Lesson 1:

This lesson demonstrates the use of *DigiElch* for running a C-Profile-Simulation for a cyclic voltammetric system (i.e. a simulation showing simultaneously how both the current curve and the associated concentration profiles are changing as function of the electrode potential). It also explains most of the commands available in the C-Profiles Menu and the options for customizing the appearance of the screen display and the drawing of the concentration profiles. It is assumed in the following that the user has worked trough Lesson0.pdf and that the file "CVSimSOcat.cvs" has been prepared and saved as described there.

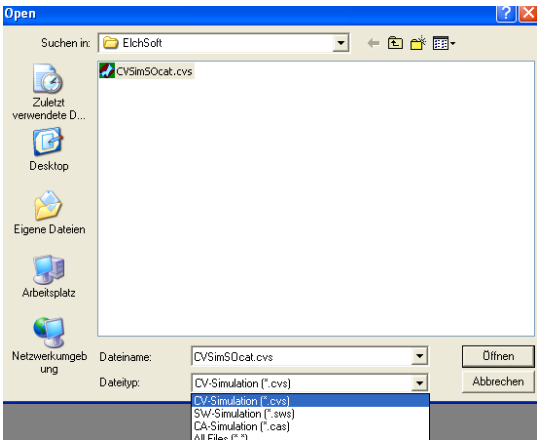
When working through the lesson, please, keep in mind that some menu commands may be disabled as long as *DigiElch* is running as trial installation.

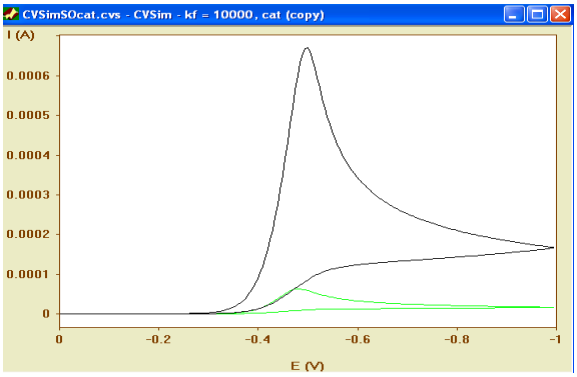
Summary

1. Running a C-Profiles-Simulation

1.1. Opening the CV-simulation document "CVSimSOcat.cvs"

Start *DigiElch* and click on File -> Open select the file type CV-Simulation (*.cvs) in the appearing standard Windows file dialog and go to the folder where "CVSimSOcat.cvs" has been saved in Lesson0. In the example below it is assumed that this file has been saved in the folder "ElchSoft". Continue with **Open** ("Öffnen")





When opening a CV-Simulation document or when creating a new one, the CV-Simulation Menu will be activated and the associated window shows the CV-current curves of all involved simulation objects as demonstrated in the above picture on the right-hand side. For running a C-Profiles-Simulation (i.e. a simulation showing simultaneously how both the current curve and the associated concentration profiles are changing as function of the electrode potential) it is necessary to leave the CV-Simulation Menu and to activate the C-Profiles Menu.

1.2. Activating the C-Profiles Menu

The C-Profiles Menu is activated by clicking on View -> Active Simulation -> Concentration Profiles () from within the CV-Simulation Menu. Unlike previous versions of *DigiElch* this command is always active (unless a simulation is just running) no matter whether the simulation of the CV-current curve has or has not yet completed. In the first case the C-Profiles Menu is activated and the concentration profiles referring to the end of the simulation are displayed on the left-hand side of the associated splitter window while the current curve is plotted on the right hand side of the splitter window as shown in the following picture. (The splitter window remains empty if the simulation object is empty or if the simulation has not yet been executed.)

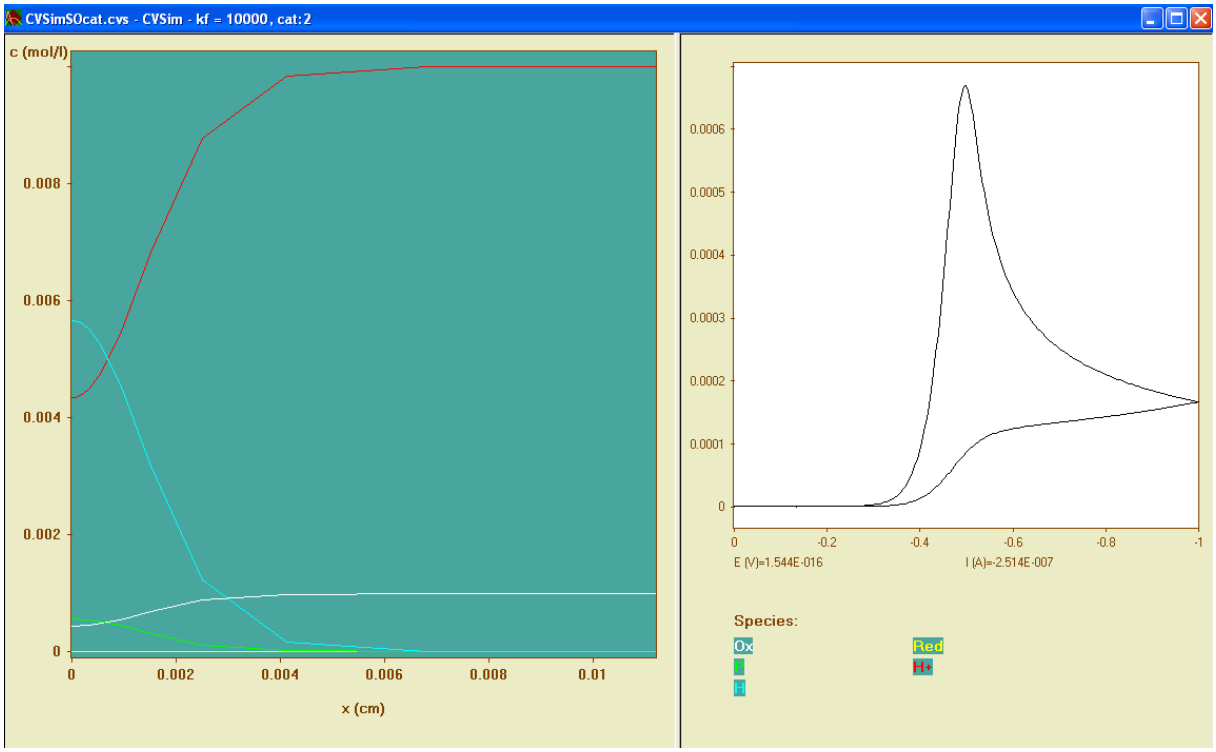
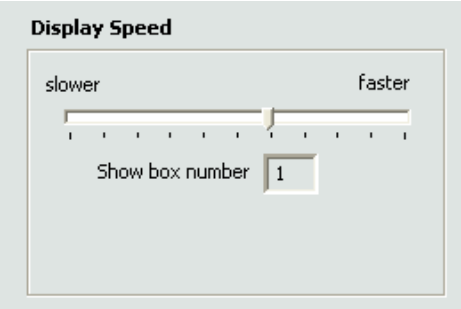


Figure 1

1.3. Running a C-Profiles Simulation using the Fixed Grid Simulator, applying the Pause/Continue command and adapting the display speed

If the simulation object is empty you must complete the input of the CV-Properties page (raised by clicking on Simulation -> Edit Properties ( )) before the command for running a C-Profiles Simulation is activated. This is not necessary for the simulations stored in the "CVSimSOcat.cvs"-file. Thus, you can directly click on Simulation -> Run -> Fixed Grid Simulator ( ) in order to see how the current curve and the concentration profiles are changing as function of the electrode potential. However, nowadays computer are usually so fast that it is hardly possible to see what is really happening. In most cases it is therefore a good idea to slow down the speed with which the concentration profiles are plotted. Press down the right mouse button while the mouse cursor is localized over the left-hand part of the splitter window showing the concentration profiles.

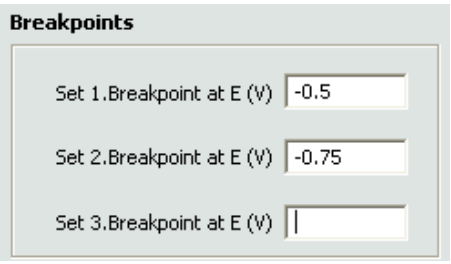


Go to Display Speed in the appearing Displaying C-Profiles-dialog box and move the pointer from the right-hand side to a mid-scale position and repeat Simulation -> Run -> Fixed Grid Simulator ( ).

The plotting of concentration profiles and current curve can be interrupted by clicking on Pause ( ). As long as the plotting is paused the menu command Pause is replaced by Continue. This enables the user to Pause and Continue plotting by clicking on one and the same menu command ( ).

1.4. Setting of Breakpoints

If the user wants to see the concentration profiles referring to a predefined value of the electrode potential it is more convenient to set a breakpoint (in the Displaying C-Profiles-dialog) as shown in the following picture.



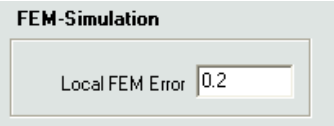
In this case the plotting is paused for the first time when reaching the potential $E = -0.5V$. It continues by pressing Continue ( ) and stops again when reaching $E = -0.75V$.

The potential and current value referring to the actual display are shown as *E(V)*- and *I(A)*- couple on the right-hand side of the splitter window immediately beneath the window part showing the CV-current curve.

1.5. Running a C-Profiles Simulation using the Adaptive Grid Simulator

As outlined in Lesson0.pdf we generally recommend working with the Fixed Grid Simulator because of its robustness and efficiency resulting from the extraordinarily high exponential convergence as far as the flux (current) computation is concerned. It leads to the surprising result that the accuracy of the simulated current curve is much better than the accuracy of the simulated concentration profiles. Indeed, looking at Figure 1 reveals that the concentration profiles were simulated on a coarse grid yielding sufficiently smooth concentration profiles only in the vicinity of the electrode surface while the concentration profiles are more and more approximated in the form of linear segments the greater the distance from the electrode. Increasing the number of boxes (grid points) in the Fixed Grid Simulator does not really overcome this problem because, due to the exponentially expanding grid, the maximum level of refinement is always introduced near the electrode.

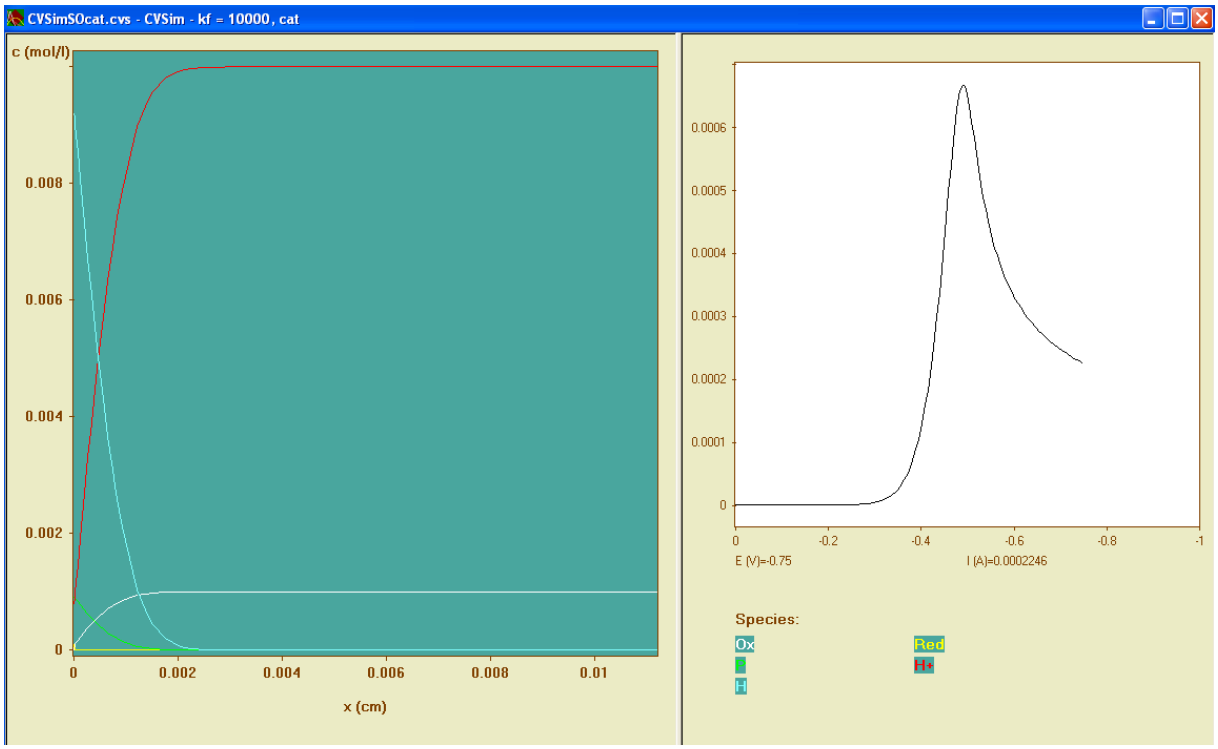
In a situation where the concentration profiles are of primary interest it is therefore more appropriate to use the Adaptive Grid (FEM) Simulator for keeping the local error in the concentration profiles below a predefined value no matter what the distance of the concentration point from the electrode surface is.



In the present case *Local FEM Error = 0.2* may be sufficient. Click on Simulation -> Edit Properties ( ), activate the Simulation Parameters page and enter this value.

Then click on Simulation -> Run -> Adaptive Grid Simulator ( ). Only 15 additional grid points are introduced in the course of the simulation. Nevertheless, relatively smooth concentration profiles are now obtained over the entire distance.

This is shown in the following picture referring to the second breakpoint, $E = -0.75V$. Of course, the profiles become smoother and smoother the smaller the value of *Local FEM Error*. Unfortunately, the optimal value can be hardly predicted in advance. In most cases it must be optimized by "trial and error". The default value *Local FEM Error = 0.005* may result in (unnecessarily) large numbers of grid points and computational costs.



2. Saving the simulation document, saving the screen display, exporting current curve and concentration profiles

2.1. Saving the simulation document

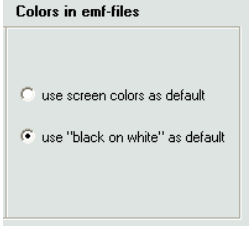
All simulations involved in a simulation document can be saved by means of a standard Windows file dialog that appears when clicking on Document -> Save ( ) or Document -> Save As. The first command works "quiet" using the default path for saving the simulation document. The second command enables the user to save the document with a new name. Document -> Save As is used instead of Document -> Save if a new document (with an empty default path) is saved for the first time. Both commands are disabled as long as the simulation is running (even if it is paused).

All chemical parameters and all simulation parameters (including the current curve) but not the settings for the screen display such as colors, fonts etc. are saved for each simulation. Note, however, that (unlike previous version of *DigiElch*) all simulated concentration profiles are stored in memory and written to the cvs-file when saving a simulation document after having completed a C-Profile Simulation. It is therefore a big difference in the size of cvs-files saved before and after having completed a C-Profile Simulation. The saving of all simulated concentration profiles is particularly useful when presenting results obtained with high computational costs (complex mechanisms comprising numerous species, systems requiring 2D-simulations) because the drawing of the concentration profiles can be immediately started without having to redo the simulation once more.

2.2. Saving the screen display

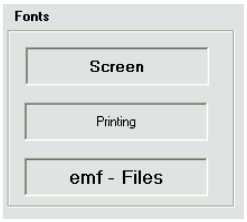
The graphics showing the concentration profiles on the screen can be saved as emf-file in enhanced Windows metafile format by clicking on Document -> Save Screen Display ( ) from within the C-Profiles Menu. This command is active only if the drawing of the concentration profiles has been paused (either manually or by setting a breakpoint as described above in 1.3. and 1.4.).

The screen display can be saved either in "black and white" or using the actual display colors (except the child window's background color which is always saved in white).

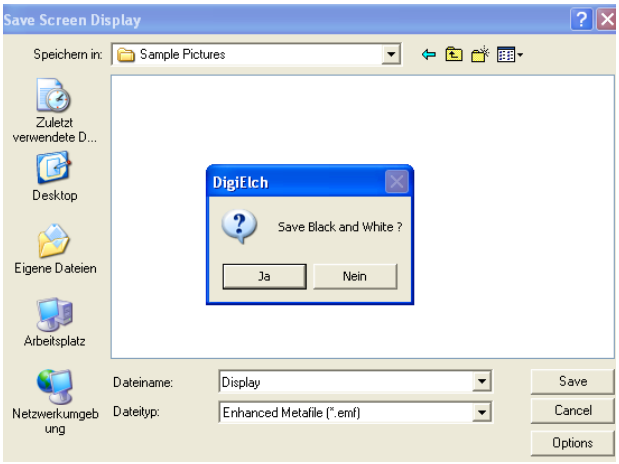


Whether the first option or the second one is used depends on the default settings of Colors in emf-files which can be adjusted by clicking on View -> Preferences ( )

The default type and size of the font used for labeling the axes in the emf-file can be adjusted independently of the screen font by means of a standard Windows font dialog that appears when clicking on emf-Files. The **Fonts** settings are available on the Preferences page raised by clicking on View -> Preferences ( )



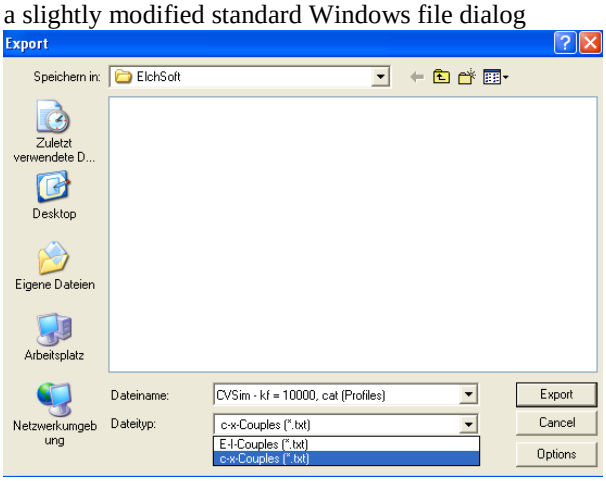
The Document -> Save Screen Display-command opens a slightly modified standard Windows file dialog.



Clicking on the button **Options** enables the user to select whether the screen display is saved in "black and white" or using the actual screen colors. This selection applies only to the actual operation and does not overwrite the default settings of Colors in emf-files on the Preferences page.

2.3. Exporting concentration profiles and/or CV-current curve

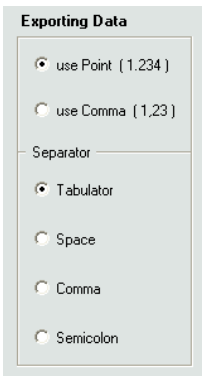
The CV-current curve and/or the simulated concentration profiles can be exported in ASCII- format by applying the Simulation -> Export ( ) – command. This command is active only if the drawing of the concentration profiles has been paused (either manually or by setting a breakpoint as described above in 1.3. and 1.4.). It opens a slightly modified standard Windows file dialog



The two different export options are described in the following:

2.3.1. Export Option: E-I-couples (*.txt)

Data exported in this way cannot be re-imported into *DigiElch*. The purpose of this export option is to export the *actual state* of the current curve (visible on the right-hand side of the splitter window) in a format that can be easily handled by third-party presentation software. For this purpose a few formatting options are provided.



By default (i.e. when selecting this export filter and pressing directly the **Export** button in the Windows file dialog box shown in 2.3.) the current curve is exported in the form of voltage-current couples using the number-format and the separator selected in **Exporting Data** available on the Preferences page which is raised by clicking on View -> Preferences ( ). This selection can be temporarily overwritten (without changing the default settings in **Exporting Data**) by clicking on the **Options** button in the Windows file dialog box shown in 2.3.

2.3.2. Export Option: c-x-couples (*.txt)

This export option works analogously as described in 2.3.1 with the only difference that the *actual state* of the concentration profiles (visible on the left-hand side of the splitter window) is exported. The concentration profiles simulated for all species are exported in the following form

general_header

species_header_1
x_1 separator C_1_1
x_2 separator C_1_2
.
.
x_N separator C_1_N

species_header_2
x_1 separator C_2_1
x_2 separator C_2_2
.
.
x_N separator C_2_N

etc.

where **N** is the number of grid points used in the simulation.

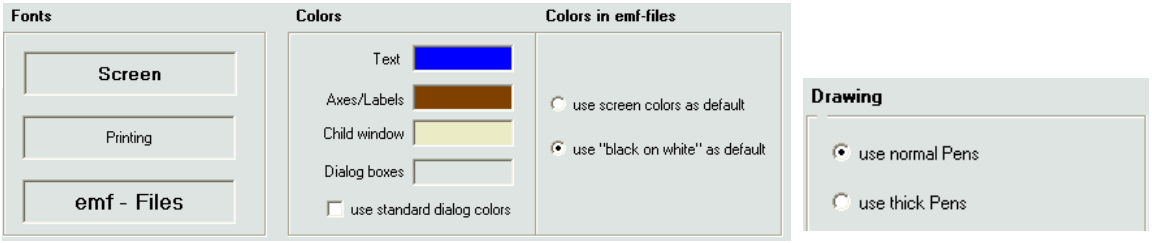
- **general_header**
  concentration profiles at E (V): E_Value
  number of species: Number_of_Species_Value
- **species_header_i**
  species name: Name_of_species_i
  number of x (cm), C[Name_of_species_i] (m/l) couples: N
- **C_i_j** is the concentration of the *i-th* species at the *j-th* grid point, and **x_j** is the distance of the *j-th* grid point from the electrode surface
- **Separator** is one of the following characters: 'Space', 'Tab', 'Comma' or 'Semicolon'
- Numbers can be formatted using either point or comma.
- The formatting of numbers and the separator can be specified by clicking on the **Options** button in the file dialog box. Otherwise, the default settings defined in the **Preferences** dialog are used.

3. Customizing colors, fonts and the drawing of concentration profiles and cyclic voltammatric current curve

The options for customizing colors, fonts and the drawing of the screen display are split into two groups: The **first group** involves options which apply to all windows associated with a CV-simulation document no matter whether CV-current curves, concentration profiles ore fitting objects are displayed. The **second group** applies only to the display shown in the left- or right-hand side of the splitter window associated with the C-Profiles Menu.

3.1. Customizing options applying to all windows

These options are compiled on the Preferences page which appears by clicking on View -> Preferences ().



The options for Colors in emf-files have already been described in 2.2. The remaining options work as follows:

Fonts

The default font and its size used for labeling the axes can be adjusted independently for screen display, printing and for the saving of the screen graphics in emf-format by means of the standard Windows font dialog that appears when clicking on the associated text field.

Colors

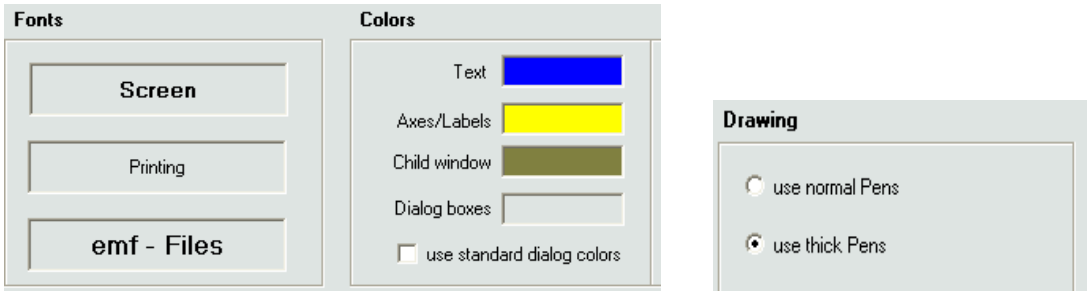
The default colors for drawing the info-text, for labeling axes as well as the child-window's background color and the color of dialog boxes can be adjusted by means of the standard Windows color dialog box that appears when clicking on the associated color field. The color shown in the field associated with Dialog boxes is only used if use standard dialog colors has not been selected. Otherwise, the color settings of the operating system are used for all *DigiElch*'s dialog boxes. Note that changing the color settings for Dialog boxes and Child window takes effect only after creating/opening a new dialog box/child window.

Drawing

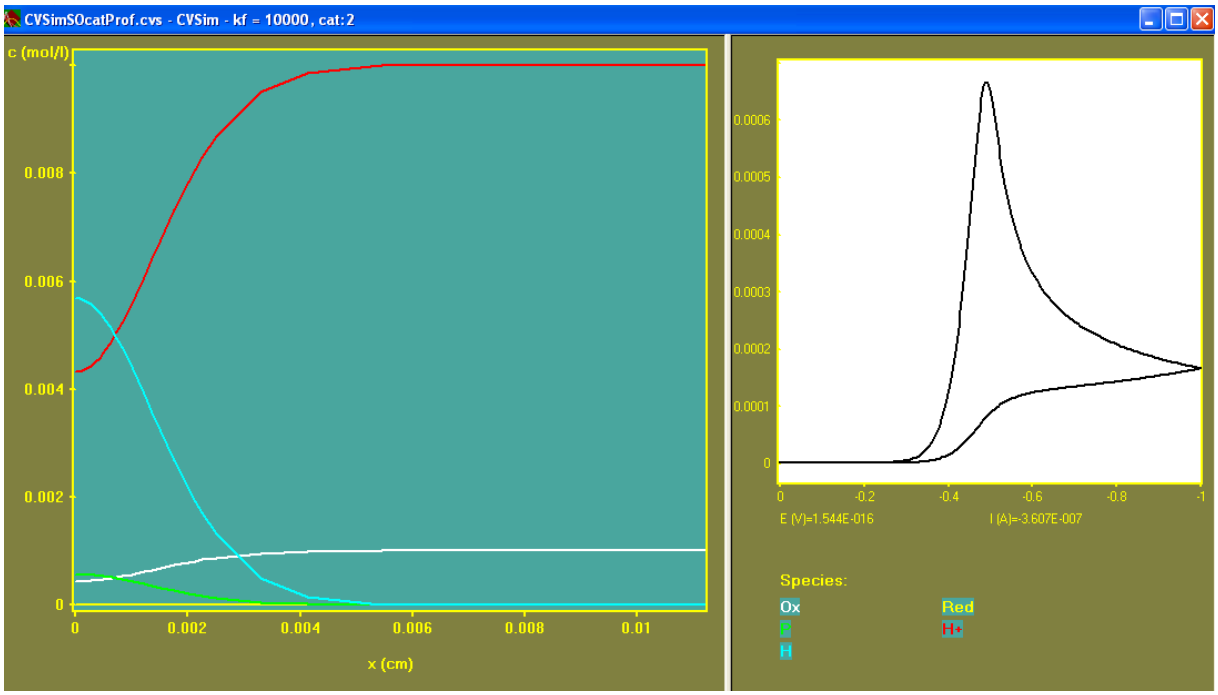
This selection decides whether a normal or a thick pen is used for printing, storing emf-files and drawing the screen display.

Example:

The settings for **Fonts**, **Colors** and **Drawing** shown above beneath 3.1. lead to the display of **Figure 1** in 1.2. Using the following settings



results in

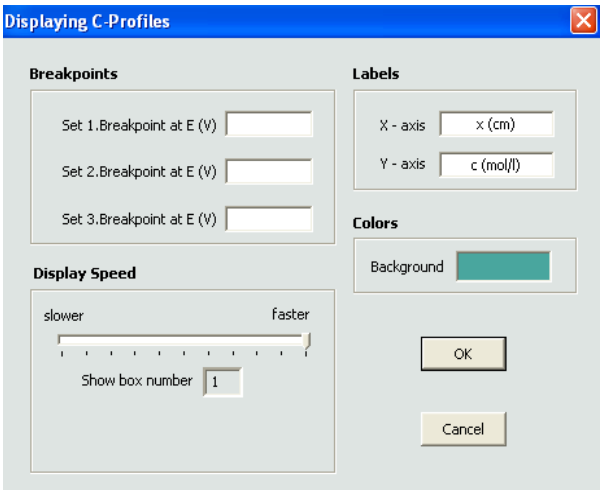


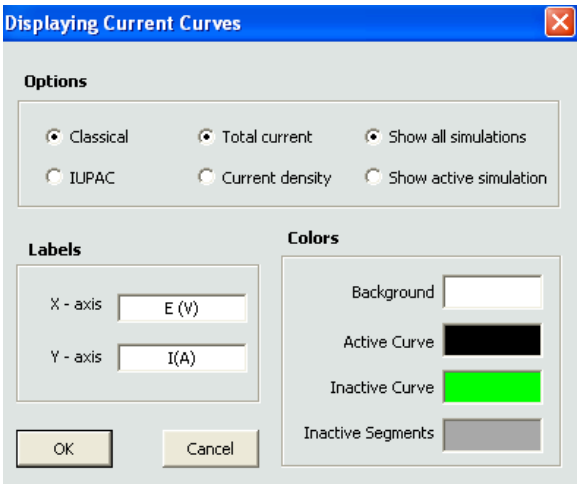
Resetting the default colors:

The default colors can be reset by clicking on View -> Reset Default Colors in *DigiElch's* start menu. The latter is active only immediately after starting *DigiElch* or when closing all child windows.

3.2. Customizing options applying only to the display shown in the left- or right-hand side of the C-Profiles splitter window

Depending on whether the mouse cursor is localized over the left- or right hand side of the splitter window, a click on the right mouse button raises one of the following dialog boxes

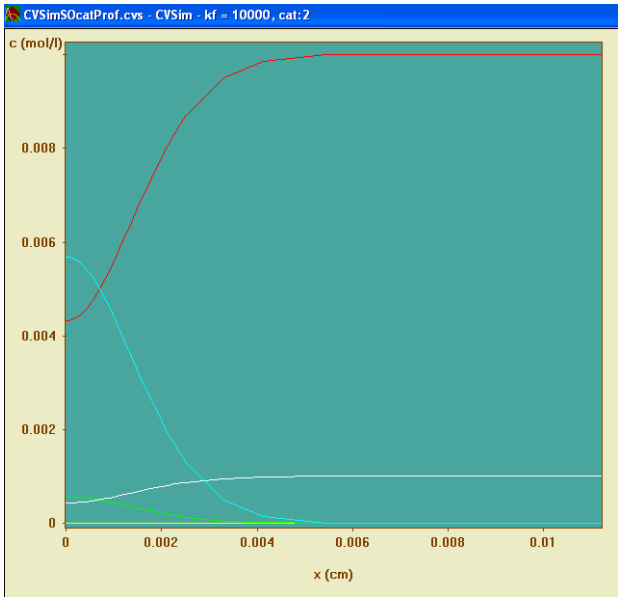


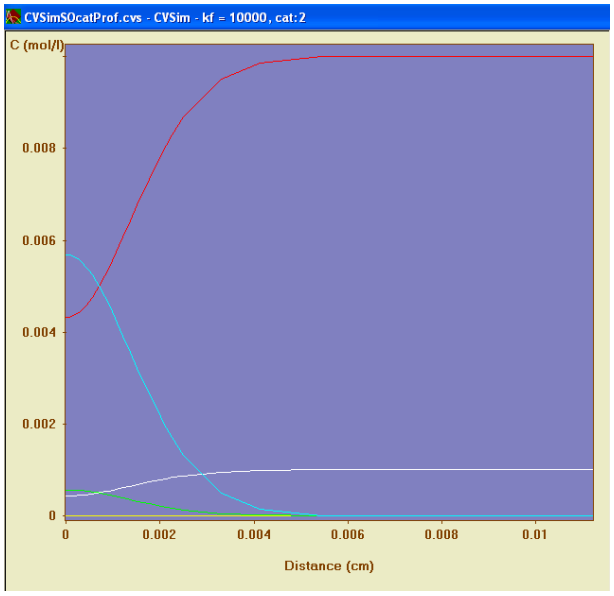


Displaying C-Profiles

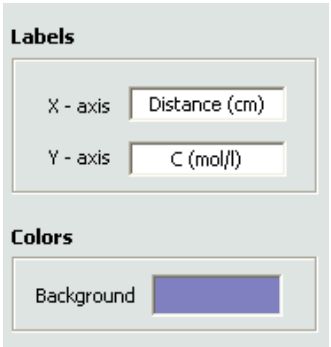
The adjustment of the Display Speed and the setting of Breakpoints has already been described above in 1.3. and 1.4., respectively.

The effect of Labels and Background is best explained by comparing the following to pictures:





The left picture refers to the settings of Labels and Background shown above, the right picture refers to the following settings



Displaying Current Curves

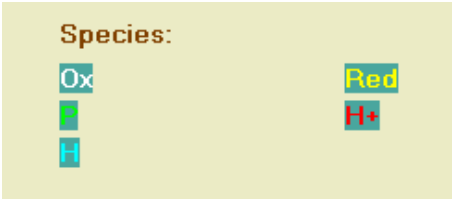
Options

- Classical/IUPAC
  if Classical is selected negative potentials are drawn from left to right and the cathotic current is positive. Otherwise positive potentials are drawn from left to right and the cathotic current is negative
- Total current/Current density
  Either the total current or the current density is plotted.
- Show all simulations/Show active simulation
  This option has no effect as long as the C-Profiles Menu is activated. In this case only the active simulation is plotted on the right-hand side of the C-Profiles splitter window. However, the selection will be taken over when returning to the CV-Simulation Menu.

Colors
The default colors for drawing the *background*, the *active CV*, the *inactive CV* and the *inactive cycles* (segments) of the active CV can be adjusted by means of the standard Windows color dialog box that appears when clicking on the associated color field. The selection for the inactive CV will be taken over when returning to the CV-Simulation Menu.

Labels
The default labels (*E(V)* and *I(A)*) used in the text that appears immediately beneath the display of the CV-current curve can be modified by changing the text in the associated text field.

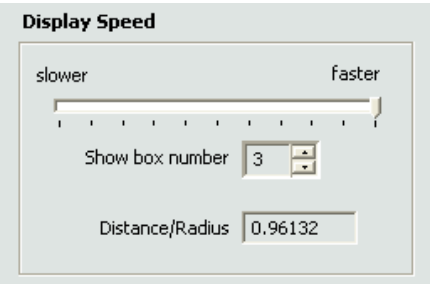
3.3. Customizing the colors used for drawing the individual concentration profiles



Double-clicking the left mouse button while the mouse cursor is localized over the rectangle where the name of a particular species appears under Species on the right-hand side of the splitter window opens a standard Windows color dialog box that can be used for modifying the color with which the concentration profile of that species is drawn.

4. Running a C-Profiles Simulation for a 2D-electrode geometry

Running a C-Profiles Simulation for a 2D-electrode geometry works analogously as described in 1.3.



However, in that case the spin control Show box number in Display Speed of the Displaying C-Profiles-dialog box is activated. This enables the user to select the y-direction for which the concentration profiles are plotted. In the present case, the electrode geometry refers to a disk electrode and the concentration profiles drawn on the screen refer to the third box in y-direction (i.e. parallel to the electrode surface). The distance of all these concentration points from the center of the electrode is given in Distance/Radius, i.e. expressed in parts of the electrode radius.