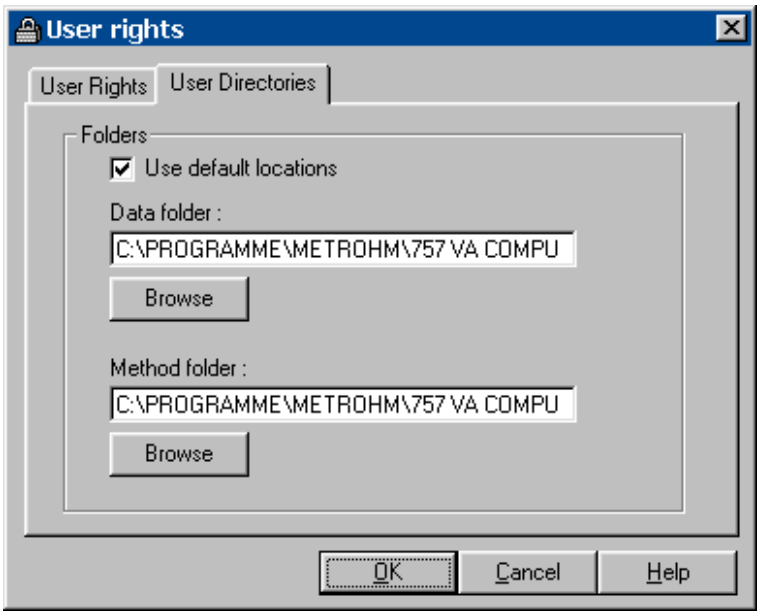
Password

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

Remove

Remove a user from the users list.

Note: Make sure not to remove all users with the **Change allowance** option enabled, otherwise the **USER RIGHTS** window cannot be opened again and the program has to be reinstalled.



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.

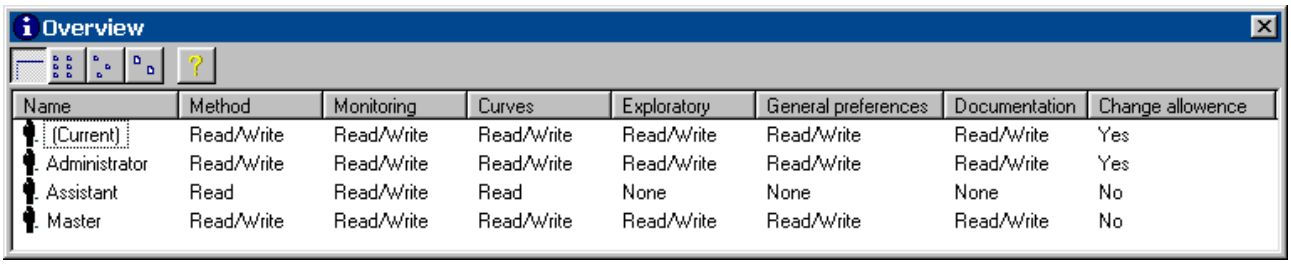
Method folder

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.

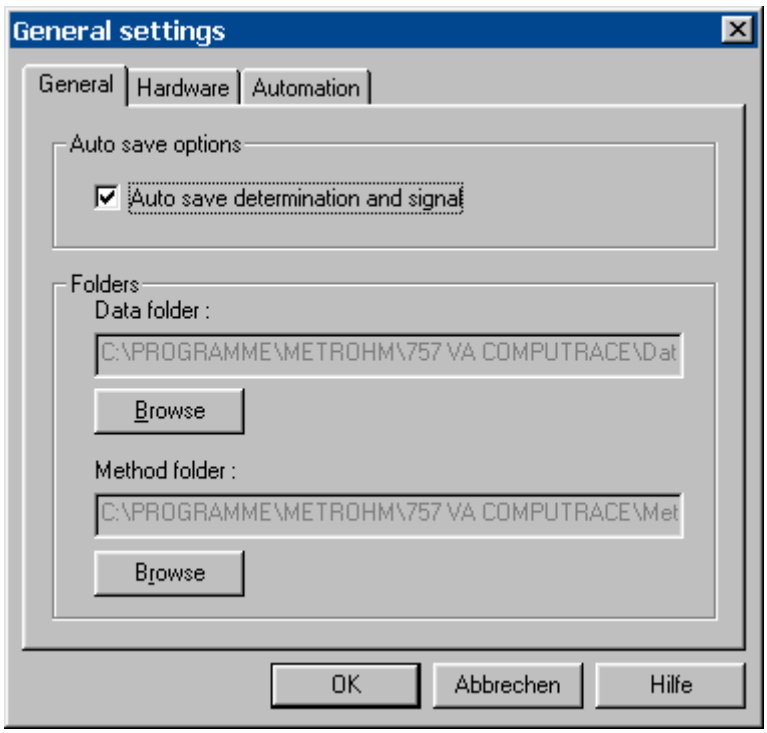
 Help.

2.7 Settings menu

General settings

MAIN WINDOW / Settings / General Settings

In the **GENERAL SETTINGS** window default settings for autosaving and storage directories can be defined with the **General** tab.



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 after the end of the measurement.

Folders

Selection of default directories.

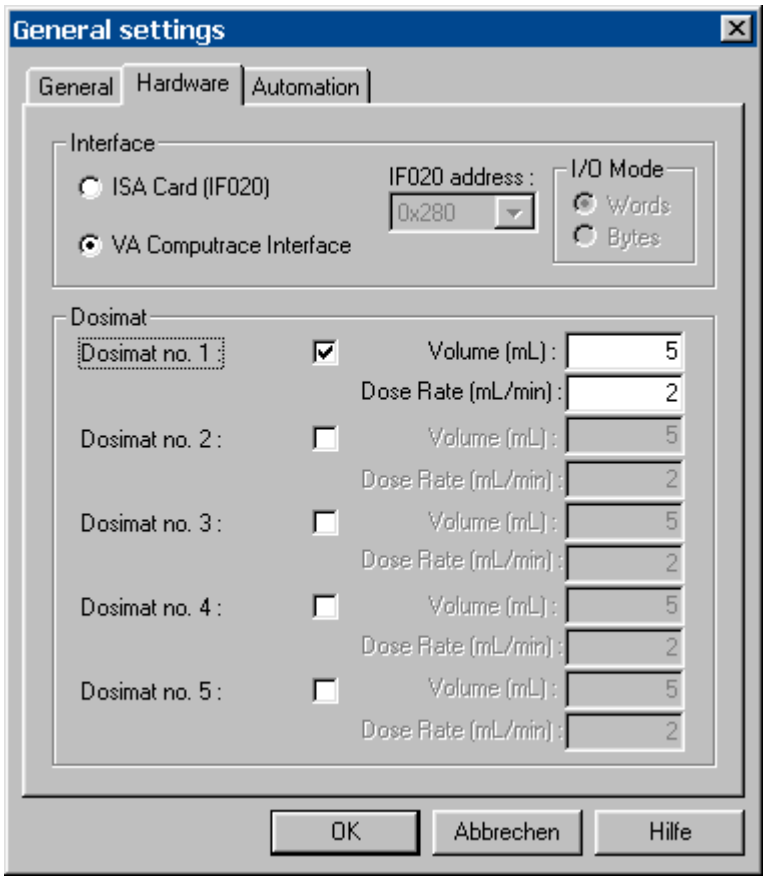
Data folder
Default directory for storage of signal files (***.sig**) and determination files (***.dth**). For changing an existing entry, use the **<Browse>** button.

Method folder
Default directory for storage of method files (***.mth**). For changing an existing entry, use the **<Browse>** button.

Hardware settings

MAIN WINDOW / Settings / General Settings

In the **GENERAL SETTINGS** window default settings for the add-on board, the VA Computrace Interface and the Dosimats can be defined with the **Hardware** tab.



Interface

Selection of the interface used to operate the 757 VA Computrace:

ISA Card (IF020)
3.757.1300 Add-on board

VA Computrace Interface
6.2155.000 VA Computrace Interface

IF020 address

IP address of the add-on board.

I/O Mode

Input/Output transfer mode for add-on board. The default setting is **Words** (16-bit communication). If the add-on board does not work, use the **Bytes** (8-bit communication) setting.

Dosimat

Settings for the 665 or 765 Dosimats connected to the remote interface of the 757 VA Computrace Stand (details see *section 1.3*).

Dosimat no. [on, off; off]
Check this checkbox for each Dosimat connected.

Volume (mL) [1, 5, 10, 20, 50 mL; 5 mL]
Volume of the exchange unit of the Dosimat

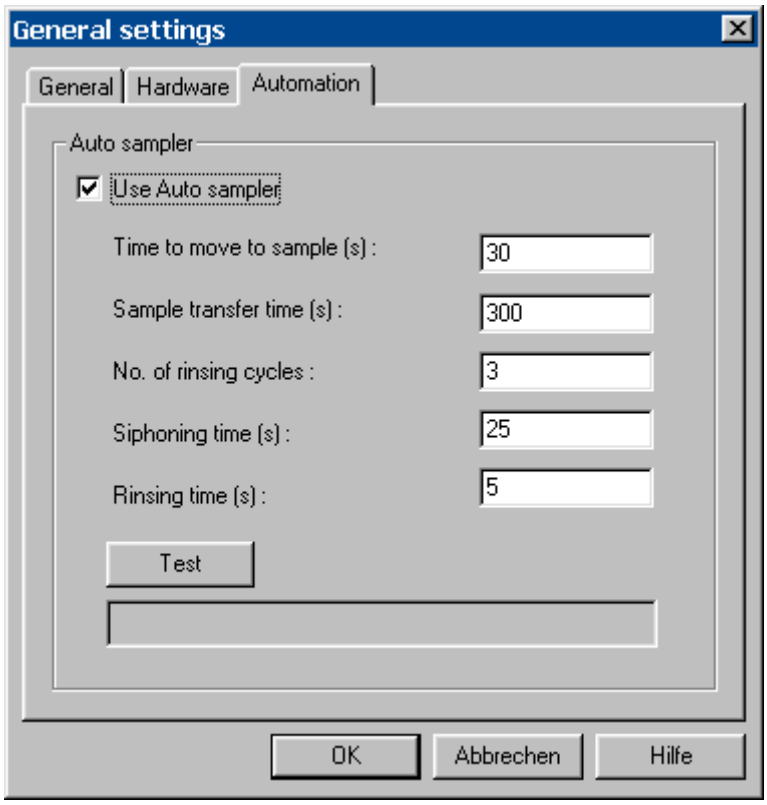
Dose rate (mL/min) [0.001 ... 150 mL/min (depending on exchange unit)]
Dosing rate of the Dosimat.

Note: If Dosimats are connected to the 757 VA Computrace Stand, the instruments must always be switched on in the sequence Dosimat → 757 → PC.

Automation

757 VA COMPUTRACE / Settings / General Settings

In the **GENERAL SETTINGS** window default settings for the operation of the **813 Compact Autosamplers** and two **772 Pump Units** can be defined with the **Automation** tab.



Use Autosampler

Enable/disable the use of the 813 Compact Autosampler. If this option is disabled, the **SAMPLE TABLE** window will not be available.

Note: **Method 2** must be set on the 813 Compact Autosampler.

Time to move to sample (s) [30 s ; 25 ... 2147483647 s]
Maximum time needed for the 813 Compact Autosampler to move from one sample to the other. (minimum time allowed: **25 s**).

Sample transfer time (s) [300 s ; 30 ... 2147483647 s]
Time to transfer the sample solution from the sample vessel to the measurement vessel using the peristaltic pump of the 813 Compact Autosampler (minimum time allowed: **30 s**).

No. of rinsing cycles [3 ; 0 ... 2147483647]
Number of rinsing cycles.

Siphoning time (s) [25 s ; 0 ... 2147483647 s]
For each rinsing cycle, the measuring vessel is siphoned off during this time using a 772 Pump Unit.

Rinsing time (s) [5 s ; 0 ... 2147483647 s]
For each rinsing cycle, the measuring vessel is rinsed during this time using a 772 Pump Unit.

Test the 813 Compact Autosampler with the set automation parameters.

Note: Before starting the test, switch on the 813 Compact Autosampler, set **Method 2** at the Autosampler and place two sample vessels filled with water on the sample rack.

For details on the use of the 813 Compact Autosampler, see *813 Instructions for Use*.

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*).

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

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

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

757 VA COMPUTRACE / Window / Sample table (F10)
The **SAMPLE TABLE** window will be opened or (if it is already open) closed (see *section 5.6*).

MAIN WINDOW / Window / Exploratory specification (F11)
The **EXPLORATORY SPECIFICATION** window will be opened or (if it is already open) closed (see *section 4.2*).

MAIN WINDOW / Window / Exploratory curves (F12)
The **EXPLORATORY CURVES** window will be opened or (if it is already open) closed (see *section 4.3*).

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 757 VA Computrace Stand. It combines the most important polarographic and voltammetric mercury electrodes in a single construction:

DME Dropping mercury electrode

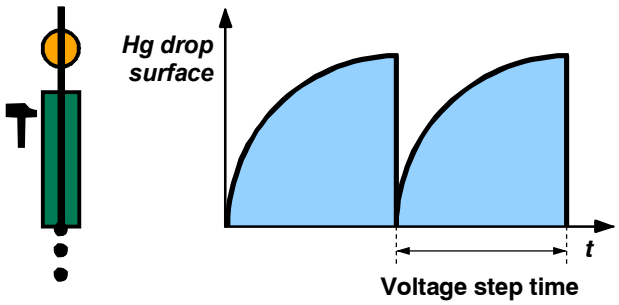
SMDE Static mercury drop electrode

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:

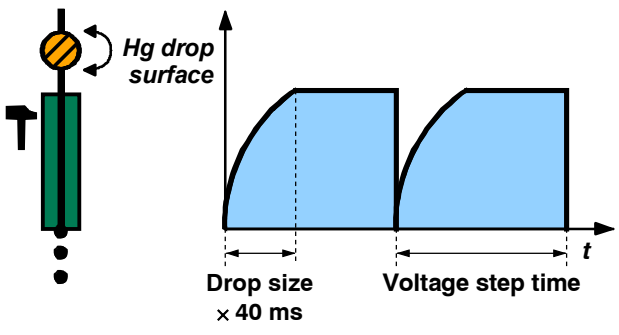
- In the exploratory mode, the DME can be used for all measurement modes except SqW, CV and PSA. In the determination mode, the DME can be used for all measurement modes except DC, SqW, CV and PSA.
- An advantage of the DME compared with the SMDE is that the MME capillary is subjected to less mechanical 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:

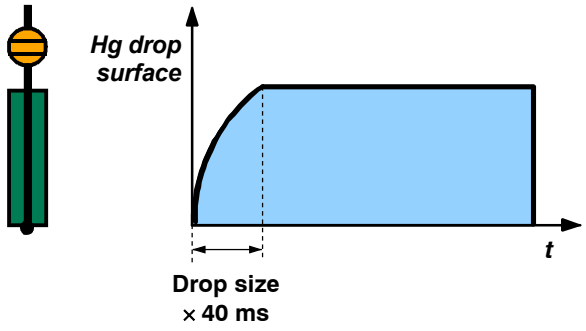
- In the exploratory mode, the SMDE can be used for all measurement modes except SqW, CV and PSA. In the determination mode, the SMDE can be used for all measurement modes except DC, SqW, CV and PSA.
- An advantage of the SMDE compared with the DME is its greater sensitivity as the electrode surface 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:

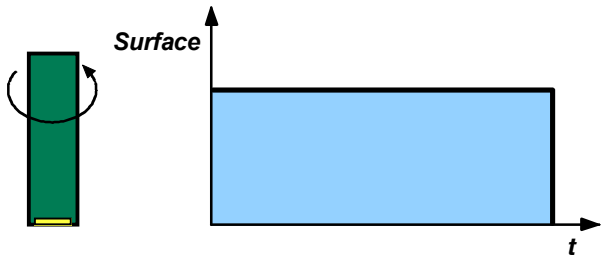
- The HMDE can be used for all measurement modes.
- The HMDE is primarily used for very sensitive stripping voltammetry in which the analyte species is not measured until it has first been electrochemically enriched.

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 757 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

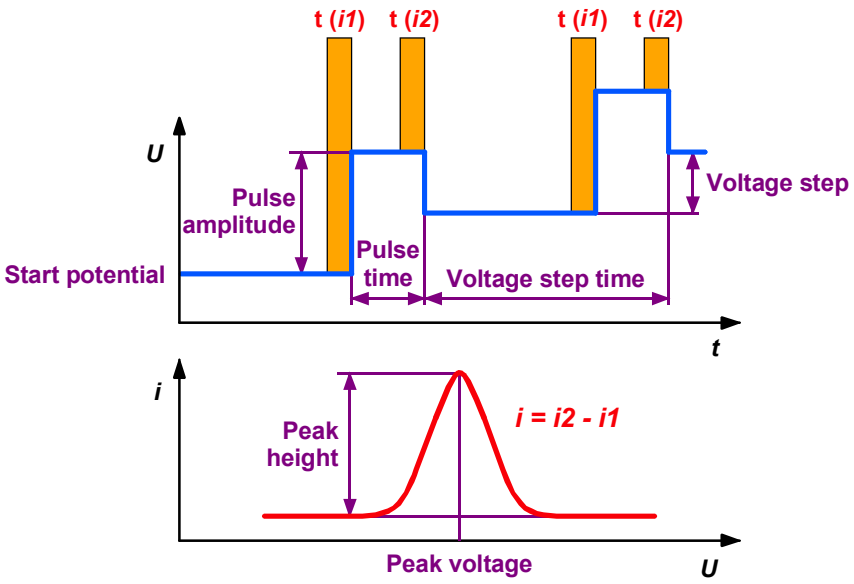
DP – Differential Pulse

General:

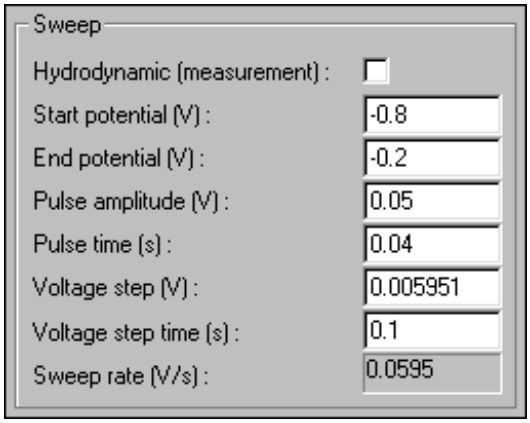
DP or **Differential Pulse voltammetry** is the most universal and frequently used voltammetric measurement mode. It is equally well suited for irreversible and reversible systems and offers a high sensitivity. The DP measurement mode can be set for the exploratory and determination mode by selecting **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 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 + 30 ms (DME)
  Voltage step time > Pulse time + Drop size × 40 ms + 10 ms (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  Pulse time ≥ 40 ms → t (*i*) = 20/16.67 ms (50/60 Hz)
  Pulse time < 40 ms → t (*i*) = 0.5 × Pulse time

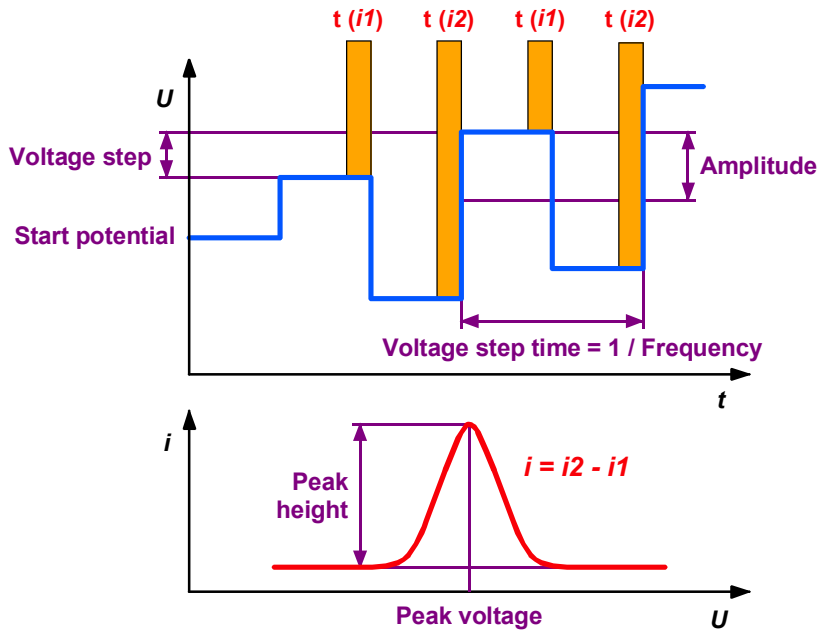
SqW – Square Wave

General:

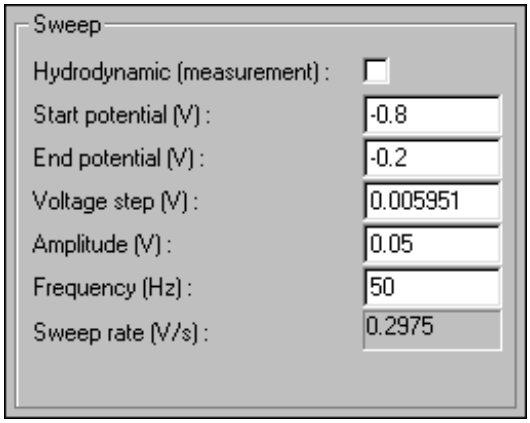
SqW or **Square Wave voltammetry** is primarly suitable for reversible electrode processes. It is used particularly for sensitive stripping voltammetric determinations at the HMDE or RDE. The SqW measurement mode can be set for the exploratory and determination mode by selecting **SqW - Square wave** 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, 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 ; 0.05 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.
- The following condition applies to the definition of the **Voltage step time**:
  Voltage step time = 1 / Frequency > 250 µs
- The measurement time **t (*i*)** is defined as follows:
  Voltage step time ≥ 80 ms → t (*i*) = 20/16.67 ms (50/60 Hz)
  Voltage step time < 80 ms → t (*i*) = 0.5 × Voltage step time

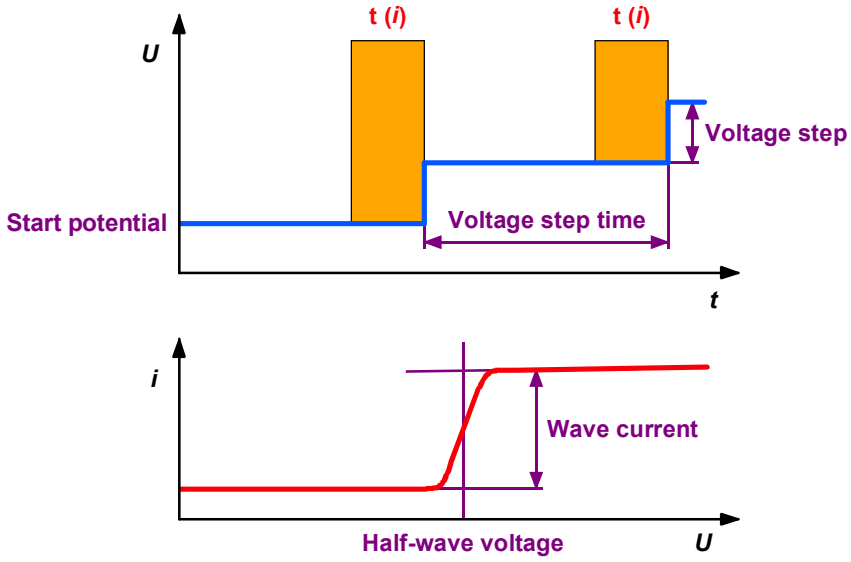
DC – Sampled Direct Current

General:

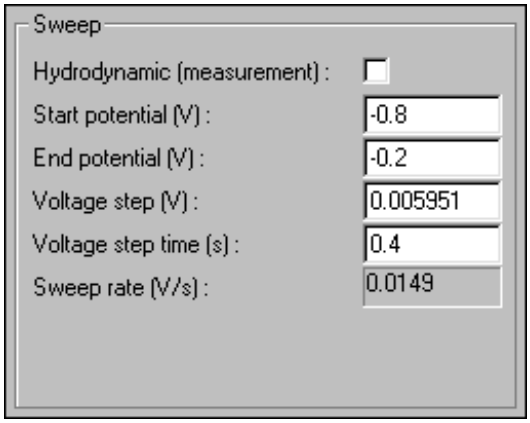
DC or **Sampled Direct Current voltammetry** is the classic, simplest voltammetric measurement mode with limited sensitivity. It is mainly used for the investigation of reversible redox systems. The DC measurement mode can be set for the exploratory and determination mode by selecting **DC - Sampled 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 > 20 ms (DME)
  Voltage step time > Drop size × 40 ms + 10 ms (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  t (*i*) = 20/16.67 ms (50/60 Hz)

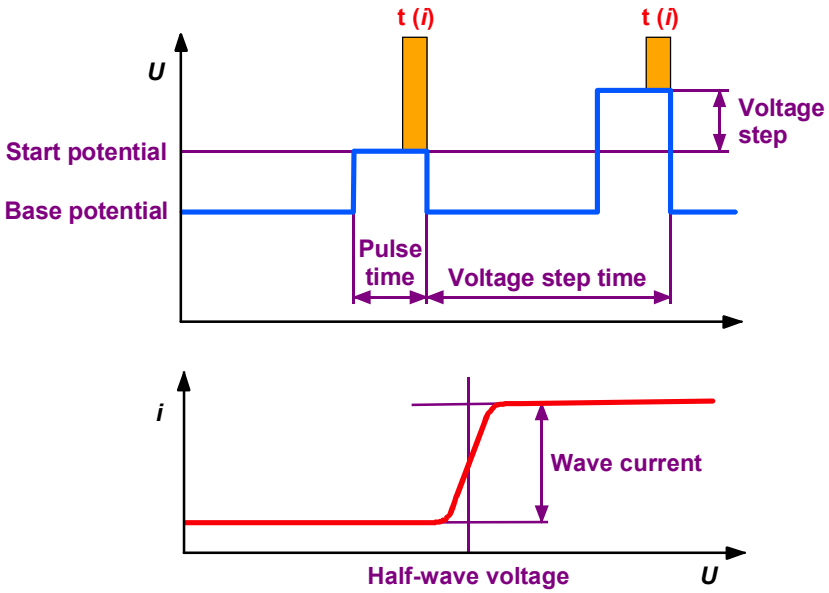
NP – Normal Pulse (for "Exploratory" only)

General:

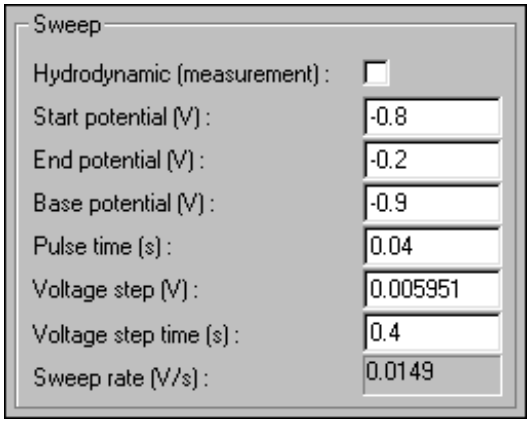
NP or **Normal Pulse voltammetry** is the classic pulse voltammetric measurement mode with direct recording of the current. It is equally well suited for irreversible and reversible systems and offers a higher sensitivity than the DC voltammetry. The NP measurement mode can only be set for the exploratory 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 ; -0.1 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.
- 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 + 30 ms (DME)
  Voltage step time > Pulse time + Drop size × 40 ms + 10 ms (SMDE)
- The measurement time **t (*i*)** is defined as follows:
  Pulse time ≥ 40 ms → t (*i*) = 20/16.67 ms (50/60 Hz)
  Pulse time < 40 ms → t (*i*) = 0.5 × Pulse time

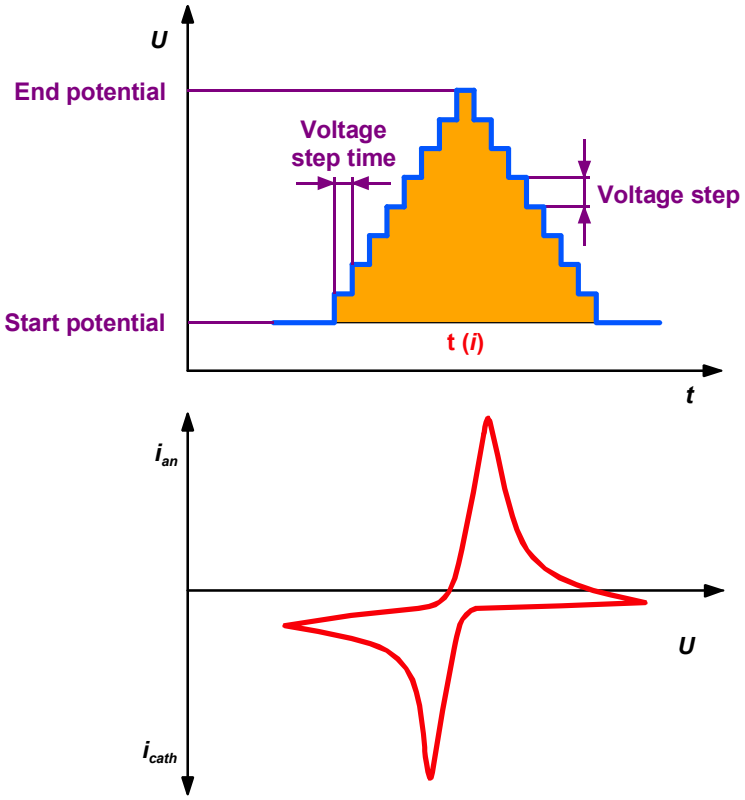
CV – Cyclic Voltammetry

General:

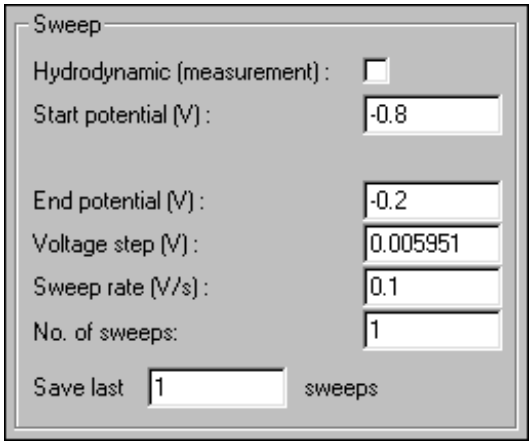
CV or **Cyclic voltammetry** is mainly used to investigate the reversibility of electrode processes and for kinetic studies. The CV measurement mode can be set for the exploratory and determination mode by selecting **CV - Cyclic voltammetry** for the **Mode** parameter in the **EXPLORATORY SPECIFICATION**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

Description:

For cyclic voltammetry, the voltage is once or several times changed at a rapid but 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 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.

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.

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

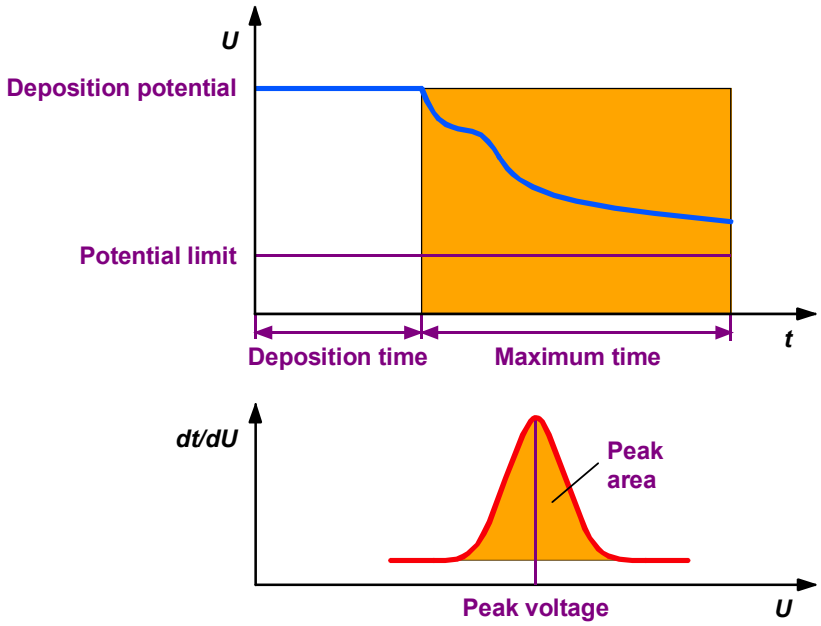
PSA – Potentiometric Stripping Analysis

General:

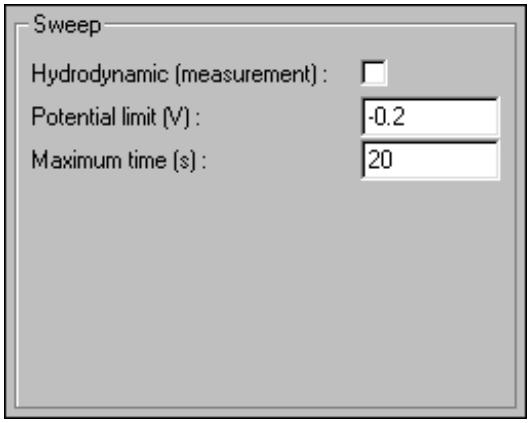
PSA or **Potentiometric stripping analysis** with chemical oxidation is mainly used to determine substances in an organic matrix with the aid of mercury film electrodes without prior digestion. The PSA measurement mode can be set for the exploratory and determination mode by selecting **PSA - Potentiometric 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 21.39 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 ; -0.1 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).

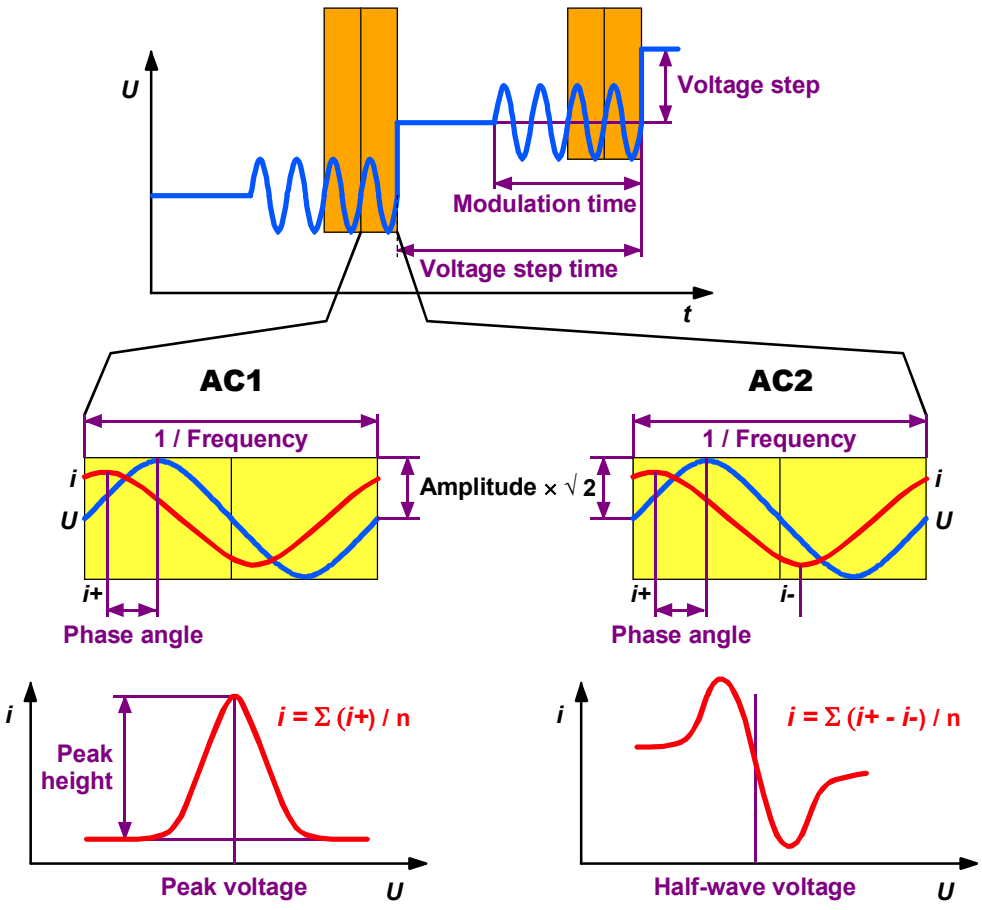
AC – Alternating Current Voltammetry

General:

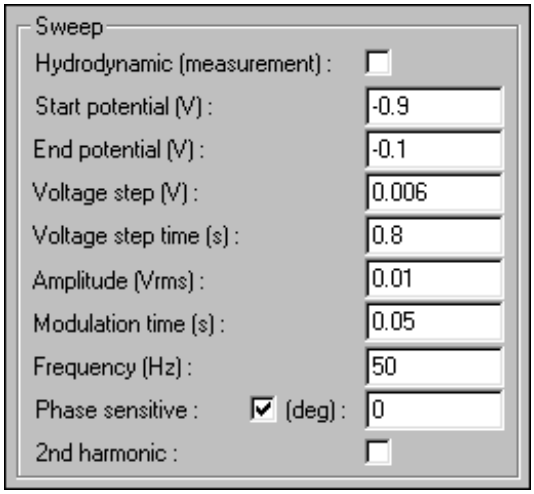
AC or **Alternating Current voltammetry** is primarly suitable for reversible electrode reactions. It is virtually completely insensitive to irreversible reactions. The AC measurement mode can be set for the exploratory and determination mode by selecting **AC - Alternating current voltammetry** for 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 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) [-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.

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**.

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°.

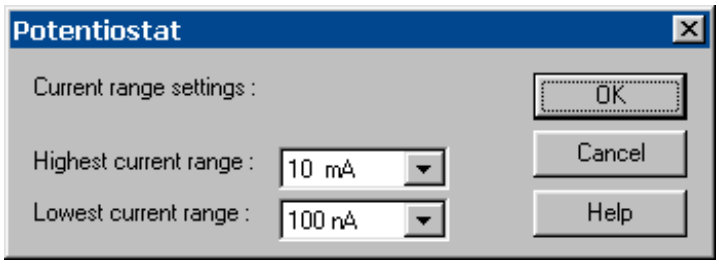
2nd harmonic [on, off ; off]
Enable/disable second harmonic current measurement (AC2).

Notes:

- The AC measurement mode can be used with all types of electrodes.
- The following condition applies to the definition of the **Modulation time**:
  Modulation time > 2 / Frequency
  Modulation time < voltage step time + 0.45 s
- The measurement time **t (*i*)** is defined as follows:
  t (*i*) = Modulation time / 2

3.3 Potentiostat

The potentiostat built-in in the 757 VA Computrace Stand normally works with full sensitivity for current measurements from 100 pA to 30 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, SqW or DC it may be sometimes helpful to limit the highest and/or lowest current range in order to avoid disturbing current leaps.



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

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

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. **Stirring**
   Optional stirring of the sample solution during preparation procedures until start of the equilibration time (details see *Stirring*).

2. **Purging**
   Optional purging of the sample solution during the **Initial purge time** (details see *Purging*).
3. **Drop formation**
   Hg drop formation at the MME if **DME**, **SMDE** or **HMDE** is selected (details see *Electrodes, section 3.1*).
4. **Conditioning cycles**
   Optional conditioning of solid state electrodes by applying cyclic conditioning sweeps (details see *Conditioning*).
5. **Cleaning**
   Optional cleaning of solid state electrodes by applying a cleaning potential during the **Cleaning time** (details see *Pretreatment*).
6. **Deposition**
   Optional electrochemical deposition for stripping voltammetry during the **Deposition time** (details see *Pretreatment*).
7. **Equilibration time**
   Optional waiting time before starting the sweep. During the **Equilibration time**, the stirring is switched off and the **Start potential** is applied to the electrodes (details see *Pretreatment*).
8. **Voltage sweep**
   Start of the voltage sweep which depends on the selected measurement mode (details see *VA measurement modes, section 3.2*).
9. **Stand-by potential**
   Optional apply of a **Stand-by potential** after the end of the voltage sweep (details see *Stand-by potential*).

Stirring

If switched on (**Stirrer > 0 rpm**), the solution in the sample vessel at the 757 VA Computrace Stand is stirred during all preparation procedure steps until the start of the equilibration time.

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

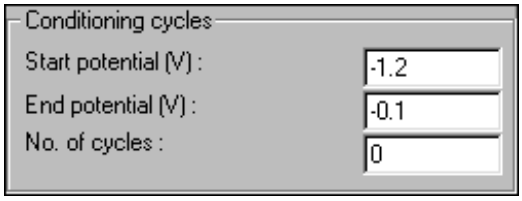
Purging

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 757 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]
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.

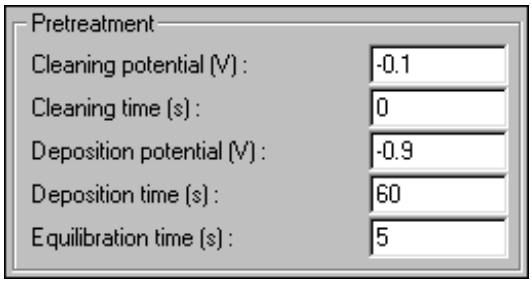
No. of cycles [0...X ; 0]
Number of conditioning cycles.

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.

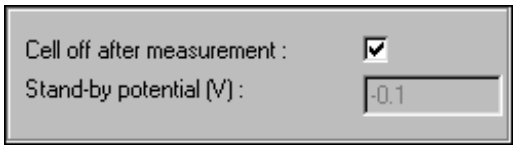
Deposition potential (V) [-5...+5 V ; -0.9 V]
Voltage applied to the electrodes during the **Deposition time**.

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 stirrer switched off and start potential applied to the electrodes.

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.



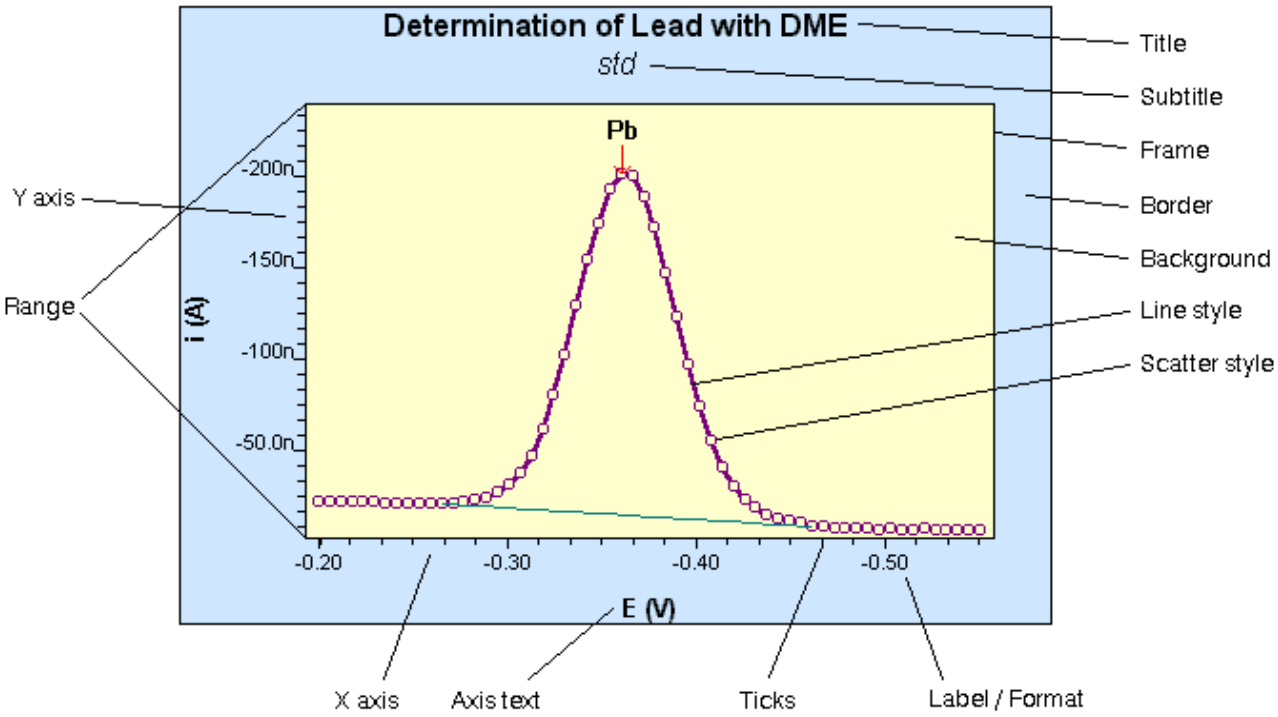
Cell off after measurement [on, off ; on]
Enable/disable the switching off of the voltage applied to the electrodes after measurement.

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 set to **off**.

3.5 Graphical settings

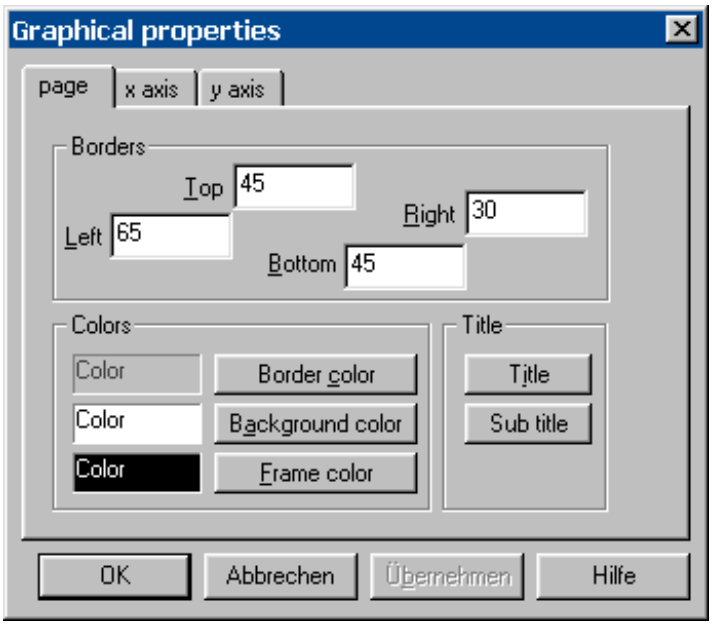
Curve window elements

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 ; 45 pt]

Left [≥ 0 pt ; 65 pt]

Right [≥ 0 pt ; 30 pt]

Bottom [≥ 0 pt ; 45 pt]
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.

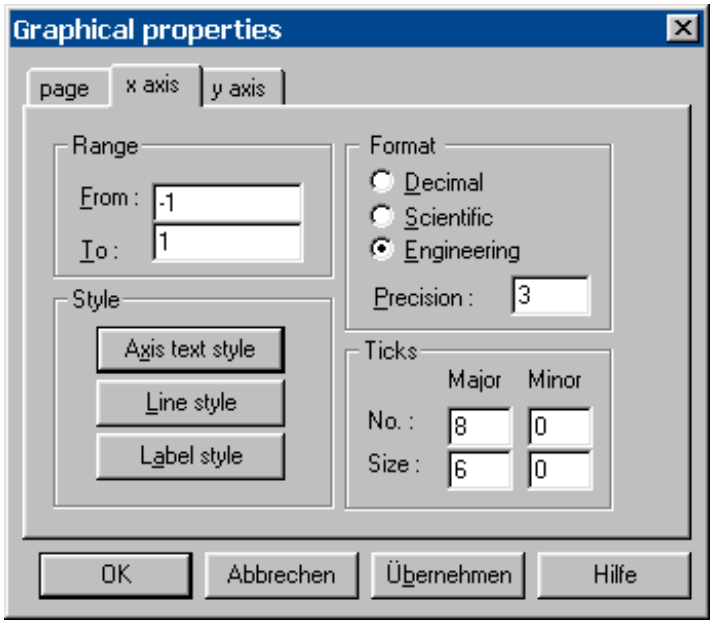
Title

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 V ; -1 V]
Lower limit for x axis (voltage).

To [-5...+5 V ; -1 V]
Upper limit for x axis (voltage).

Range (for y axis)

From [> 0 ; -1e-10]
Lower limit for y axis
(current for VA techniques, dt/dE for PSA).

To [> 0 ; 1e-10]
Upper limit for y axis
(current for VA techniques, dt/dE for PSA).

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 *page 54*).

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]

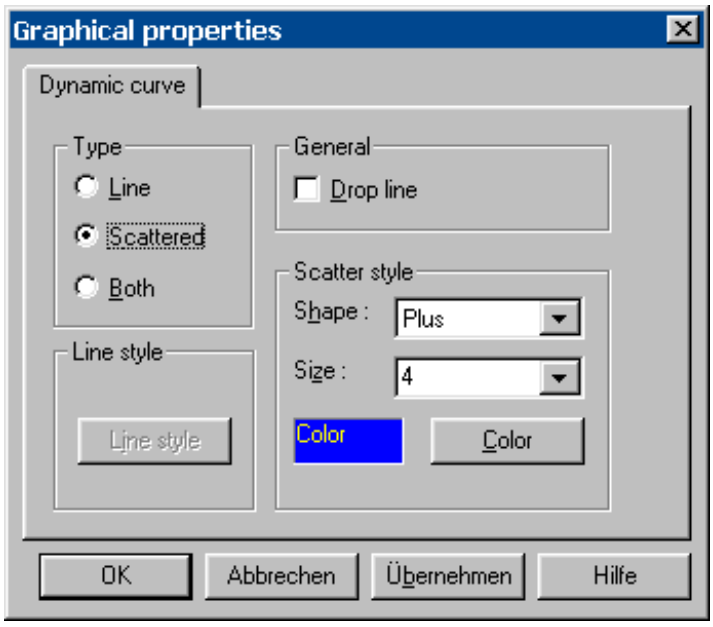
Number of major or minor ticks for x or y axis. In some cases this number will not be applied exactly but be fitted automatically to the next possible value for axis graduation.

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 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 *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.

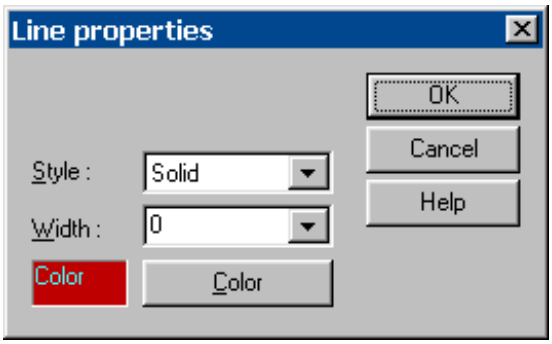
Size [1...12 ; 4]
Size of the symbol in points.

Color

Color of the symbol.

Line properties

Definition of line properties for axes or curve lines.



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 seven 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

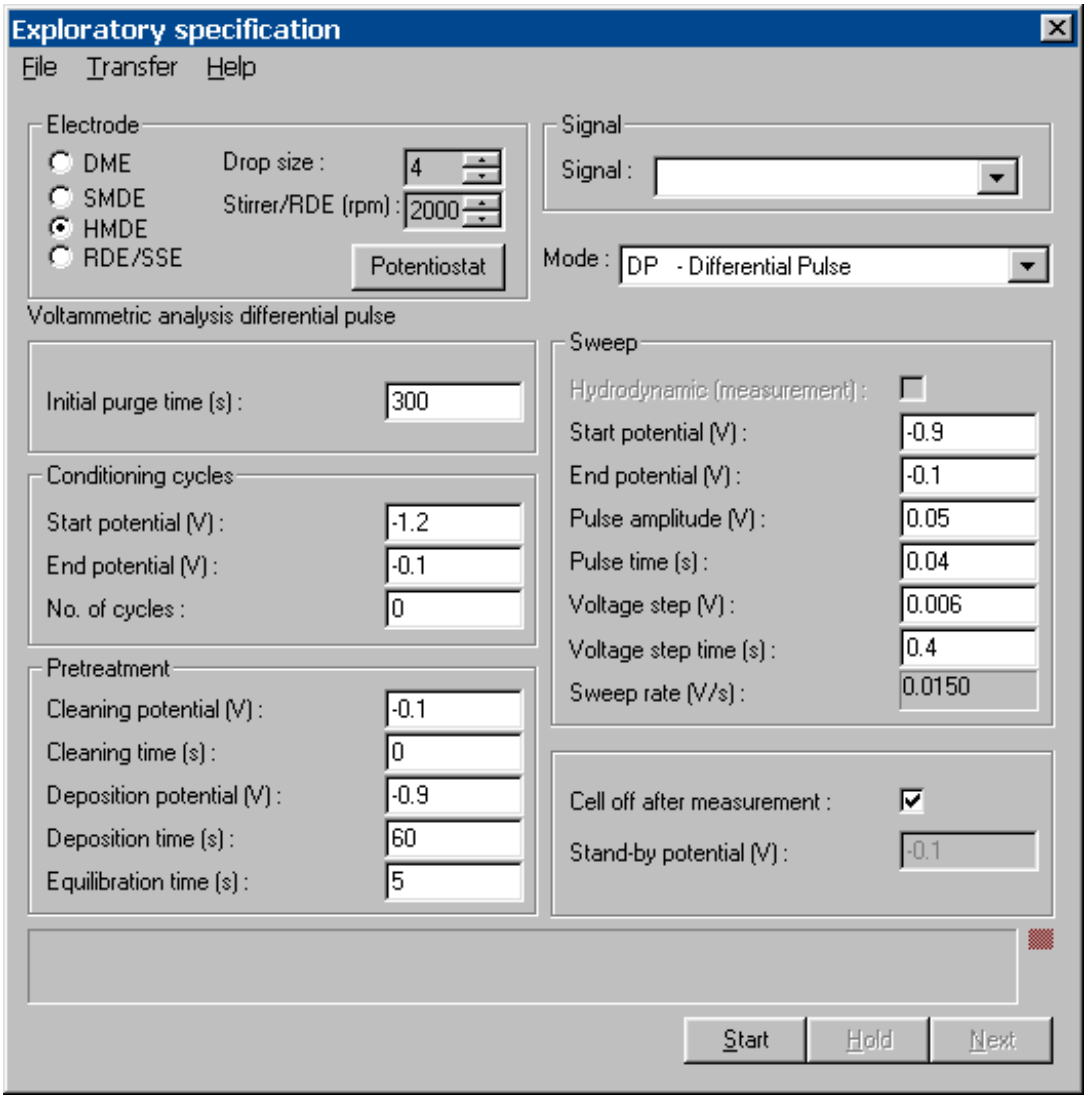
MAIN WINDOW / Window / Exploratory specification (F11)
The **EXPLORATORY SPECIFICATION** window will be opened or (if it is already open) closed.

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*.



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 see *Purging*, *section 3.4*

Conditioning cycles see *Conditioning*, *section 3.4*

Pretreatment see *Pretreatment*, *section 3.4*

Signal	Selection of a signal file to be shown with the **Selected signal properties**. An asterisk ***** marks the signal file whose parameters are loaded.
Mode	Selection of VA measurement mode, see *VA measurement modes*, *section 3.2*
Sweep	Parameters of the selected VA measurement mode, see *VA measurement modes*, *section 3.2*
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. After selection of the file to be loaded you are asked **Do you want to load the measurement parameters?**. If you click **<Yes>**, the measurement parameters are loaded into the **EXPLORATORY SPECIFICATION** window.

EXPLORATORY SPECIFICATION / **File** / **Save signal as ...**
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 ACSII 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).

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.

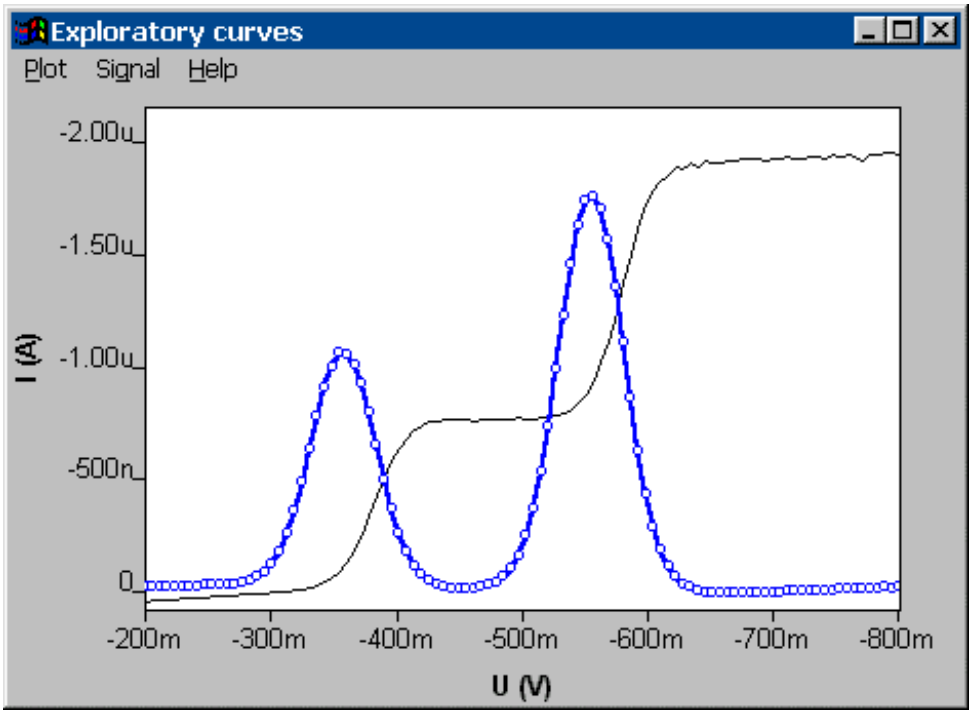
Continue measurement
Continue an interrupted measurement.

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 always displayed with positive values at the top and negative values at the bottom.

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*).

Line style

The line properties for axes 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.

Change labels

EXPLORATORY CURVES / **Plot** / **Change Y axix 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 SPECIFICATION** window.

EXPLORATORY SPECIFICATION / **Signal** / **Clear**

Remove the selected signal curve from the **EXPLORATORY CURVES** window.

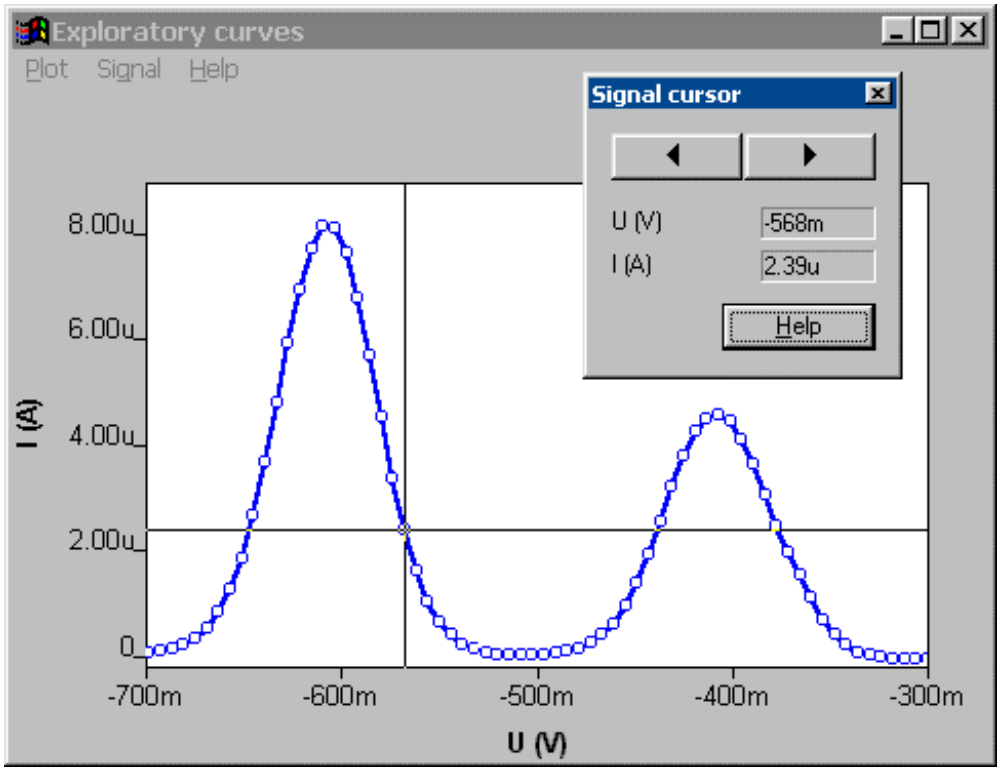
EXPLORATORY SPECIFICATION / **Signal** / **Clear all**

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.



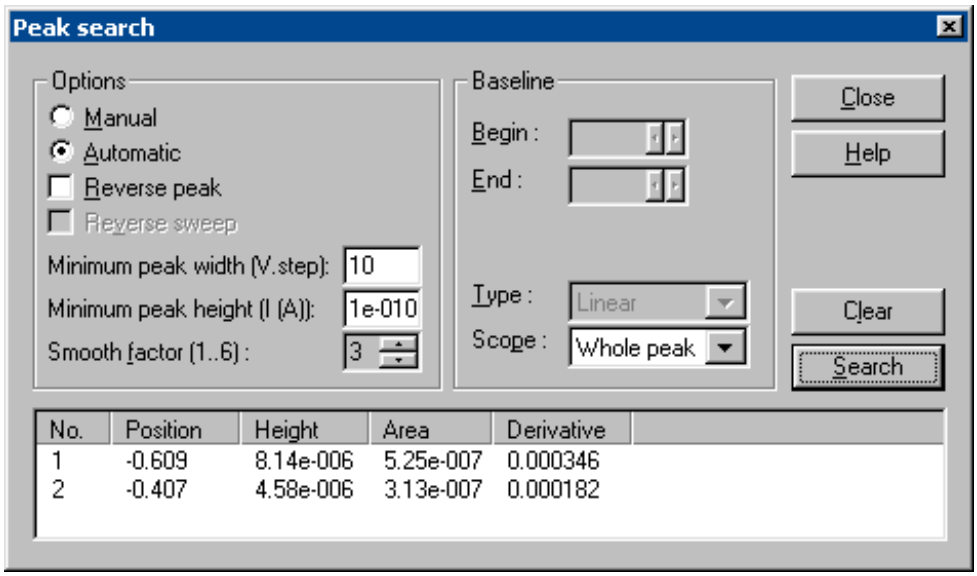
Move cursor to the next or to the preceding measurement point on the selected signal.

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).

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) [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 pressing the ↑ or ↓ key.
If the automatic peak evaluation is selected, **n/a** is displayed and the field can not be edited.

End (V) **[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 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 ; 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.

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.

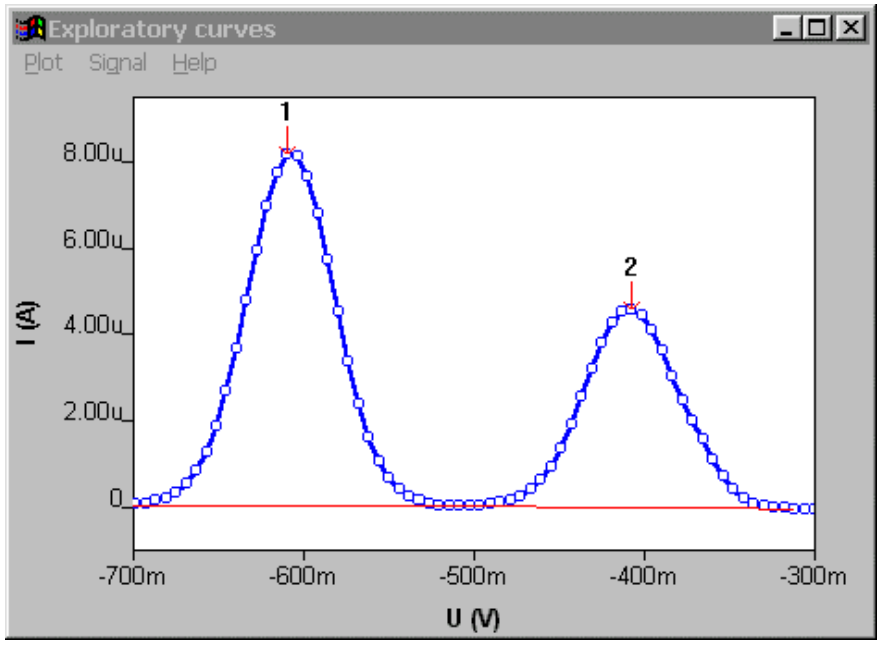


Table of results

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 peak*).

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

Copy All or **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.

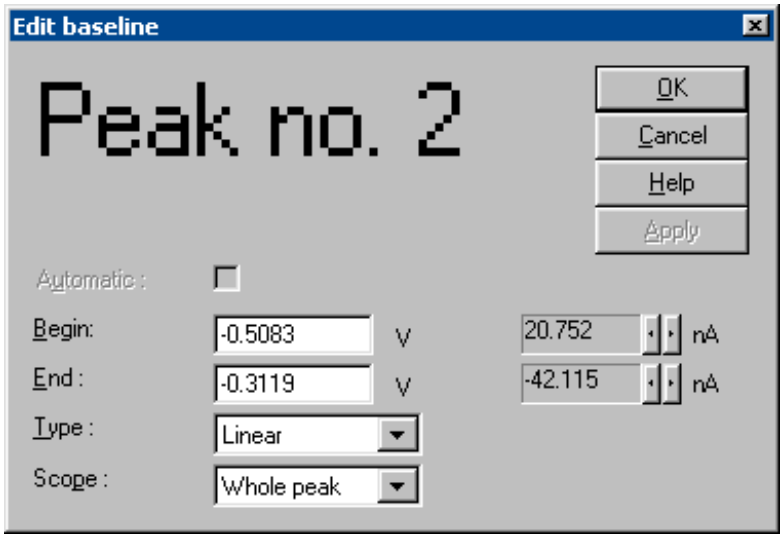
Height (A)
Calculated peak height from the baseline to the peak maximum.

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.

Edit peak

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 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 in the first field or by clicking the buttons of the second field indicating the current value.

Type of baseline [Linear, Polynomial, Exponential ; 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

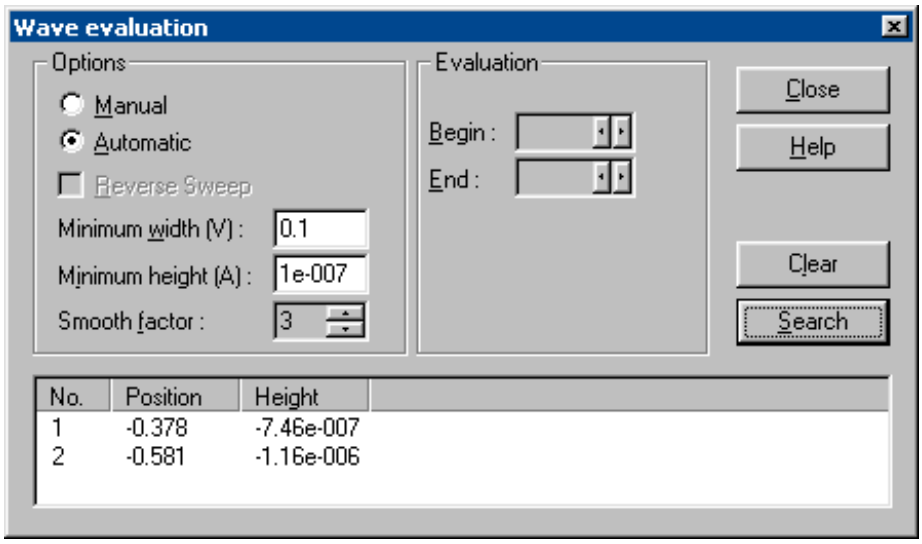
Start peak evaluation with the current parameters entered in the **EDIT PEAK** window.

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 **PEAK SEARCH** 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.

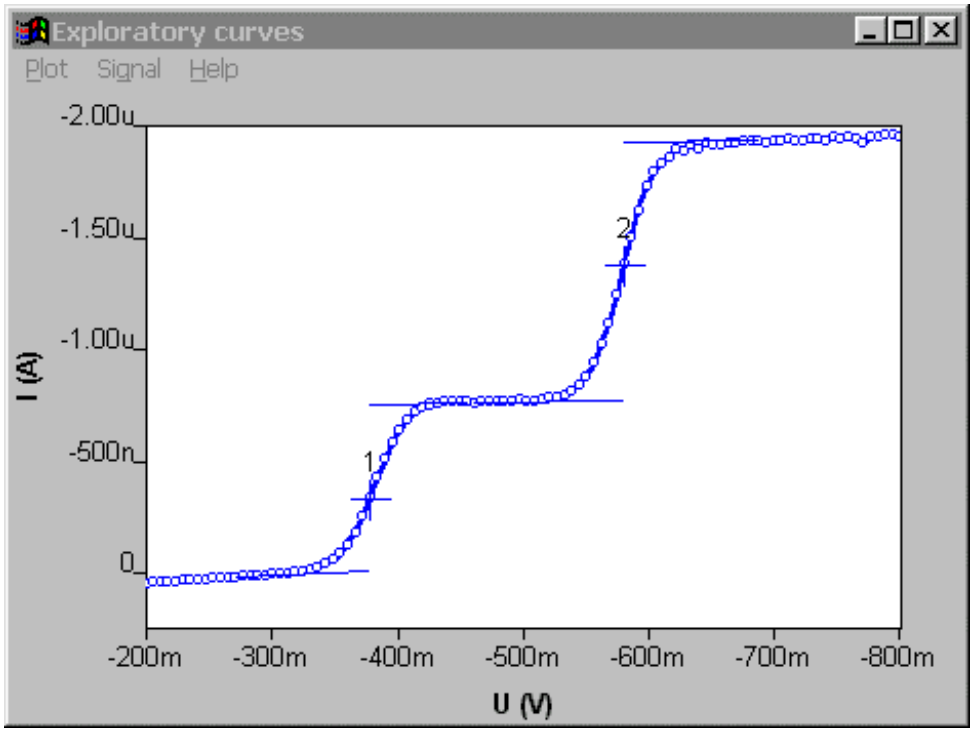


Table of results

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 results line to the clipboard.

Copy All or **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.

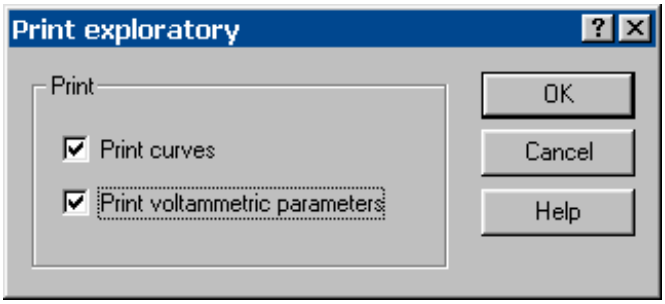
Position (V)
Calculated half-wave potential of the wave.

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.

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 six 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, 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.

757 VA COMPUTRACE / Window / Sample table (F10)

The **SAMPLE TABLE** window will be opened or (if it is already open) closed.

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. If the method has been changed since loading, the message **The file already exists. Overwrite?** appears. Click **Yes** to overwrite the method file or **No** to cancel saving.

MAIN WINDOW / File / Save method as ...

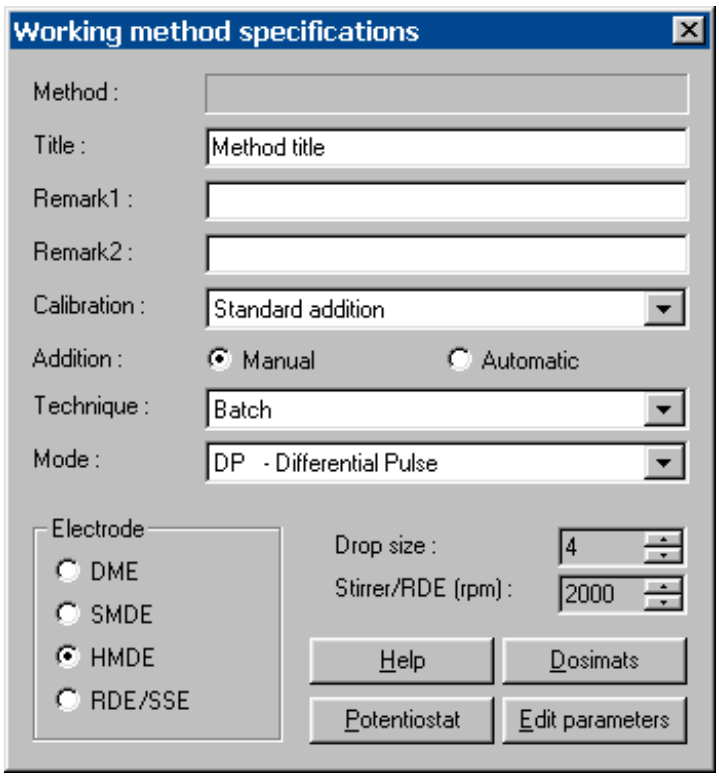
Save the current method loaded in the working memory as a new file. Enter name and directory for storage of the method file.

757 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.

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 **<Dosimats>** 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.

Calibration [*see below* ; Standard addition manual]
Selection of calibration mode (see also *section 5.7*):

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 Dosimats are defined in the **DOSIMATS** 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 Dosimats are defined in the **DOSIMATS** window.

Addition [Manual, Automatic ; Manual]
Selection of manual or automatic standard addition or recording of calibration curves:

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

Automatic
Automatic standard addition or recording of calibration curves using one or several Dosimats.

Technique [*see below* ; Batch]
Selection of measurement technique:

Batch
Measurement without solution exchange.

Batch with solution exchange
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.

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

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*).

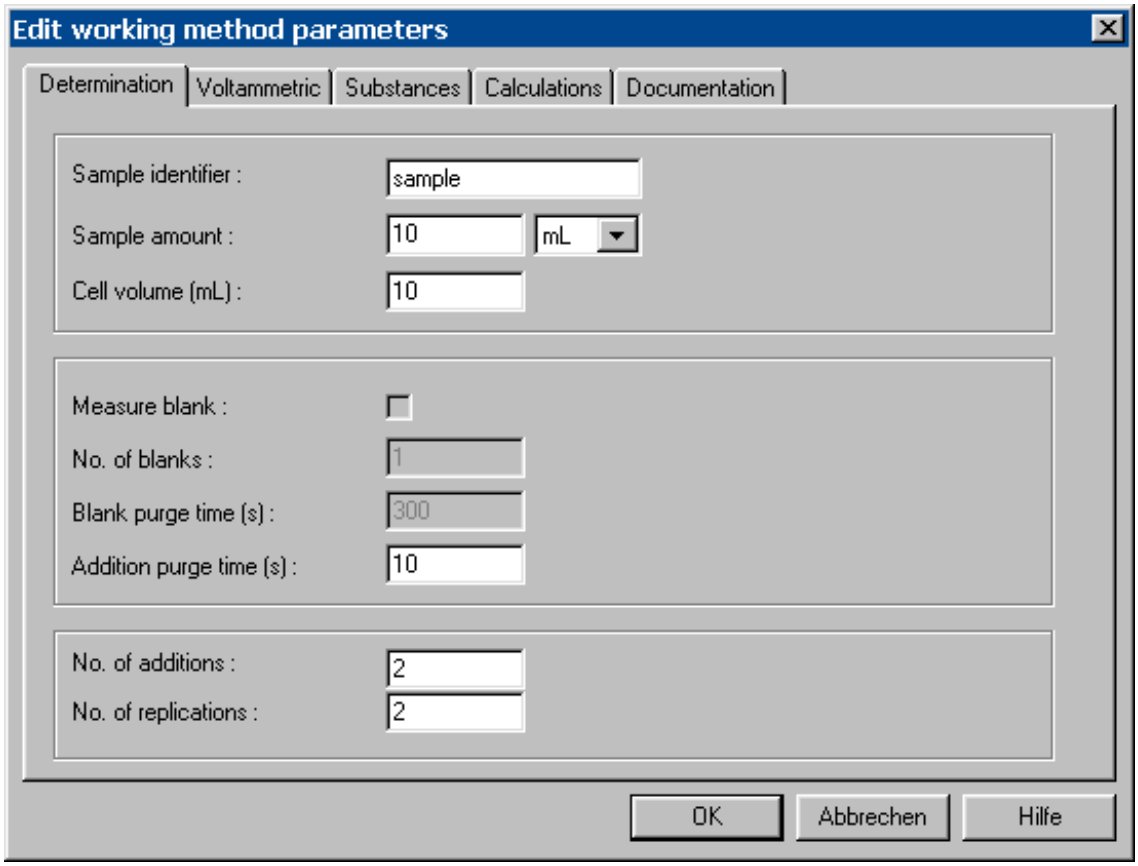
Dosimats — Dosimat settings (see *Dosimats*).

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

Edit parameters — Edit working method parameters (see *Determination*, *Voltammetric*, *Substances*, 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 mode and measurement technique.



Sample identifier [16 characters ; "sample"]
Identification for sample.

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.

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 **Mass conc.** calculated refer to this cell volume.

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. The blank curve is only recorded once (no replications).

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).

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** (for the first measurement, the **Initial purge time** is used).

No. of additions [0...28 ; 2]

Number of additions of standard addition solutions or 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 ;]

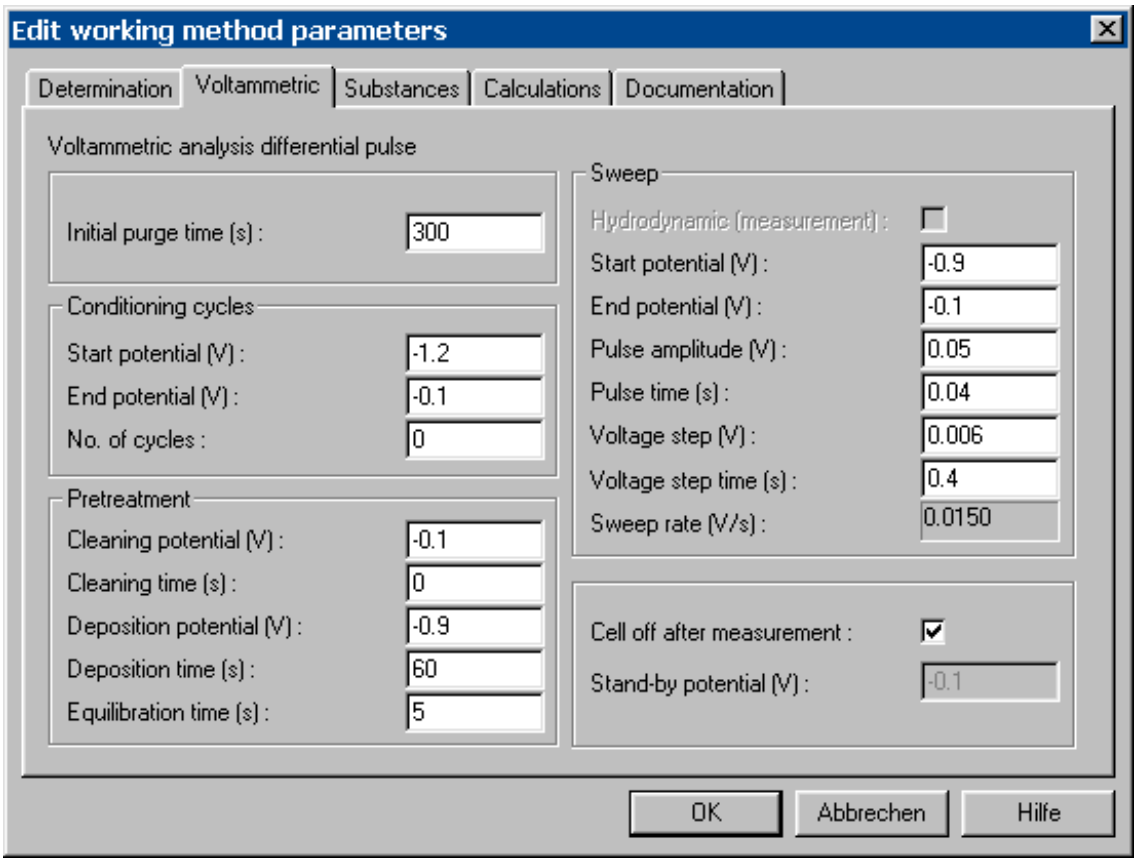
Selection of the determination file with the recorded calibration curves to be used if **Sample with calibration curve** is selected for **Calibration**.

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

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

Voltammetric

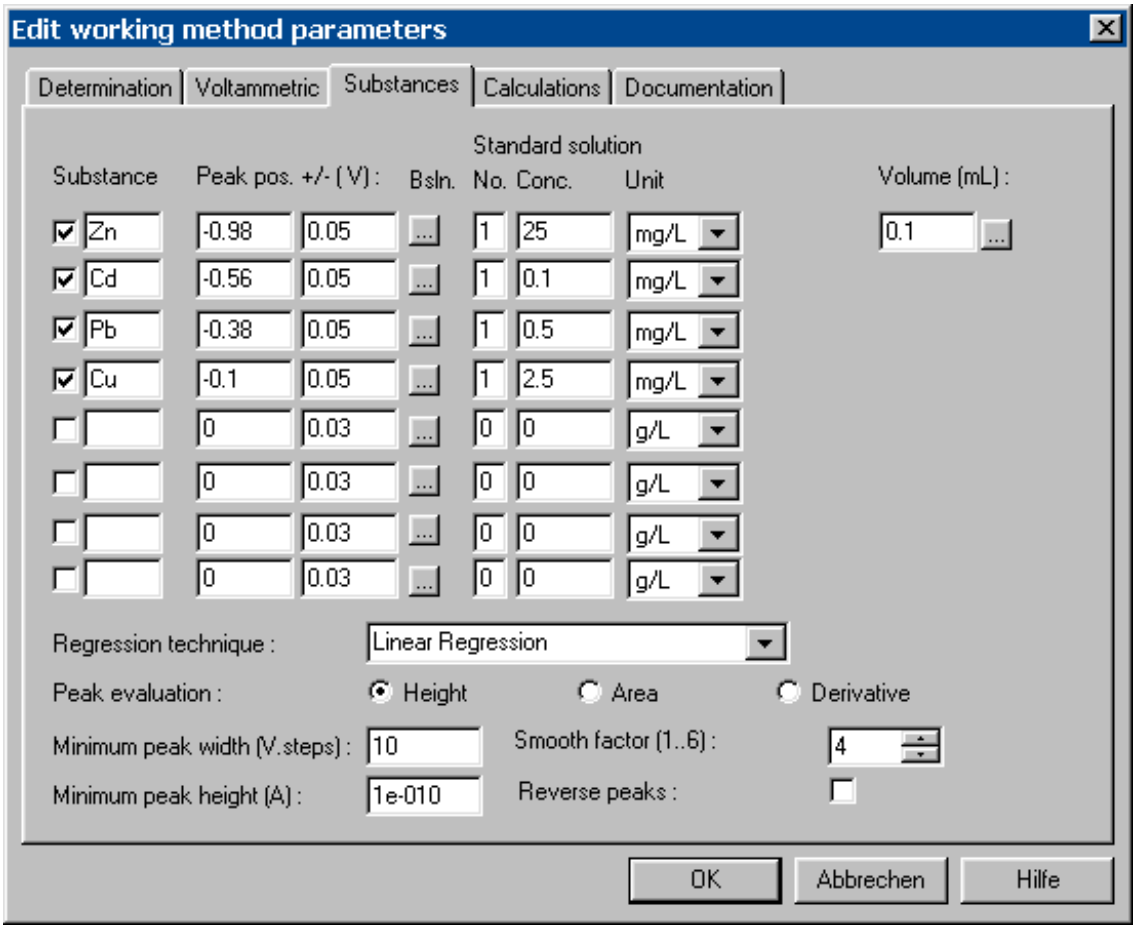
The **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window contains parameters for preparation procedures and VA measurement modes. The parameters displayed depend on the measurement mode selected in the **WORKING METHOD SPECIFICATIONS** window.



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

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 depend on the calibration technique selected in the **WORKING METHOD SPECIFICATIONS** window.



Substance [8 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*). Click the ... button to open the **BASELINE** window for the selected substance.

Standard solution

Definition of addition solutions for standard addition or recording of calibration curves. These pa-

rameters are not displayed if **Batch with solution exchange** is selected for **Technique**.

No. [1...5 ; 0]

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

Conc. [> 0 ; 0]

Value for concentration of addition solution.

Unit [µg/L...g/µL ; g/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*). 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*). 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** 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** 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** is selected for **Calibration**.

Peak evaluation [Height, Area, Derivative ; 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.

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

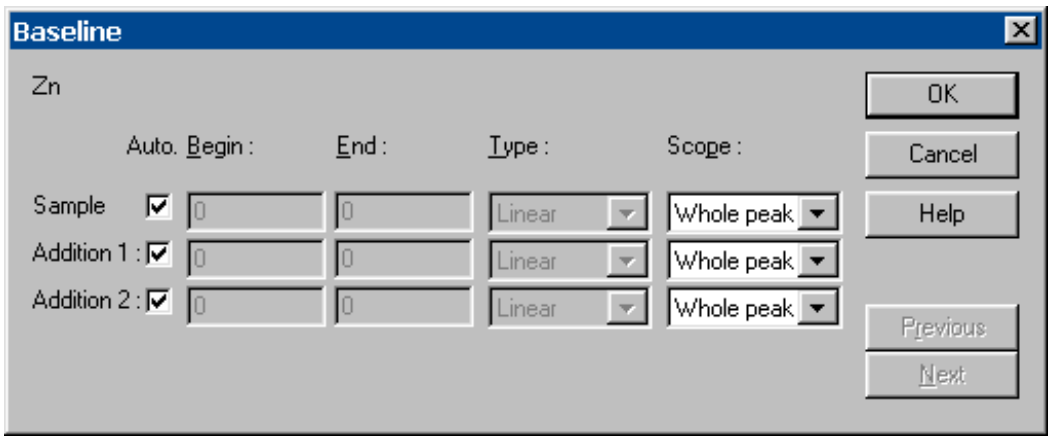
Smooth factor [1...6 ; 4]
Smoothing power of the Savitzky/Golay smoothing of the baseline (**1** = minimum smoothing, **6** = maximum smoothing).

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

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

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

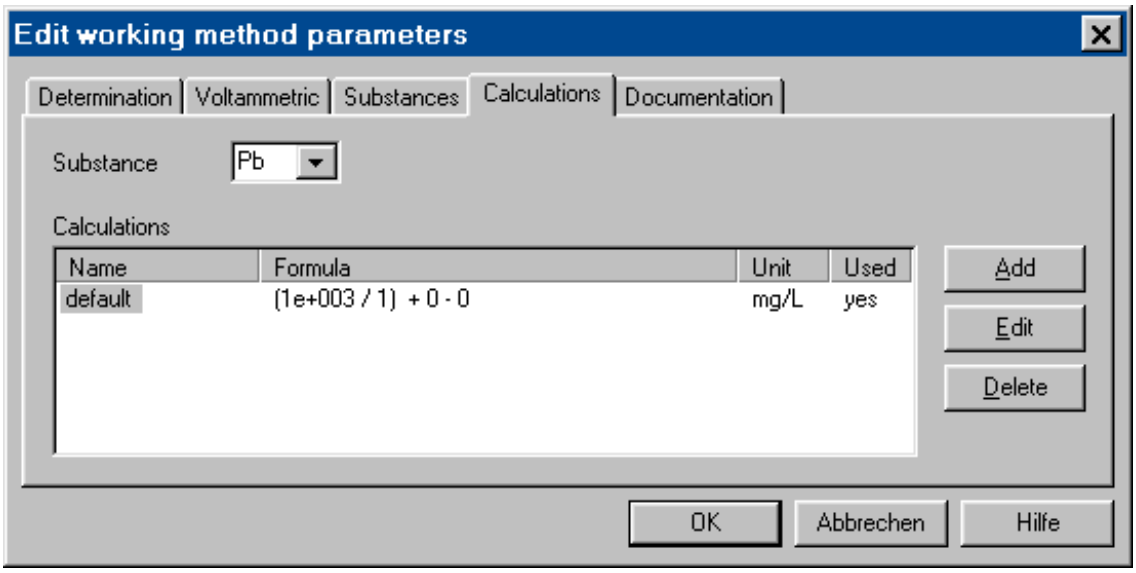
Scope **[Whole peak, Front end, Rear end ; Whole peak]**
Selection of the range for baseline evaluation.

Previous — Switch to the previous page of this window.

Next — Switch to the next page of this window.

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**.

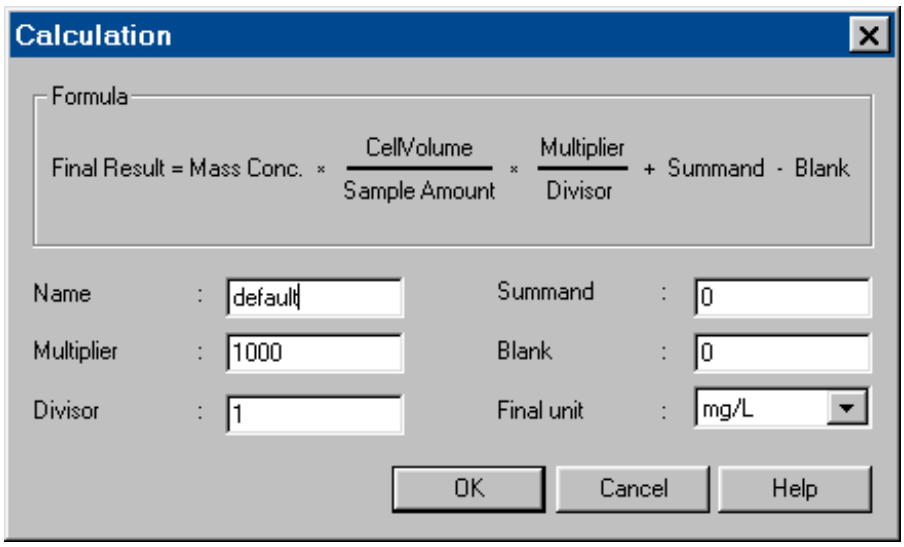
Add — Add a new calculation formula. The **CALCULATION** window for edition of the formula is automatically opened.

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

Delete — Delete the selected formula.

Calculation

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.

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

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

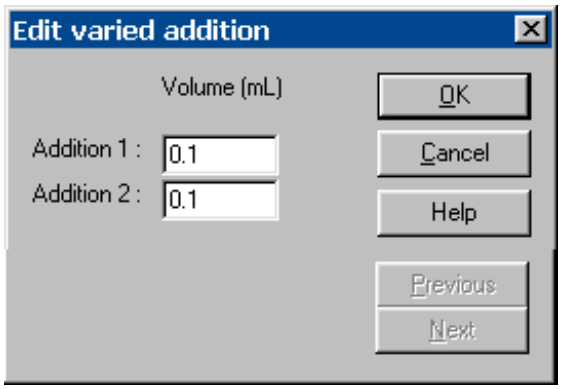
Summand [any number ; 0]
Summand for calculation formula.

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

Final unit [pg/µL...g/L ; g/L]
Final result unit.

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.



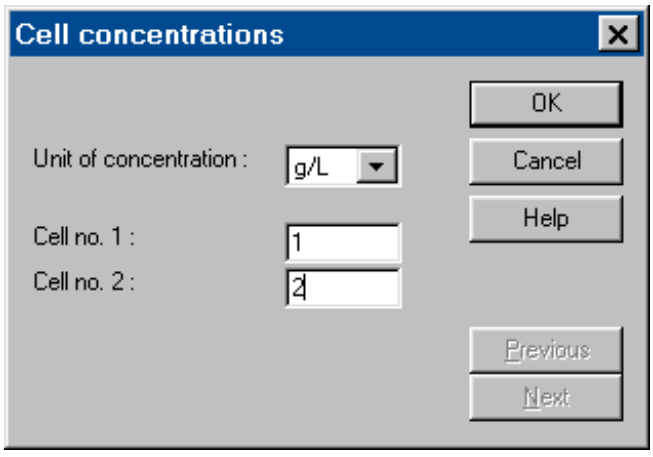
Volume (mL) [> 0.01 mL ; 0 mL]
Addition volume for each addition.

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/µL...g/L ; g/L]
Unit for concentration of solution X.

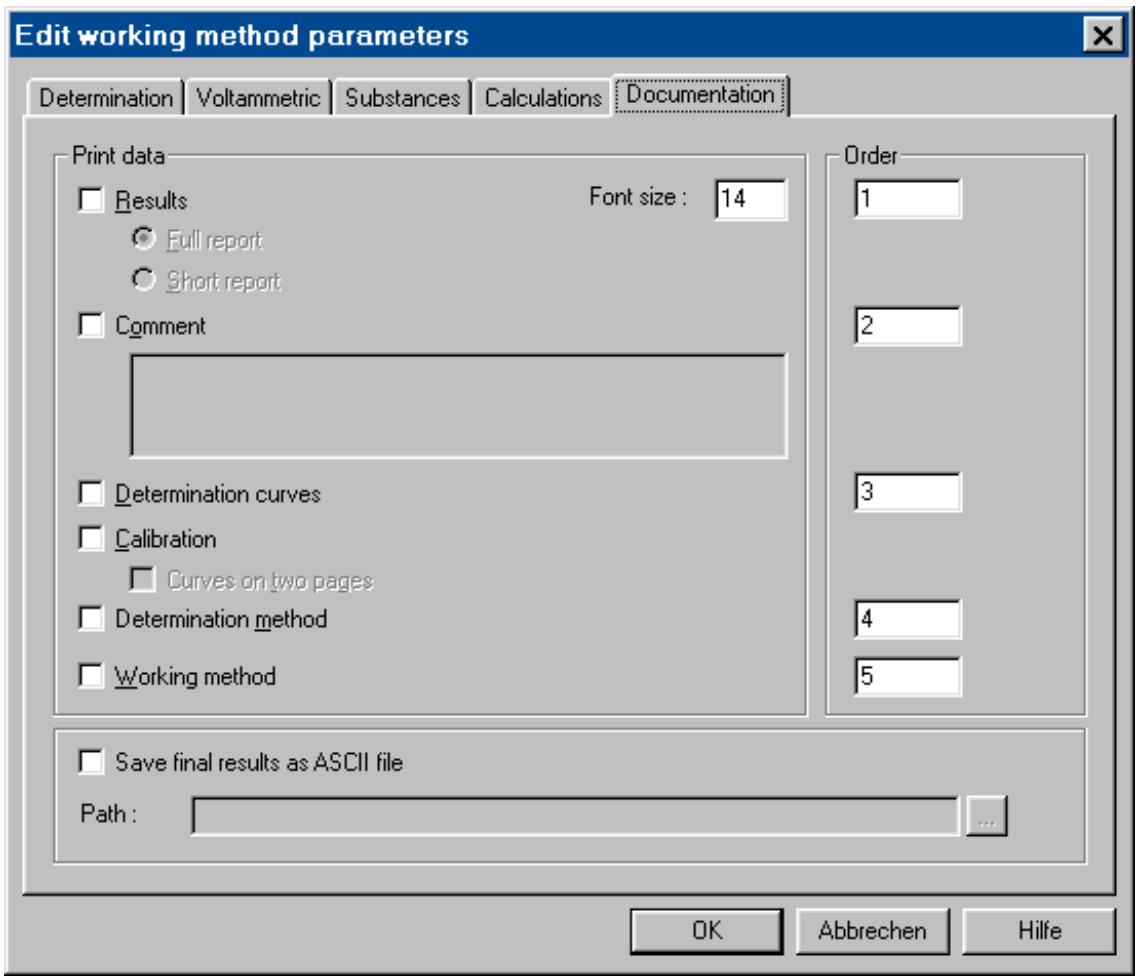
Cell no. X [> 0 ; 0]
Value for concentration of solution X.

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 memory.

Order [1...6 ;]

Order of printout for the element.

Save final results as ASCII file

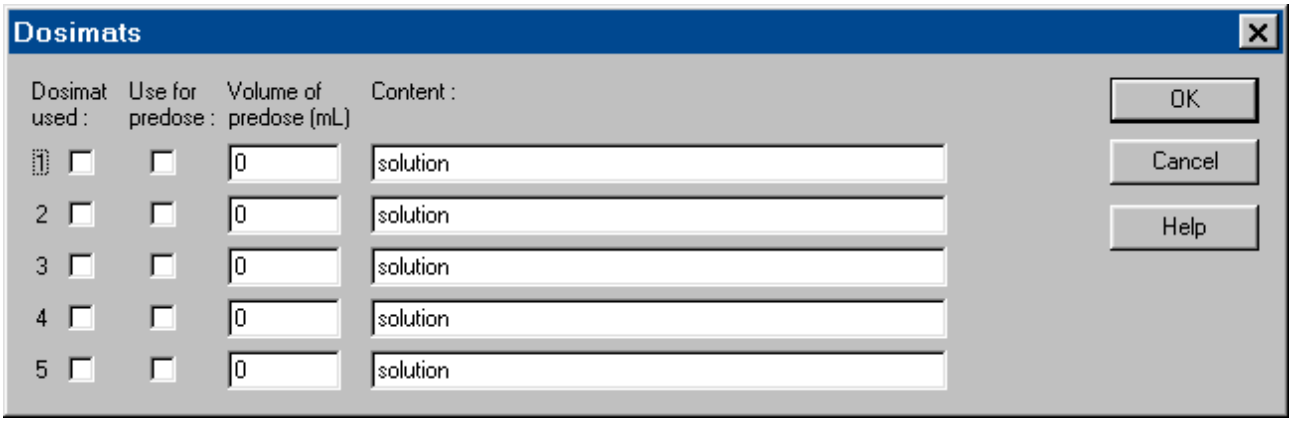
Automatic storage of the full report into an ASCII file.

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

Dosimats

The automatic use of 665 or 765 Dosimats for the addition of solutions has to be defined in the **DOSIMATS** window which is opened by clicking the Dosimats button in **WORKING METHOD SPECIFICATIONS** window.

Note: Make sure, that the desired Dosimat has also been checked on the **Hardware** tab of the **GENERAL SETTINGS** window (see *section 2.7*).



Dosimat used [on, off ; off]

Checkbox for Dosimats used for automatic addition of solutions. For the addition of standard solutions, the Dosimat 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 Dosimat for addition of an auxiliary solution (e.g. buffer) at the start of the determination.

Volume of predose (mL) [> 0.01 mL ; 0 mL]

Volume of the auxiliary solution (e.g. buffer) to be added at the start of the determination.

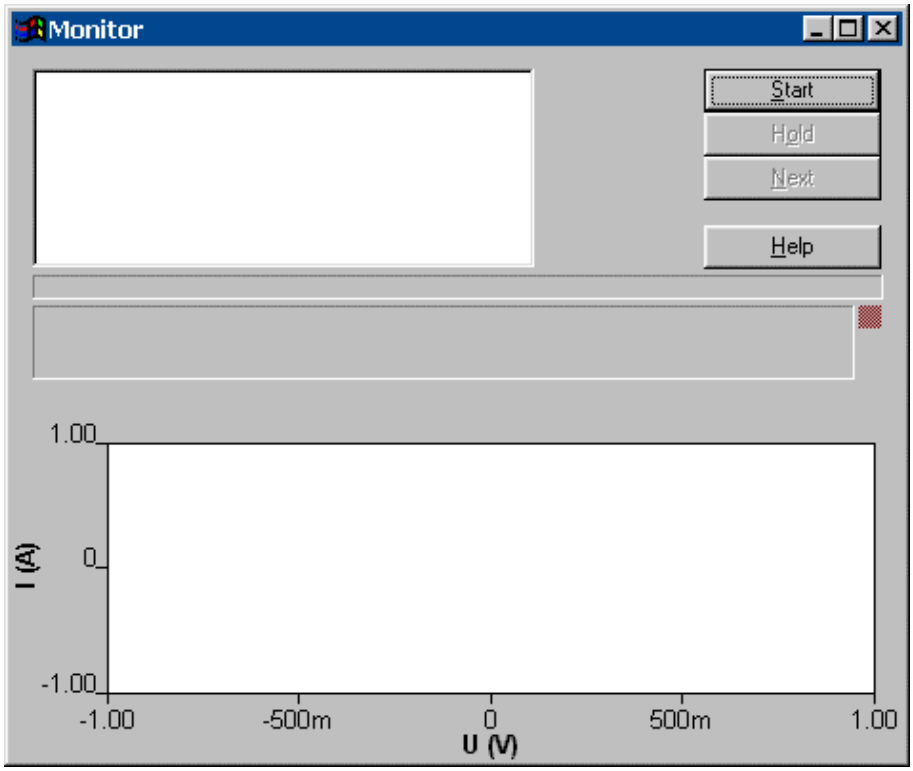
Content [46 characters ; "solution"]

Remarks regarding the solution.

5.3 Monitor

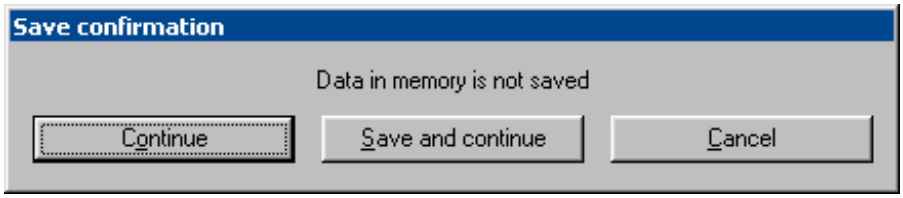
Start determination

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 appears.



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.

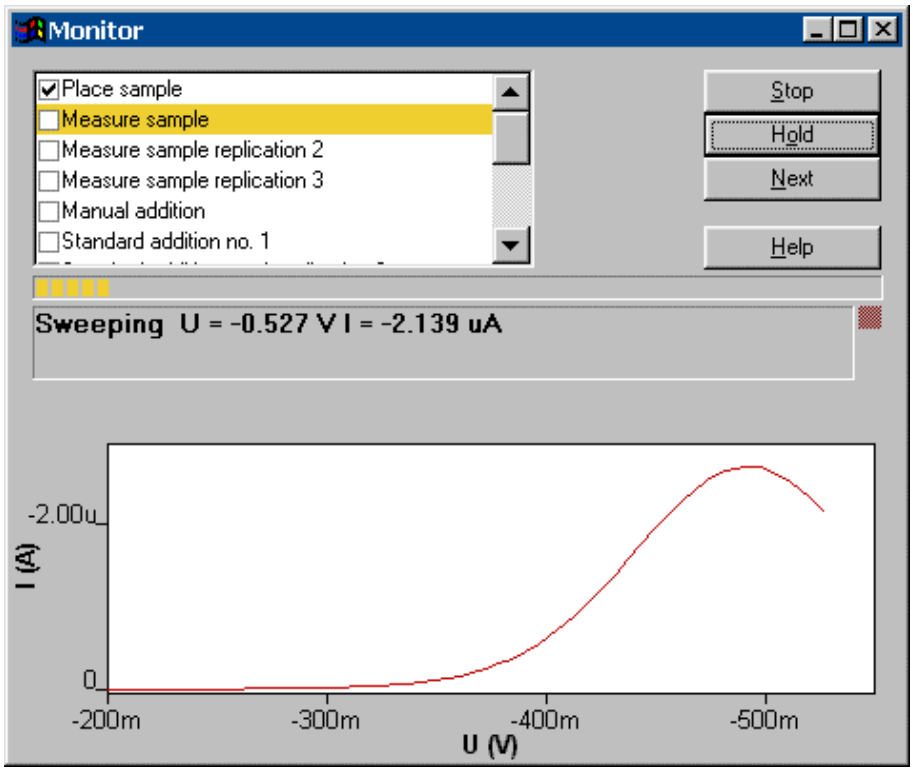
Hold determination
Interrupt running determination.

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

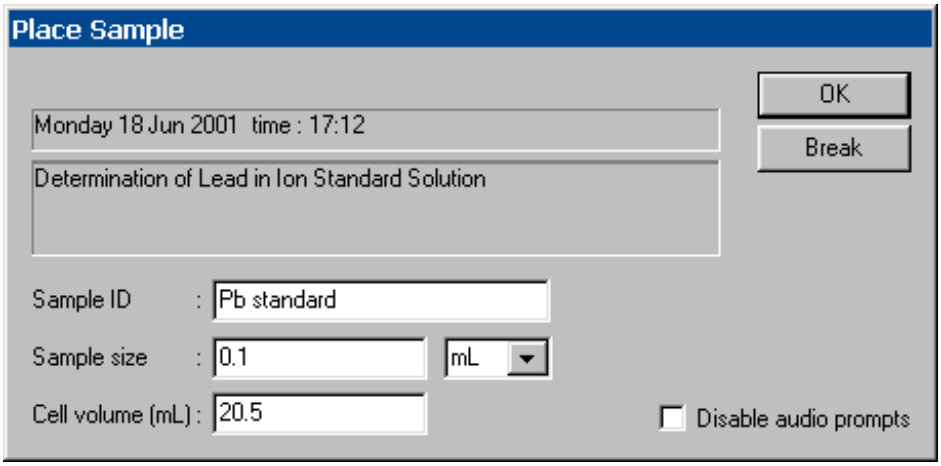
For some steps in the operation sequence additional windows demanding an action or entry of the user appear.

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 **MMDDHHMM** (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. **02041109_std.dth**).

Sample ID [16 characters ; "std"]

Identification for sample.

Sample size [> 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.

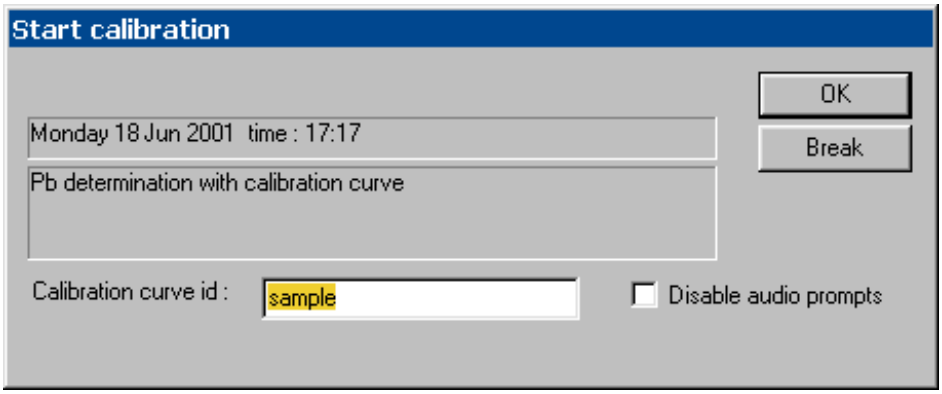
Cell volume (mL) [> 0 mL ; 10 mL]

Total volume of solution (sample + auxiliary solution, e.g. buffer) in the measuring vessel at the start of the determination. The sample concentrations **`Mass conc.`** calculated refer to this cell volume.

Add the sample 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 **MMDDHHMM** (month-day-hour-minute) and the **Sample ID** are used as default for the name of the determination file with the recorded calibration curve to be saved automatically (e.g. **02041109_std.dth**).

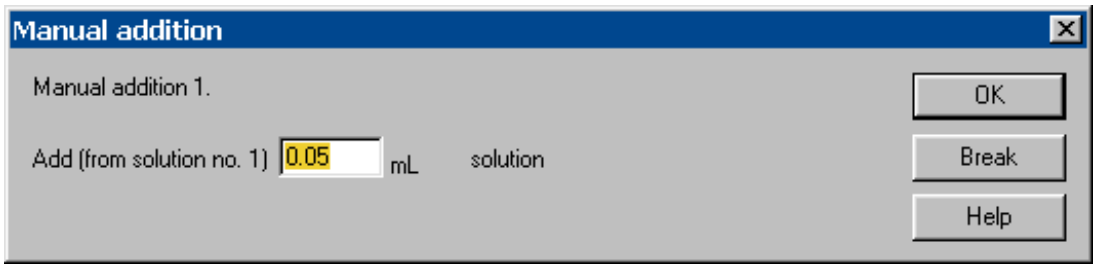
Calibration curve id [16 characters ; "std"]

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 PROPERTIES** window (details see *Axisproperties*, *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 *Curveproperties*, *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. If the determination has been changed since loading, the message **The file already exists. Overwrite?** appears. Click **Yes** to overwrite the determination file or **No** to cancel saving.

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.

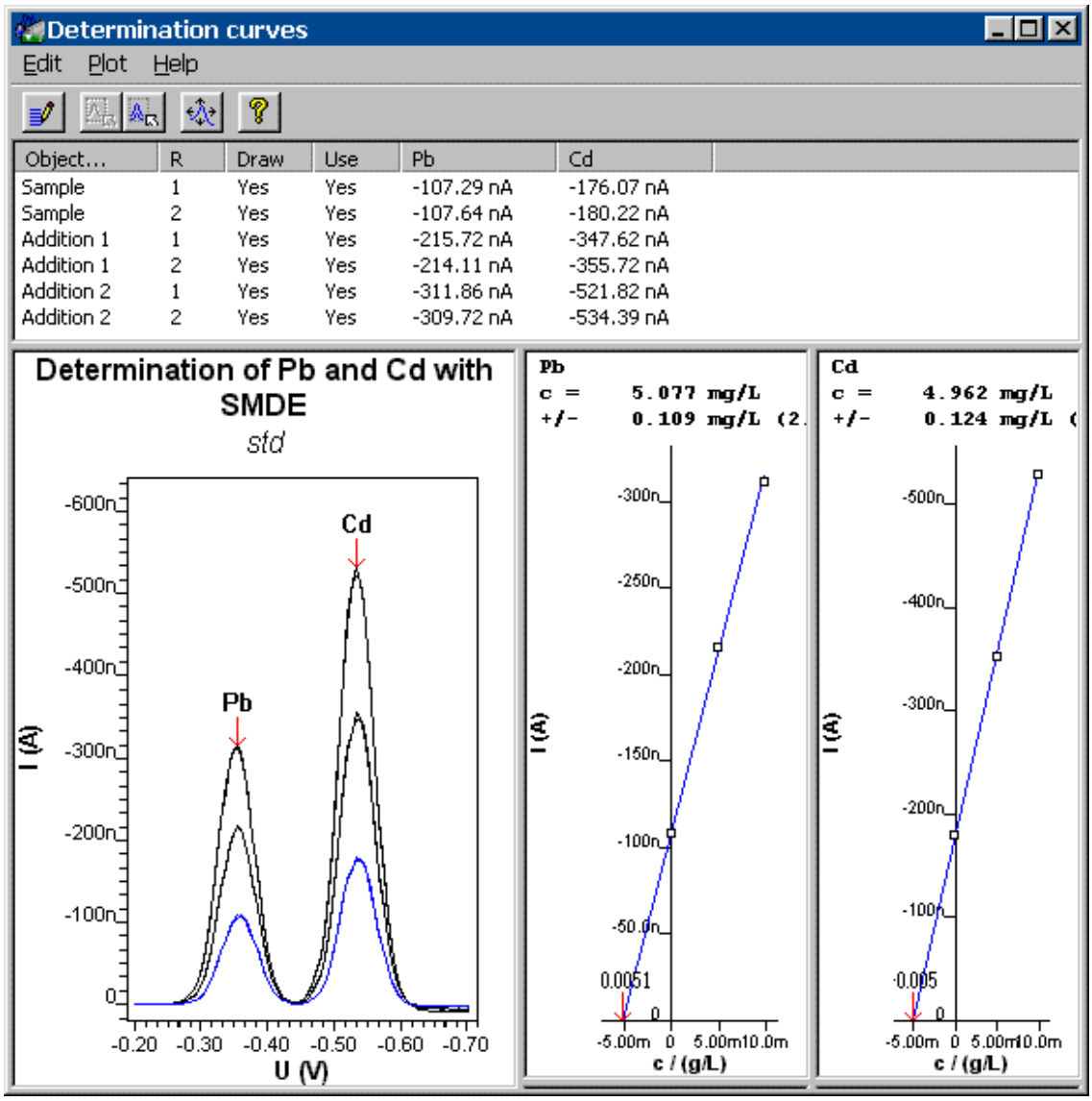
Copy parameters to working method

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.

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

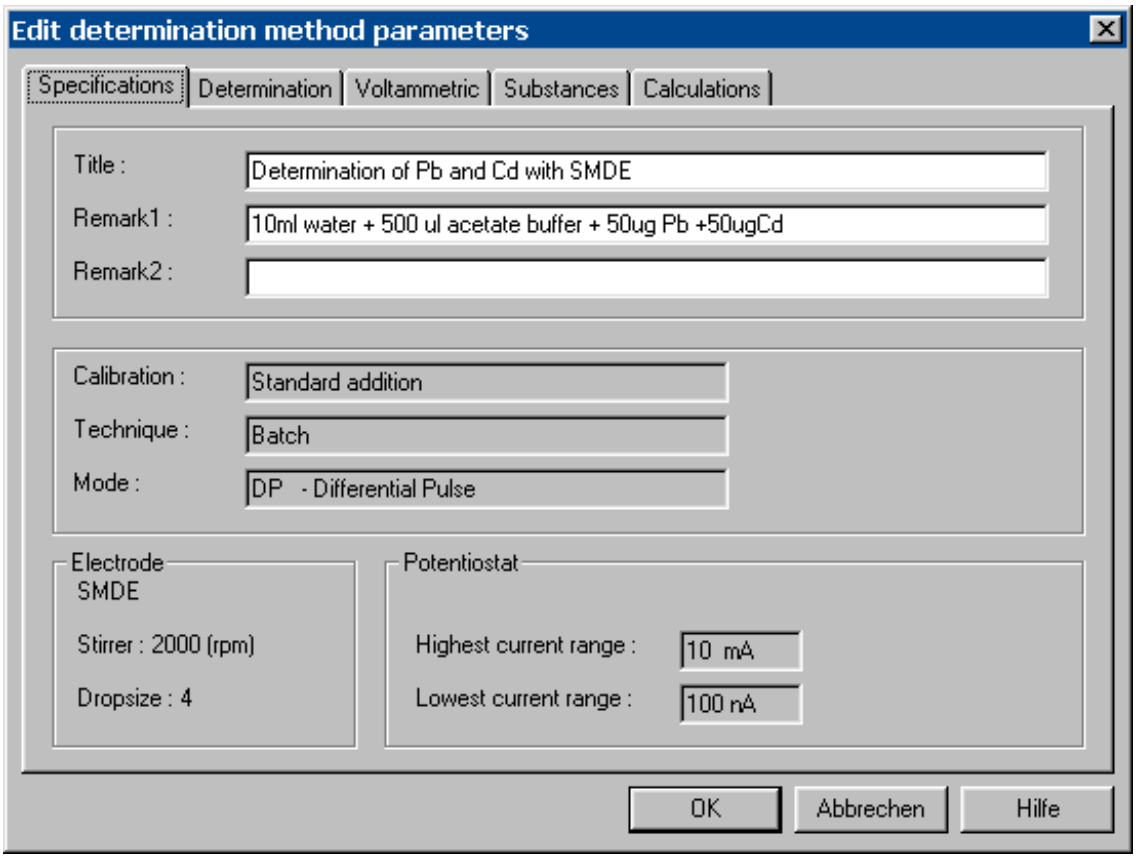
DETERMINATION CURVES / Edit / Determination method parameters

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: These parameters will not automatically be used for the next measurement. To do this, use the **Copy parameters to working method** command (see *section 5.3*).

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*).

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 3.1*).

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 3.1*).

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** 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 **Substances** tab of the **EDIT WORKING METHOD WINDOW**, *section 5.2*.

Edit addition parameters

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.

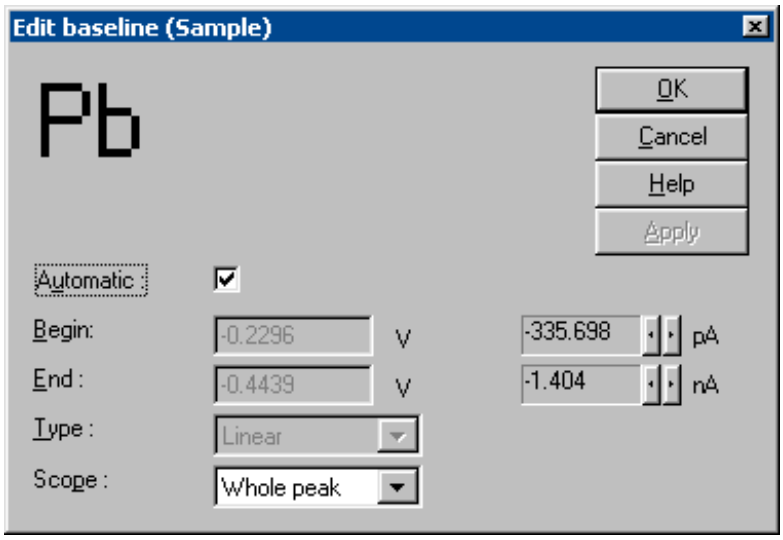
DETERMINATION CURVES / **Edit** / **Addition parameters** / **Draw**
Enable/disable the drawing of the curve selected in list of curves. The entry in the **Draw** column of the list is changed.

DETERMINATION CURVES / **Edit** / **Addition parameters** / **Show selected**
Show 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** / **Show all**
Show all available curves. The entries in the **Draw** column of the list are set to **Yes** for all curves.

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 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 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 ; 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**".

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*).

Line style

The line properties for axes or 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.

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.

```
==================== METROHM 757 VA COMPUTRACE (5.757.0020) ====================
 Determ.     : 07171553_5ppm CdPb SMDE bl.dth
 Sample ID   : std
 Creator     : ---               Date :                    Time:
 Modified by : ---               Date :                    Time:
 User        :                   Date : 2001-08-07         Time:  16:48:20
--------------------------------------------------------------------------------
 Cell volume:   10.000 mL
 Sample amount: 10.000 mL
--------------------------------------------------------------------------------
 Method  :  Pbhm.mth
 Title   :  Determination of Lead and Cadmium with SMDE
 Remark1 :  10ml water + 500 ul acetate buffer + 50 ug Pb
 Remark2 :  buffer
--------------------------------------------------------------------------------
  Substance : Pb                                                  Comments
  Mass conc.:    5.034  mg/L                                      ----------
  MC.dev.   :    0.016  mg/L      (    0.31%)
  Mass      :   50.339  ug
  Add.mass  :   50.000  ug

              VR     V    nA      I.mean  Std.Dev. I.delta   Comments
              ----  -----  ------  ------  -------  -------   ----------
              1-1   -0.361  -99.1  -99.2   0.193
              1-2   -0.361  -99.4
              2-1   -0.361 -196.1  -196.2  0.155    -96.9
              2-2   -0.361 -196.3
              3-1   -0.355 -290.7  -290.3  0.524    -94.2
              3-2   -0.355 -290.0

  Substance : Cd                                                  Comments
  Mass conc.:    4.961  mg/L                                      ----------
  MC.dev.   :    0.010  mg/L      (    0.19%)
  Mass      :   49.613  ug
  Add.mass  :   50.000  ug

              VR     V    nA      I.mean  Std.Dev. I.delta   Comments
              ----  -----  ------  ------  -------  -------   ----------
              1-1   -0.539 -176.3  -176.1  0.355
              1-2   -0.533 -175.8
              2-1   -0.539 -350.0  -350.2  0.284    -174.1
              2-2   -0.533 -350.4
              3-1   -0.533 -520.5  -520.4  0.165    -170.2
              3-2   -0.533 -520.3


 Substance    Calibr.    Y.reg/offset   Slope        Std.Dev.
 ---------    --------   ------------   -----------  ------------
       Pb     std.add.   -9.926e-008    -1.972e-005   1.923e-010
       Cd     std.add.   -1.761e-007    -3.549e-005   3.164e-010

 Solutions
--------------------------------------------------------------------------------

  No. Content                                          Vol. (mL) Predose (mL)
  --- ------------------------------------------------ --------- --------------



 Final results                        +/- Res. dev.   %     Comments
 ----------------------------------   -----------------   ----------

 Pb:
 Pb           = 5033.876  µg/L         15.514       0.308

 Cd:
 Cd           = 4961.325  µg/L         9.595        0.193
```

The **RESULTS** window comprises the following parts:

Header

Metrohm 757 VA Computrace
Name of manufacturer and instrument.

(5.757.0020)
Version number of PC software.

Determination data

Determ.
Name of determination file.

Sample ID
Identification for sample (see **Sample identifier** on the **Determination** tab).

Creator
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.

Note: Irrespective whether fields have been modified or not, the modification date is entered into the **Modified by** line if the **EDIT DETERMINATION PARAMETERS** window is closed by clicking **<OK>** .

User Name of the current logged-in user who reloaded a saved determination with **Date** and **Time** of loading (identical information as for **Creator** if the report has been printed or opened at the end of the determination).

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*).

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.

Substance evaluation

Substance
Substance name (see **Substance** on the **Substances** tab, *section 5.2*).

Mass conc.
Calculated substance mass concentration referring to the total volume of solution (**Cell volume**) in the measuring vessel at the start of the first sweep.

MC.dev.
Absolute and relative total deviation of the calculated substance mass concentration **Mass conc.**.

Mass
Absolute substance mass in the measuring vessel.

Add.mass
Substance mass added in every standard addition (only available for constant additions).

Peak evaluation

VR Number of variation and replication.

V Evaluated peak voltage (V).

A;W;A/V {for PSA: s/V;s;s/(V^2*V)}
Calculated eval. quantity (height, area, or derivative)

i.mean; P.mean; mean
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
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).

Calibration data

Substance

Substance name (see **Substance** on the **Substances** tab*, section 5.2*).

Calibr.

Calibration technique **std.add.**, **rec.cc.**, or **smp.cc.** (see **Calibration** on the **Specifications** tab*, section 5.4*).

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.

Mean deviat.

Calculated mean deviation of the measured values about the standard addition or calibration curve.

Solutions

No. Number of Dosimat used for addition or predose.

Content

Remarks regarding the solution (see **Content** on the **DOSIMATS** window*, section 5.2*).

Vol. (mL)

Volume of the exchange unit installed on the Dosimat (see **Volume** on the **Hardware** tab*, section 2.7*).

Predose (mL)

If the Dosimat is used for solution predose, the message **Predose X.X mL** is displayed in this column.

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

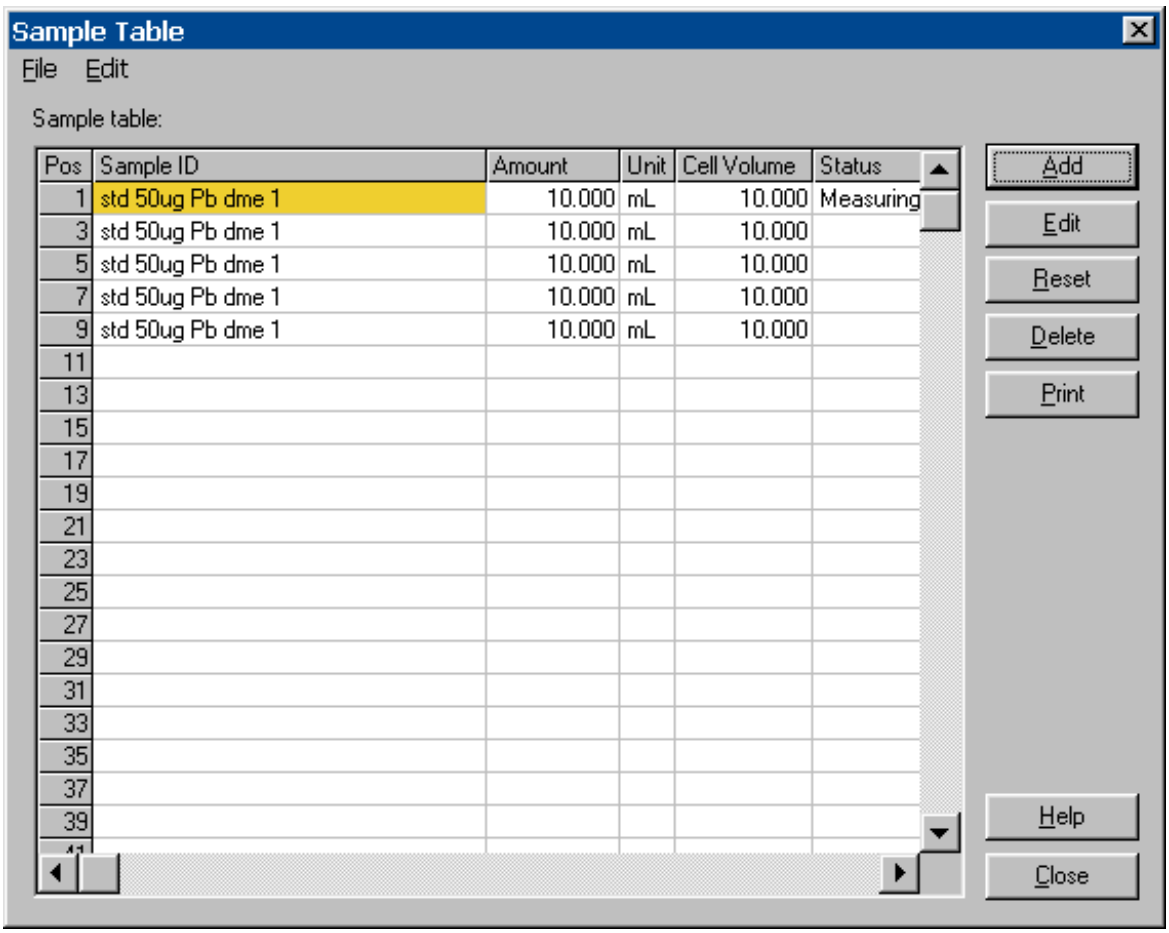
Text selected in the **RESULTS** window can be copied to the clipboard by selecting the **Copy to clipboard** option of the context sensitive menu.

RESULTS / Select all
Select the whole text in the **RESULTS** window.

RESULTS / Copy to clipboard
Copy the selected text to the clipboard.

5.6 Sample table

The **SAMPLE TABLE** window shows the sample data of the loaded sample table.



Pos. [1, 3, 5 ... 127; read only]
Position of the sample on the sample rack of the 813 Compact Autosampler. Only odd numbers are displayed, since for every sample a vessel containing rinsing solution must be placed at the even sample rack positions.

Sample ID [16 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 **`Mass conc. calculated`** refer to this cell volume.

Status [read only]
Display of sample determination status: **Measuring**, **Done** or "empty" (ready for start).

Add
Add a new sample data row. The **SAMPLE** window for entry of **Sample ID**, **Sample amount**, **Sample unit**, and **Cell volume** is opened.

Edit
Edit the selected sample data row. The **SAMPLE** window for modification of **Sample ID**, **Sample amount**, **Sample unit**, and **Cell volume** is opened.

Reset
Reset the **Status** of the sample data rows to "empty" in order to restart the current sample table.

Delete
Clear the contents of the selected sample data row.

Print
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.

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.

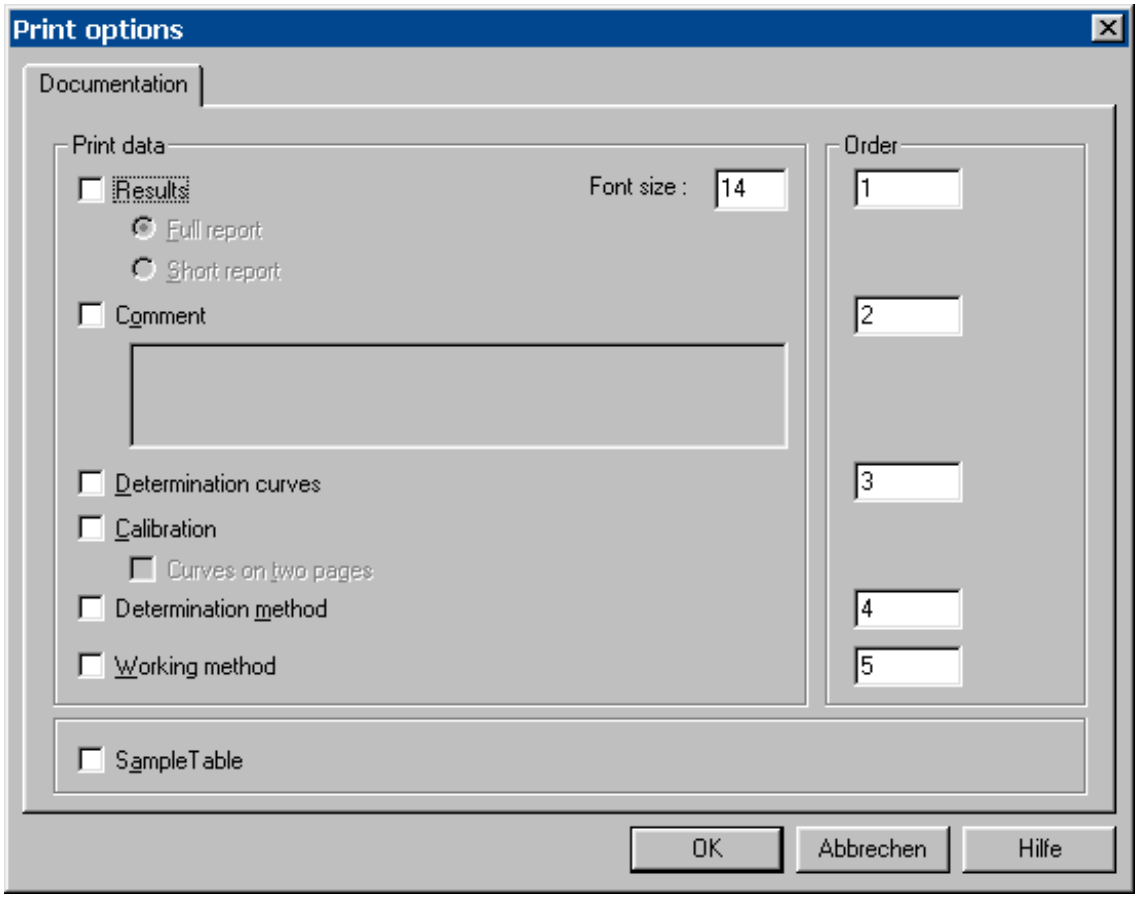
SAMPLE TABLE / Edit / Delete
Clear the contents of the selected sample data row.

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 Add-on board via TCP/IP connection or to the VA Computrace Interface via USB connection. The data acquisition at the VA Computrace Stand is started and controlled by the Add-on board or VA Computrace Interface, which receive and store 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 757 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
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, 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:

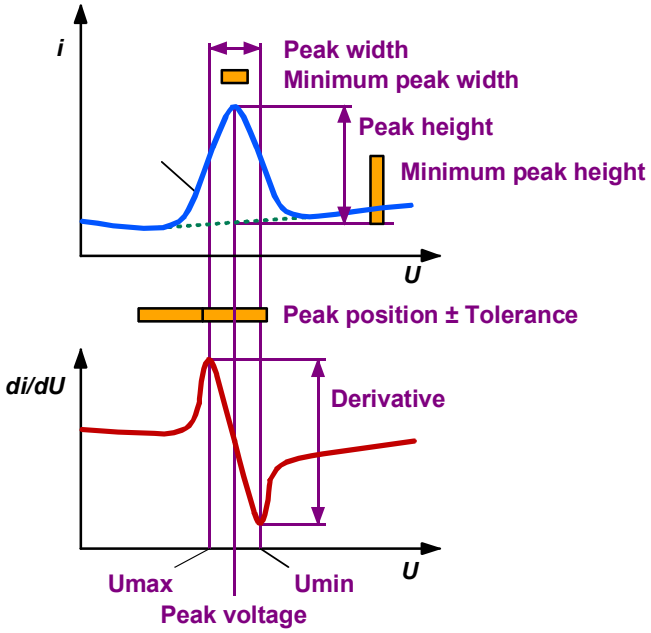
1	3-point weighed moving average
2	5-point weighed moving average
3	7-point weighed moving average
4	9-point weighed moving average
5	11-point weighed moving average
6	13-point weighed moving average

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**

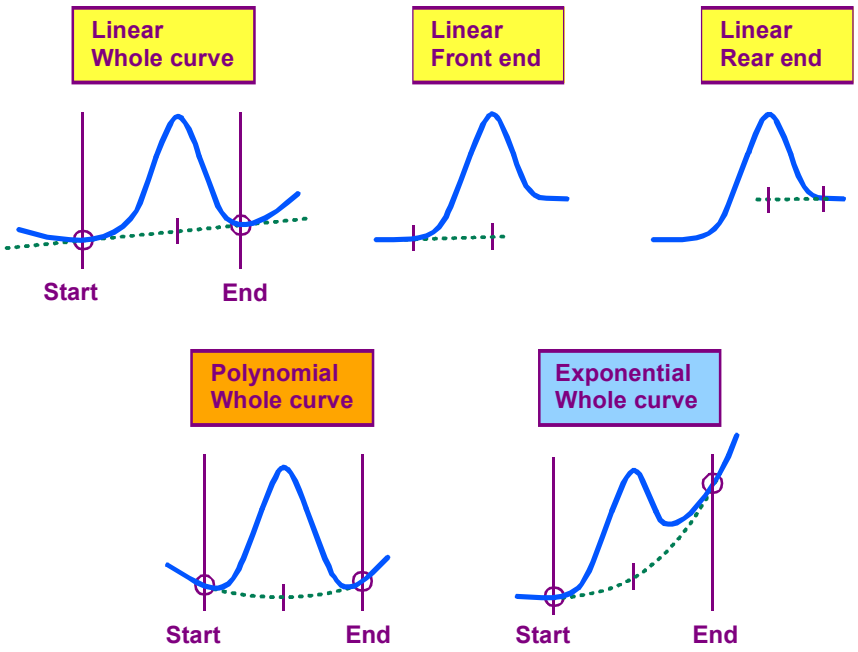
Peak height test: **Peak height > Minimum peak height**

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

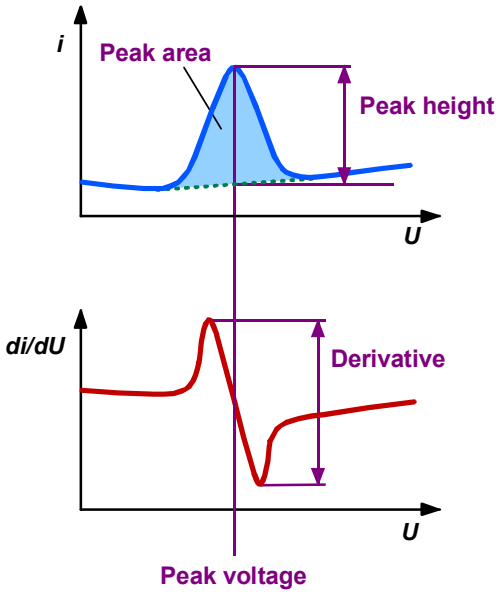
Recognized peaks are evaluated using approximated baselines. The calculation of a baseline for a smoothed substance peak is determined by the baseline parameters set for this substance in the **BASELINE** window (see *section 5.2*). The following possibilities exist for baseline calculation:



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 *section 5.2*). With the aid of the calculated baselines, the set evaluation quantity **Height**, **Area** or **Derivative** is determined for each substance peak and displayed as a result.



Content calculation

With polarographic and voltammetric methods, the measured evaluation quantities (**Height**, **Area** or **Derivative**) 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 757 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 mass concentration ***c*(s)** which is defined by the found substance mass **Mass** and the sample amount in the measuring vessel **Sample amount**:

$$c(\mathrm{s}) = \mathrm{Mass} / \mathrm{Sample\ amount}$$

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 *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 Dosimat using the **Predose** 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 Dosimat. 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

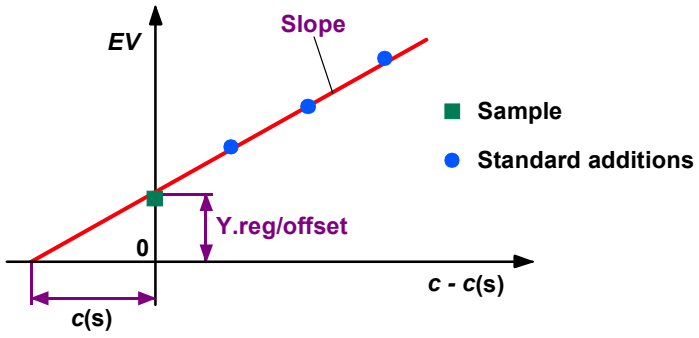
3. **Determination of standard addition curve**
For the calculation of the linear standard addition curve, the parameters ***a*** and ***b*** of the linear regression curve **y** = ***a*** + ***b*****x** are calculated by weighted least square minimization with **y = EV** and **x** = ***c* – *c*(s)**. 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 MC.dev.**
The total deviation of the calculated substance mass concentration **Mass.conc.** is determined using a linear error calculation. Independent of the number of measurements, the total deviation **MC.dev.** is always calculated in a way that **Mass.conc.** ±**MC.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 method for the majority of the applications possible with the 757 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 **`Mass`** and **`Add.mass`** 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.
- 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:

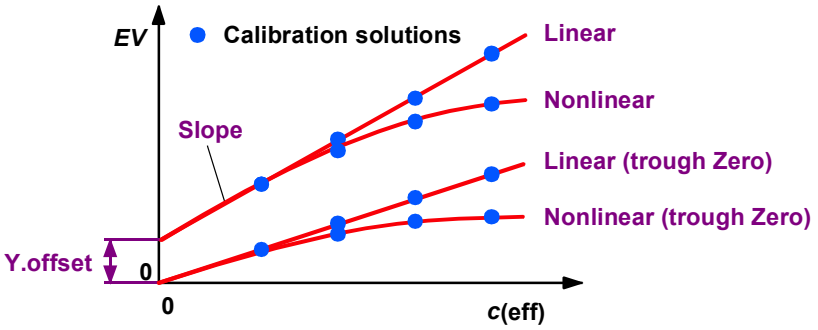
`EV(n)`	Evaluation quantity of a single measurement for calibration solution **n**
`mean(n)`	Mean value of all evaluation quantities for calibration solution **n**
`Std.dev.(n)`	Standard deviation of the individual value **`EV(n)`** = ***s*(n)**
***c*(eff,n)**	Effective mass concentrations of the calibration 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**
$\mathbf{y} = \boldsymbol{b}\mathbf{x}$	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)**

   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

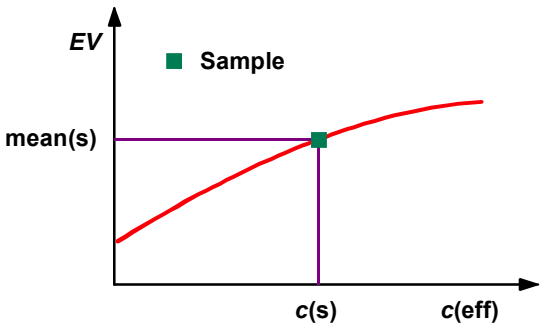


3. **Measurement of sample solution**
The sample solution with the unknown mass concentration ***c*(s)** of the sample is measured one or more times (defined by **No. of replications**). This gives:

`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:

$$\texttt{mean(s)} = d\,c(s)^4 + b\,c(s) - a$$



5. **Calculation of result deviation MC.dev.**
   The total deviation of the calculated substance mass concentration **Mass.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 **MC.dev.** is always calculated in a way that **Mass.conc.** ± **MC.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.

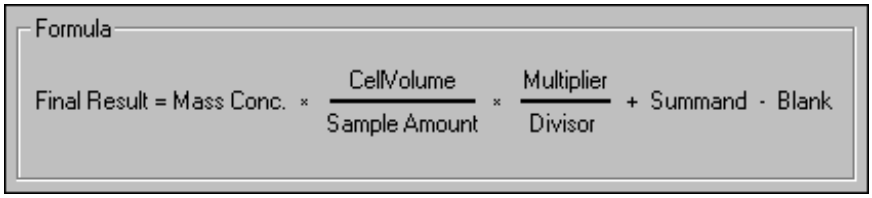
With regard to optimum accuracy and scatter, a number of **rules** must be observed with calibration curves:

- **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 **mass 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 Manual control

6.1 Computrace control

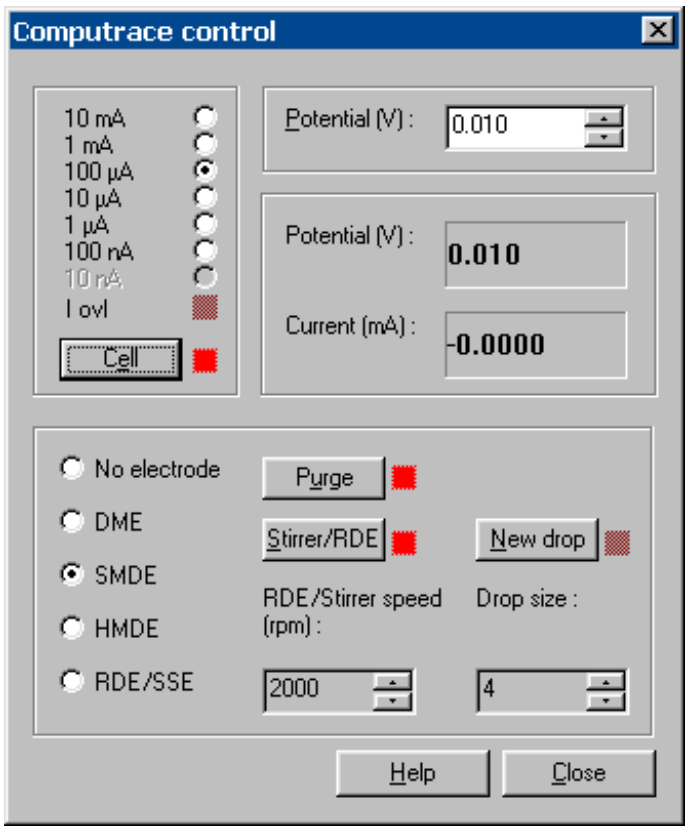
Computrace control selection

MAIN WINDOW / Utility / Computrace control

Start manual control of the 757 VA Computrace Stand.

Computrace control window

The **COMPUTRACE CONTROL** window serves for manual control of the 757 VA Computrace Stand.



10 mA ... 100 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 757 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.

Stirrer/RDE Switch on/off stirrer/RDE with the set **RDE/Stirrrer 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).

6.2 Dosimat control

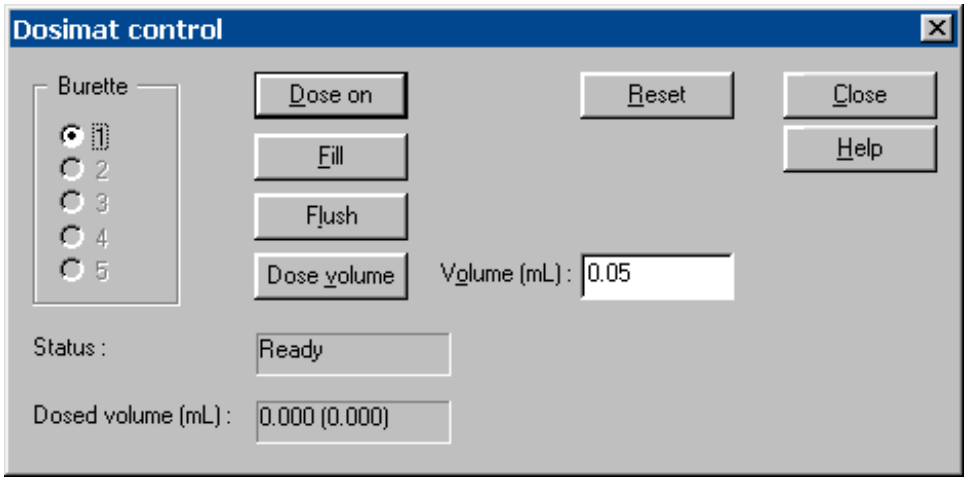
Dosimat control selection

MAIN WINDOW / Utility / Dosimat control

Start manual control of the 665 or 765 Dosimats connected to the 757 VA Computrace Stand.

Dosimat control window

The **DOSIMAT CONTROL** window serves for manual control of the Dosimats connected to the 757 VA Computrace Stand.



Burette

Selection of the Dosimat to be controlled manually.

Dose on

Switch on dosing by Dosimat. The solution is dispensed until the **<Dose off>** button is pressed.

Fill

The burette cylinder of the Dosimat is filled.

Flush

The burette cylinder of the Dosimat is emptied and refilled.

Dose volume

Dose the set **Volume**.

Volume (mL) [> 0.01 mL ; 0 mL]

Volume to be dosed.

Status [read only]

Display of the current Dosimat status.

Dosed volume (mL) [read only]

Display of current volume dispensed since last filling (first value) and accumulated volume if the display is not reset after filling (value in brackets).

Reset

Reset **Dosed volume** display and fill burette cylinder.

6.3 Film deposition

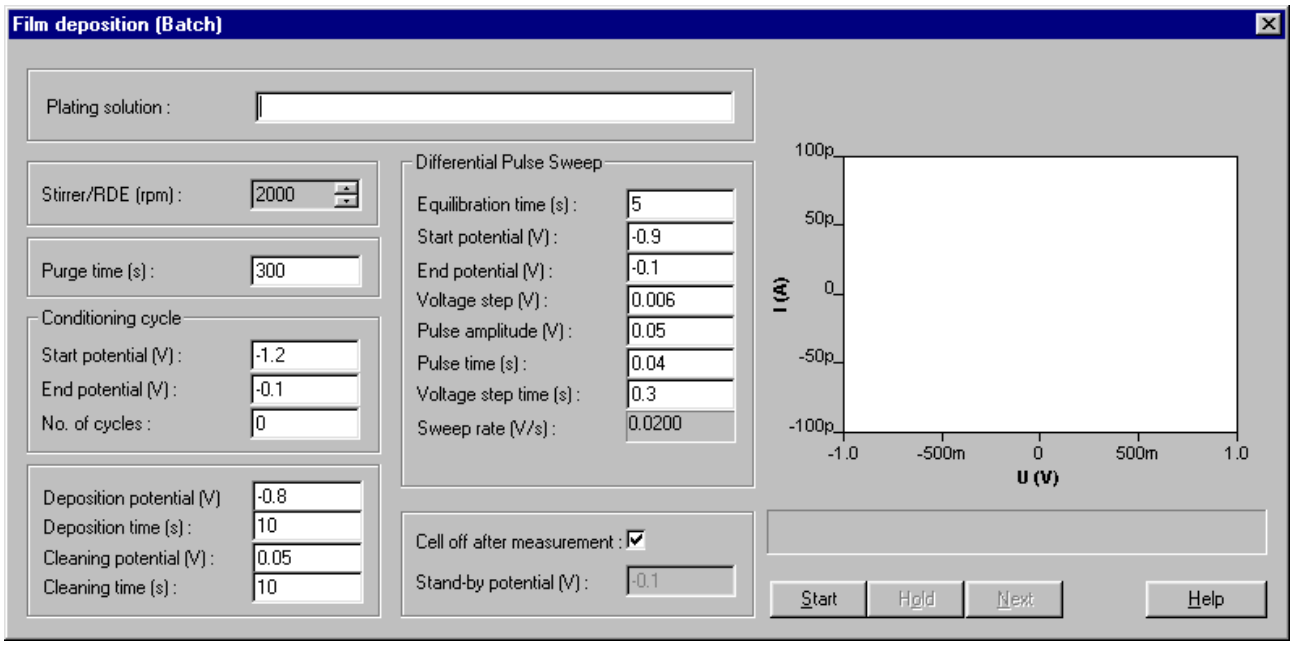
Film deposition selection

MAIN WINDOW / Utility / Film deposition

Start Hg deposition for solid state electrodes in the 757 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 757 VA Computrace Stand.



Plating solution [XXX characters ;]

Name of plating 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 ; -0.9 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.

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.

Sweep

Parameters of DP sweep used at the end of the film deposition for checking the electrode, see *VA measurement modse*, *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**.

6.4 Cleaning procedure

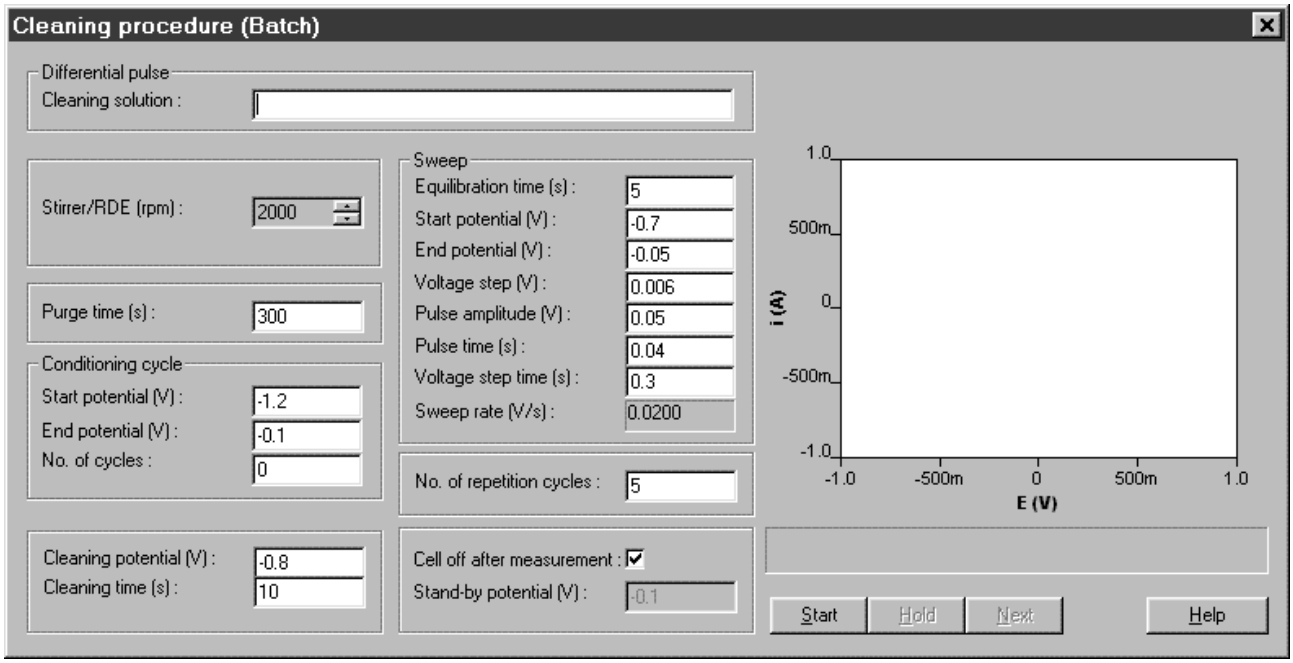
Cleaning procedure selection

MAIN WINDOW / Utility / Cleaning procedure

Start cleaning procedure for solid state electrodes at the 757 VA Computrace Stand.

Cleaning procedure window

The **CLEANING PROCEDURE** window serves for electrochemical cleaning of solid state electrodes at the 757 VA Computrace Stand.



Cleaning solution [XXX 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 ; -0.1 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.

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 ; 0]
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**.

7 How to ...?

7.1 Installation and program start

Install Dosimats for automatic addition

1. Connect 665 or 765 Dosimats to the 757 VA Computrace Stand (see *Installation of Dosimats*, *section 1.3*).
2. Make hardware settings for Dosimats (see *Hardware settings for Dosimats*, *section 1.3*).
3. Define the addition or predose solution in the **DOSIMATS** window (see *Dosimats, section 5.2*).

Switch on the instruments and start program

1. Switch on Dosimats (if present) and 757 VA Computrace Stand.
2. Make sure that the mains adapter of the VA Computrace Interface is connected to the mains.
3. Switch on 813 Compact Autosampler and 731 Relay Box (if present).
4. Switch on PC.
5. Start 757 VA Computrace software (see *Starting the 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**).

7.2 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. Select the desired user in the list of all users and change his user rights (see *User rights*, *section 2.6*).
3. Close the **USER RIGHTS** window by clicking **<OK>**.

7.3 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>**.

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. Select the directory for storage of the signal files in the **Data folder** field using the **<Browse>** button. Please note that a user specific data directory can be defined in the **User Directories** tab.

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  button (see *Performing measurements*, *section 4.2*).

Evaluate signal peaks automatically

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 SPECIFICATION** / **Signal** / **Peak search**. The **PEAK SEARCH** window is opened.
3. Set the parameters **Reverse peak**, **Reverse sweep** (for CV only), **Minimum peak width**, **Smooth factor**, **Minimum peak height**, and **Scope** for peak evaluation (see *Peak search*, *section 4.2*).
4. Click the  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 **EXPLORATORY SPECIFICATION** 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 SPECIFICATION** / **Signal** / **Peak search**. The **PEAK SEARCH** window is opened.
3. Check the **Manual** option.
4. Set the parameters **Reverse peak**, **Reverse sweep** (for CV only), **Minimum peak width**, **Smooth factor**, and **Minimum peak height** for peak evaluation (see *Peak search*, *section 4.2*).

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  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 **EXPLORATORY SPECIFICATION** 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 SPECIFICATION** / **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 4.2*).
4. Click the  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 **EXPLORATORY SPECIFICATION** 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.

7.4 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**. Confirm the question **The file already exists. Overwrite?** by clicking **<Yes>**.
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 665 Dosimats should be used for addition or predose, click 

and set the parameters to the desired values (see *Dosimats*, *section 5.2*).
7. If necessary, click 

and limit the **Highest current range** or **Lowest current range** in the **POTENTIOSTAT** window (see *Potentiostat*, *section 3.3*).
8. Click 

and set the parameters on the tabs **Determination**, **Voltammetric**, **Substances**, **Calculations** and **Documentation** (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 

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.

7.5 Determinations

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

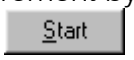
1. If you want to save the loaded and modified determination under the same name, click on  or **MAIN WINDOW** / **File** / **Save determination**. Confirm the question **The file already exists. Overwrite?** by clicking **<Yes>**.
2. If you want to save the loaded determination under a new name, click 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. Select the desired directory for automatic storage of determination files in the **Data folder** field.

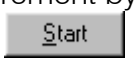
Perform a determination

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*).
4. If desired, modify the loaded method (see *How to edit the working method*).

5. Place the analysis solution in the measuring vessel at the 757 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 757 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 757 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 ρ(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 µLl Pb ion standard solution ρ(Pb) = 1 g/Ll (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 µlI Pb ion standard solution ρ(Pb) = 1 g/lI (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 813 Compact Autosampler

1. Install the 813 Compact Autosampler (see *section 1.3*).
2. Click on **MAIN WINDOW** / **Settings** / **General settings** and select the **Automation** tab.
3. Check the **Use Autosampler** option, modify the parameters for automation as desired and close the **GENERAL SETTINGS** window.
4. Close the VA Computrace program and restart the program.
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 modifiy them if need be.
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*).
9. If desired, modify the loaded method (see *How to edit the working method*).
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 813 Compact 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.

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**. Confirm the question **The file already exists. Overwrite?** by clicking **<Yes>**.
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. Check 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.

7.6 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*).
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**, **Cell volume**, and the number of standard 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 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 757 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 **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*).
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.
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**, **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 

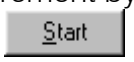
button.
10. Close the **EDIT WORKING METHOD PARAMETERS** window by clicking **<OK>**.
11. Place the sample solution in the measuring vessel at the 757 VA Computrace Stand.
12. Click on  or **MAIN WINDOW** / **Window** / **Monitor** to open the **MONITOR** window.

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 665 or 765 Dosimats. Proceed as follows:

1. Install Dosimats to the 757 VA Computrace Stand (see *How to install Dosimats*).
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*).
5. Select **Standard addition** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
6. Select **Automatic** in the **Addition** field of the **WORKING METHOD SPECIFICATIONS** window.
7. Click Dosimats to open the **DOSIMATS** window.
8. Check the Dosimats which are should be used for standard addition in the **Dosimat used** field (see *Dosimats, section 5.2*).
9. Close the **DOSIMATS** window by clicking **<OK>**.
10. Click Edit parameters 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.
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 Dosimat 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 757 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>**.

7.7 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*).
4. Select **Record calibration curve** 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 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 757 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*).
4. Select **Record calibration curve** 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.
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 757 VA Computrace Stand.
12. Click on  or **MAIN WINDOW** / **Window** / **Monitor** to open the **MONITOR** window.

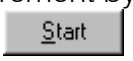
13. Start the measurement by clicking the  icon in the **MAIN WINDOW** or the  button in the **MONITORING** window.
14. Enter the **Calibration curve id** (used as part of the determination file name) in the **START CALIBRATION** window and click **<OK>**.
15. Each time a solution exchange is required 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 solution to the measuring solution using 665 or 765 Dosimats. Proceed as follows:

1. Install Dosimats to the 757 VA Computrace Stand (see *How to install Dosimats*).
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*).
5. Select **Record calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
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 Dosimat 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 757 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*).
4. Select **Sample with calibration curve** in the **Calibration** field of the **WORKING METHOD SPECIFICATIONS** window.
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 757 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>**.

7.8 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 757 VA Computrace Stand.
2. Put the plating 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 757 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 757 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.

7.9 Diagnostic procedures

Check the purging

1. Connect the inert gas to the 757 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 757 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 757 VA Computrace Stand (see *Hardware Manual*).
2. Make sure that the inert gas pressure is 1 ± 0.2 bar.
3. Add 10 mL ultrapure water to the empty measuring vessel at the 757 VA Computrace Stand.
4. Add 0.25 mL potassium chloride *c*(KCl) = 1 g/L (Metrohm No. 6.2308.020) to the measuring vessel.
5. Click on  or **MAIN WINDOW** / **Utility** / **Computrace control** to open the **COMPUTRACE CONTROL** window.
6. Select **DME** and click on  .
7. Mercury flows out of the capillary. The typical natural drop time is in the range of 1 - 5 sec. If the natural drop time is smaller than 0.5 sec, change the capillary and/or needle at the MME (see *Hardware Manual*).

8. Select **SMDE** and click on New drop.
9. A small drop is formed and removed in intervals. The drop size has to be reproducible and the drop has to be removed in every interval.
10. If the drop is not removed reproducibly, adjust the tapper mechanism (see *Hardware Manual*).
11. Select **HMDE** and click on New drop.
12. A small new drop is formed and stays at the end of the capillary. The drop should remain for at least 1 min. Otherwise the capillary and/or the needle should be changed (see *Hardware Manual*).

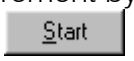
Perform a linearity test with the dummy cell

For testing the linearity of current measurement, the dummy cell of the 757 VA Computrace Stand is used with the test method **Test757_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 **Test757_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 757 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 Start 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.

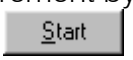
Perform a peak test with the dummy cell

For testing the peak measurement, the dummy cell of the 757 VA Computrace Stand is used with the test method **Test757_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 **Test757_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 757 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 test

The requirements of GLP (Good Laboratory Practice) include the periodic testing of analytical instruments with regard to reproducibility and accuracy using **standard operating procedures**. Metrohm suggests the procedure described below as the standard operating procedure for testing the 757 VA Computrace Stand:

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. Perform the linearity test with the dummy cell (see *How to perform a linearity test*).
4. Perform the peak test with the dummy cell (see *How to perform a peak test*).
5. Click on  or **MAIN WINDOW** / **File** / **Load method**.
6. 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.
7. Add 20 mL ultrapure water to the empty measuring vessel at the 757 VA Computrace Stand.
8. Add 0.5 mL potassium chloride c(KCl) = 3 mol/L (Metrohm No. 6.2308.020) to the measuring vessel.
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. The **PLACE SAMPLE** window appears.
11. Add 100 µL Pb ion standard solution ρ(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
12. The sample solution is measured three times. Then the **MANUAL ADDITION** window appears.
13. Use a pipette to add 100 µL Pb ion standard solution ρ(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
14. The sample solution spiked with standard addition solution is measured three times. Then the **MANUAL ADDITION** window appears.

15. Use a pipette to add 100 µL Pb ion standard solution ρ(Pb) = 1 g/L (Metrohm No. 6.2301.100) into the measuring vessel and click the **<OK>** button.
16. The sample solution spiked again with standard addition solution is measured three times. Then the **END OF DETERMINATION** window appears.
17. Click the **<OK>** button. The determination is saved automatically and the result report is printed out.
18. To assess the recorded lead determination, the results printed out in the full report for the mass concentration of lead **`Mass conc.`** and its total scatter **`MC.dev.`** are used. The limit values of these two results depend greatly on the care taken in the preparation of the analysis solution and in the dispensing of the standard addition solutions. When the procedure is carried out properly and carefully, the following results should be expected:
    - **Accuracy = 95 ... 105 %**
      `Final Results: Pb =  0.95 ... 1.05 g/L`
    - **Scatter ≤ ± 3 %**
      `Res. dev  ≤  ± 0.03 g/L (± 3 %)`
19. If desired, the reproducibility can be determined by performing the **`Testpb`** method several times and comparing the results obtained for the mass concentration **`Mass conc.`**.

8 Troubleshooting

8.1 General procedure for error messages

Error messages and warnings are displayed in the **CT757** window. Read the information about the possible causes and the procedure for their rectification and click the **<OK>** button.

8.2 Connection problems

Error message "Could not start the embedded system"

If this error message appears after starting the VA Computrace program, the VA Computrace Interface is not running properly. Proceed as follows:

1. Close the VA Computrace programProgramm.
2. Remove the cable to the mains adapter from the VA Computrace Interface.
3. Reconnect the mains adapter to the VA Computrace Interface.
4. Restart the VA Computrace program.

Error message "Cannot reach the hardware"

If this error message appears after starting the VA Computrace program, the 757 VA Computrace Stand is not switched on. Proceed as follows:

1. Switch off the 757 VA Computrace Stand.
2. Wait at least 2 sec.
3. Switch on the 757 VA Computrace Stand.
4. Click the **<Retry>** button in the **CT757** window.

8.3 Software problems

Error message "No access to software"

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 (see *Software installation*, *section 1.3*).

Error message "The file 'ecousb.sys' is needed"

This message indicated 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.

8.4 Dosimat problems

Dosimat does not work

1. Check if the Dosimat is switched on.
2. Check the connecting cable between the Dosimat and 757 VA Computrace Stand.
3. Click on **MAIN WINDOW** / **Settings** / **General settings** and check the entries on the **Hardware** tab of the **GENERAL SETTINGS** window (see *Hardware settings for Dosimats*, *section 1.3*).
4. Exit/restart the 757 VA Computrace software.
5. Activate the Dosimat in the **DOSIMAT** window for every method used (see *Dosimats*, *section 5.2*).
6. Check if a solution number **No.** is defined on the **Substances** tab of the **EDIT WORKING METHOD PARAMETERS** window.

Note: If Dosimats are connected to the 757 VA Computrace Stand, the instruments must always be switched on in the sequence Dosimat → 757 → PC.

Irreproducible standard additions with 765 Dosimat

1. Click on  or **MAIN WINDOW** / **Utility** / **Dosimat control** to open the **DOSIMAT CONTROL** window (see *Dosimat control window*, *section 6.2*).
2. Select the desired Dosimat in the **Burette** field.
3. Click the 

button to empty and refill the exchange unit installed on the Dosimat.
4. Check if there are air bubbles left in the glass cylinder of the exchange unit. If this is the case, repeat the flushing procedure by clicking the 

button.
5. Close the **DOSIMAT CONTROL** window.
6. Check the **Dose rate** parameter on the **Hardware** tab. The maximum dosing rate for use of the 6.1824.000 4-way microtip is 2.5 mL/min.

Wrong volume display with Dosimat

If the exchange unit at the Dosimat is changed without resetting the Dosimat, the volume display during dispensing may be wrong. Proceed as follows:

1. Switch off the Dosimat.
2. Close the **757 VA Computrace** program.
3. Switch off the 757 VA Computrace Stand.
4. Switch on the Dosimat.
5. Switch on the 757 VA Computrace Stand.
6. Start the **757 VA Computrace** program.

8.5 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 be always 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 for the investigation of reversible redox systems.
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, 1^{st} derivative) is primarily suitable for determinations based on reversible redox reactions and is virtually completely insensitive to irreversible reactions.
5. **AC2** (Alternating Current, 2^{nd} derivative) is also primarily suitable for determinations based on reversible redox reactions. Compared with the AC1MODE measurements, an increase in sensitivity, resolution and separation efficiency is often obtained.
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 Voltammetry) is mainly used to determine substances in an organic matrix by means of mercury film electrodes without prior digestion and deaeration. Only analytes which form an amalgam can be analyzed.
8. **CV** (Cyclic Voltammetry) is mainly used to investigate electrode processes and for kinetic studies.

8.6 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 or 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 if necessary or 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

With **all MME types**:

1. Have stirring or degassing been switched off during the measurement?
2. Check contact between needle and capillary. 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 or replace sealing needle (see *Hardware Manual*).
2. If the electrode drops much too quickly: reduce the **Voltage step time** on the **Voltammetric** tab of the **EDIT WORKING METHOD PARAMETERS** window.

With **HMDE**:

1. If the electrode surface is overcharged: check deposition potential and time.
2. If no drops are at the capillary: change the capillary or replace sealing needle (see *Hardware Manual*).

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 or 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 (inverse voltammetry) instead of DME or SMDE.

With **HMDE**:

1. Has the complex former been forgotten? (adsorptive 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 or replace sealing needle (see *Hardware Manual*).

With **RDE/SSE**:

1. The background current is too high: repolish 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 complex former?
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 complex formers).
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 or 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 adsorption voltammetry.

With **RDE/SSE**:

1. Electrode surface overcharged: 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. Addition solution with metal complexing solution (time reaction).

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 757 VA Computrace Stand in the factory, a purging time of 3...5 min usually suffices.

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 alkalis or alkaline earths (e.g. acetate buffer) 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*). The use of chloride Cl^- free bridging electrolyte solutions (e.g. KNO_3 sat.) is recommended as a countermeasure.

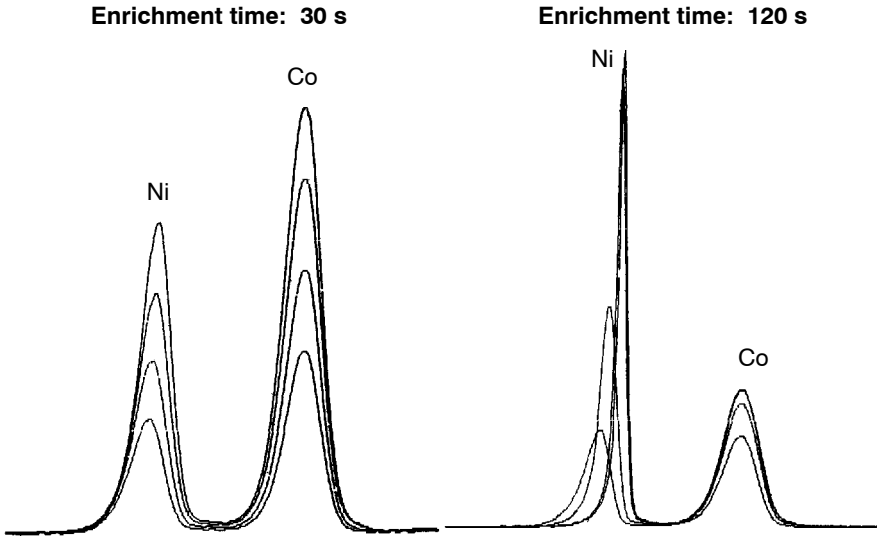
Overcharging of the working electrode

Under unfavorable conditions (high concentrations and/or long enrichment times), the enrichment of species at polarized electrodes leads to overcharging phenomena such as non-linear standard addition curves or splitting into multiple peaks which are caused by saturation and different deposition forms.

A **shorter enrichment time** usually solves the problem. The following rule of thumb holds: In general, enrichment 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 enrichment even with concentrations $\rho > 100$ µg/L (e.g. DP voltammetry at the HMDE or also at the DME).

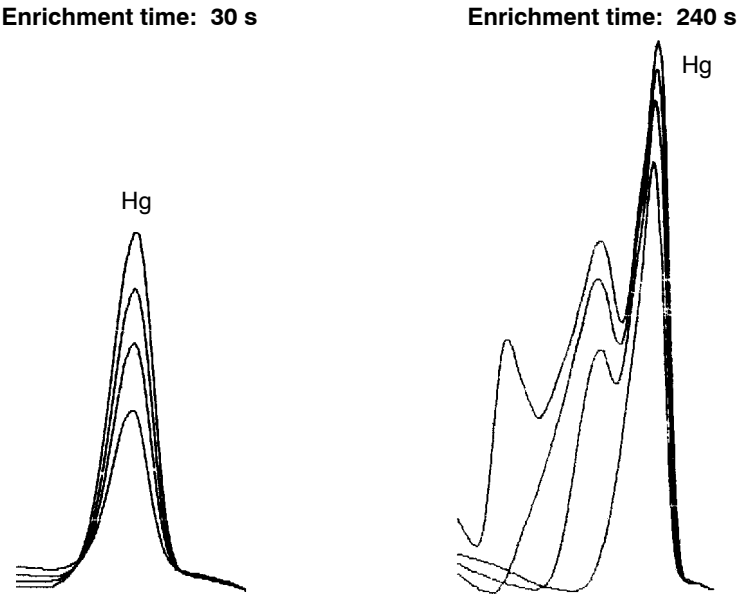
The effects of an enrichment time which is too long are shown by the following two examples:

- **Nickel and cobalt determination in the trace region by cathodic adsorption stripping voltammetry (with dimethylglyoxime complexes)**
  Prolongation of the enrichment 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:



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:

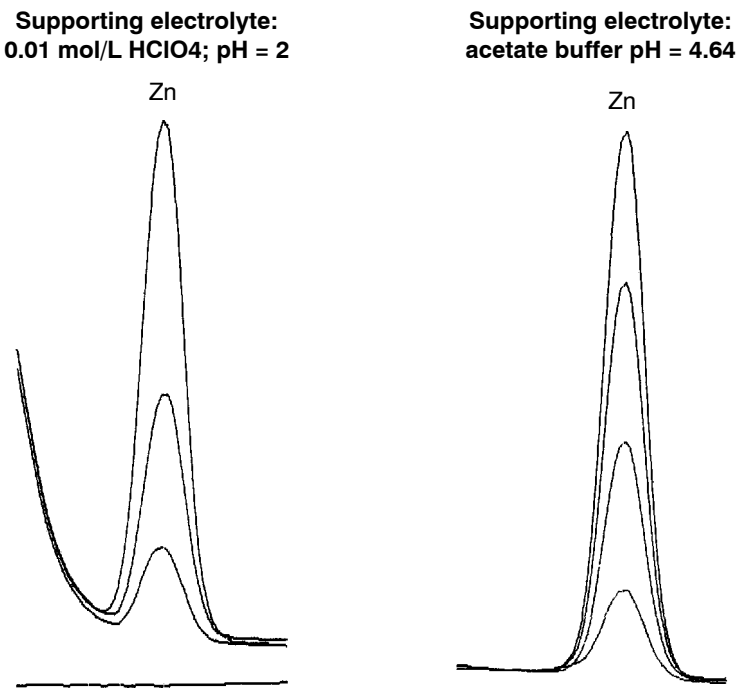


Analysis solution:	100 µg/L Hg
Supporting electrolyte:	HClO4/HCl
Standard addition:	with 1 µg Hg
Electrode:	Au-RDE

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).



Analysis solution:	deionised water
Standard addition:	with 50 ng Zn
Electrode:	HMDE (enrichment 60 s at –1.2 V)

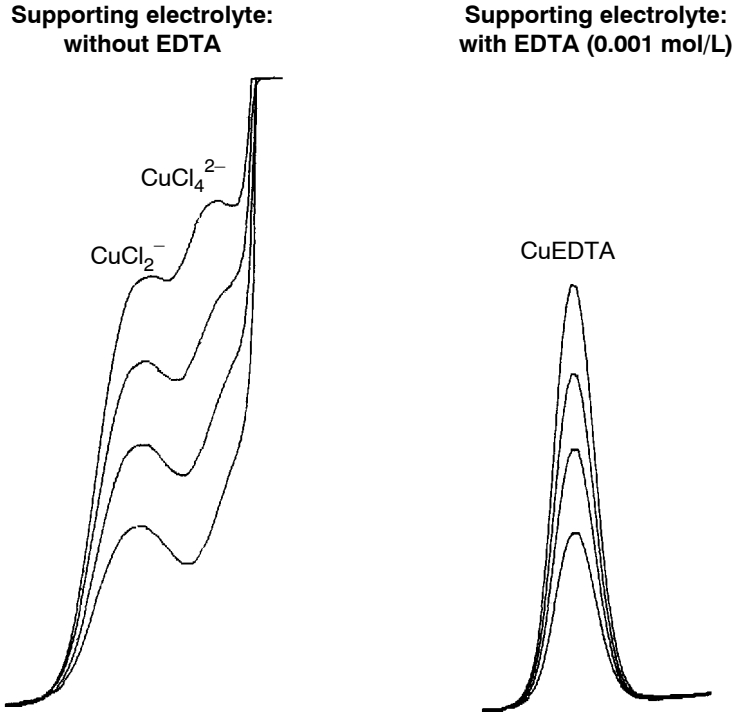
Complex formation

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 which 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 $CuCl_2^-$.)



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*), changing the pH value, changing the supporting electrolyte concentration, modifying or changing the supporting electrolyte, use of complexing agents (see *Complex formation*), longer enrichment times and changing the measurement technique.

If the curvature of the baseline can not or only partially be eliminated by the above measures, the 757 VA Computrace offers the possibility to approximate a curved baseline by selecting **Polynomial** or **Exponential** for the baseline **Type** (see *Baseline, section 5.2*).

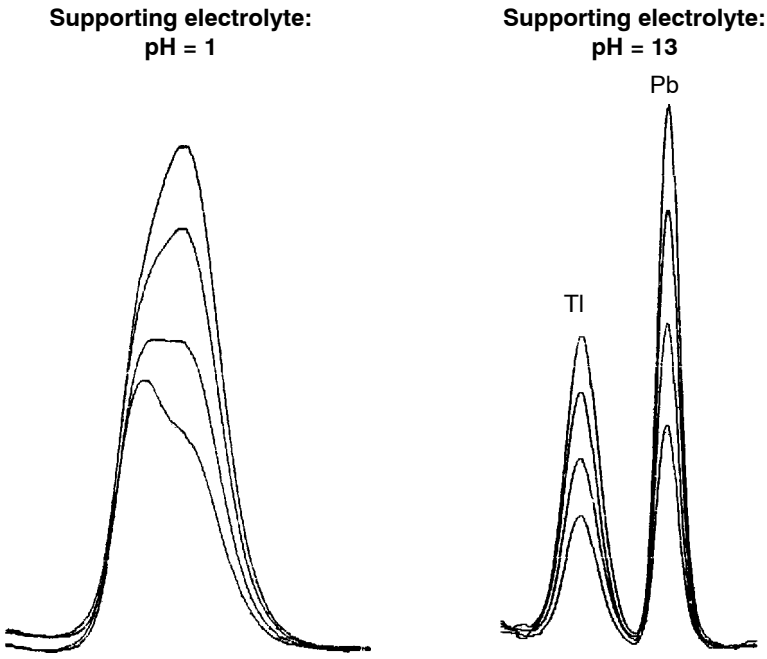
A further possibility to evaluate peaks on curved baselines involves the background subtraction after measuring a blank solution, in particular when the curved baseline can be clearly attributed to the supporting electrolytes (see *Determination, section 5.2*).

Peak overlapping

If the peak overlapping has reached a critical level at which the calculated peak height or peak area is falsified by the neighbouring 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 (see example below), changing the supporting electrolyte concentration, changing the supporting electrolyte, use of complexing agents (see *Complex formation*), longer enrichment 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 both 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.

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Index

A

B

C

D

E

F

G

H

I

L

M

N

O

P

Q

R

S

T

U

V

W

Z