Lesson 3:

This lesson uses the experimental data files included in the Fitting.cvs – file (which is installed together with *DigiElch*) for demonstrating how the potential steps used during data fitting can be individually specified for each target file. Note that experimental CVs are usually measured with small potential steps (less than or equal to *1 mV*). In version 2 of *DigiElch* exactly the same potential steps were used by the fitting procedure. Such an approach becomes very time consuming if dozens of experimental CVs are involved in a fitting project and the optimal mechanism or sensible starting values are not yet known. *DigiElch 4* enables the user to execute the data fitting with a diluted data set by selecting fitting potential steps which are different from the experimental ones.

For the purposes of this lesson real experimental CVs referring to the electrochemical reduction of a nickel chelate complex (denoted as *NiL*) in the absence and presence of 2,2'-dipyridyl (denoted as *DP*) have been imported into CV-simulation documents. The following files are included in the Lesson 3.zip archive:

- *NiLACN.cvs*
  Real experimental CVs of *NiL* measured in acetonitrile (without *DP*).

- *NiLDP1.cvs, NiLDP2.cvs, NiLDP3.cvs, NiLDP4.cvs, NiLDP5.cvs, NiLDP6.cvs*
  Real experimental CVs of *NiL* in the presence of 6 different DP concentrations

- *Start.cvs*
  CV-Simulation document containing an estimated mechanism and sensible starting parameters.

Please work through Lesson1 to learn how to prepare ASCII-files (use-files) which can be imported by *DigiElch*.

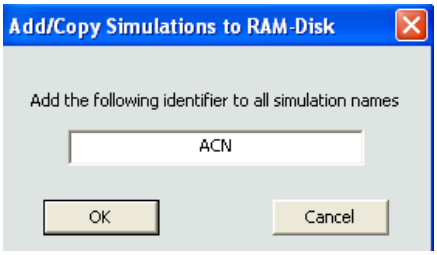
It is assumed that the reader of this lesson has already worked to the previous lessons and is familiar with basic operations such as entering, editing and deleting reaction equations. When working through the lessons, please, keep in mind that a few menu commands are disabled in the not activated program running as trial installation.

Using the RAM-Disk for setting up the fitting project

I. Start *DigiElch*

II. Open ( ) the file *NiLACN.cvs* included in the Lesson 3.zip archive. (In order to see that analytical concentrations for a species *NiL* and a species *DP* are really stored in this file click on Simulation -> Edit Properties ( ). The appearing dialog box shows all parameters imported from the experimental use-file)

III. Click on Document->Add Simulations to RAM-Disk(), enter "ACN" as Identification String in the appearing dialog box and continue with OK



The Identification String helps us to distinguish RAM-disk files referring to different documents. The string may be empty. In the present case the prefix "ACN" indicates files referring to experiments conducted in acetonitrile.

IV. Repeat II and III for the files *NiLDP1.cvs, NiLDP2.cvs, NiLDP3.cvs, NiLDP4.cvs, NiLDP5.cvs, NiLDP6.cvs* but enter "DP1", "DP2", "DP3", "DP4", "DP5" and "DP6" as Identification String.

All experimental data are internally saved now in the RAM-DISK used by the fitting procedure. It is therefore a good idea to save the RAM-DISK content to avoid steps the repetition of II to IV when restarting/resuming data fitting. Thus click on Document->Save RAM-Disk to save the RAM-Disk content let's say as "Data.rmd". Then close all open documents before continuing.

Fitting the charge transfer parameters in the absence of DP

The *NiL* complex exhibits a (quasi) reversible one-electron reduction step in acetonitrile in the absence of DP. Thus, in the first step we are going to setup a fitting project for a simple charge-transfer mechanism using only the target CVs referring to acetonitrile (Identification String "ACN") in the absence of DP.

1. Generate a new ( ) CV-Simulation document and click on Data Fitting -> Prepare Fitting Project to activate the Fitting Menu. Then enter the following mechanism and starting parameters

	Charge-Transfer Reaction	E° (V)	α λ (eV)	ks (cm/s)
1	NiL + e = NiL-	-1	0.5	1
2				

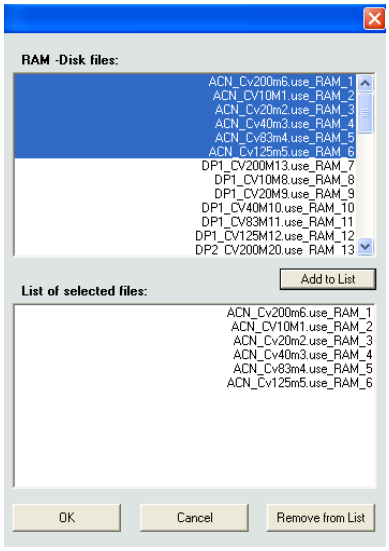
Make sure that standard potential, *E° (V)*, and heterogeneous rate constant, *ks (cm/s)*, are selected for being optimized by the fitting procedure (see Lesson2 point 10 for more details). The selection is indicated by plotting the associated parameter value in magenta.

Also make sure that the diffusion coefficient of *NiL* has been selected for being optimized and that it is linked to the diffusion coefficient of species NiL^- as shown in the following picture (see Lesson2 point 11 for more details)

	Species	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	NiL	1E-005	1	1
2	NiL-	1E-005	0	0
3				

The analytical concentration entered for *NiL* is imported from the experimental files during data fitting. The value entered in Canal does therefore not matter but at least one analytical concentration must be different from zero to enable the Run command for the fitting procedure.

2. Click Data Fitting -> Select Target Curves from RAM-Disk ( ), select all files with the prefix "ACN" to the List of Selected Files and finish with **Ok.**

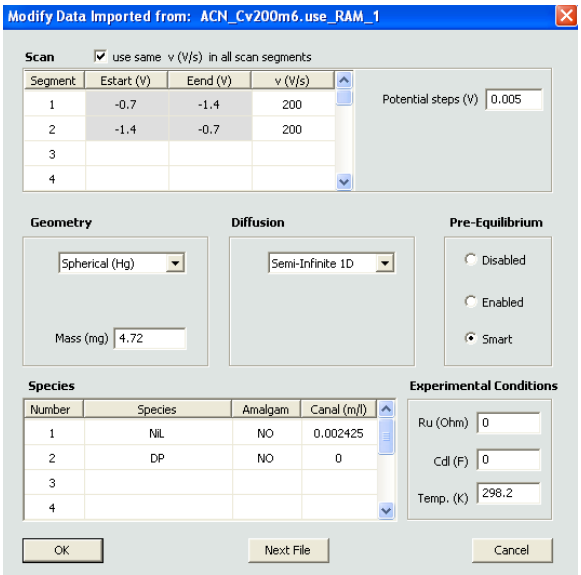


Note that the prefix defined in the Identification String and the extension _RAM_i (*i* is an index) is added to each file name in order to ensure that

- it can be easily recognized to which experiment the file refers
- a unique file name is generated

3. In principle data fitting could be started now by clicking on Data Fitting->Run Fitting Procedure ( ). In that case, data fitting is executed using the same *1-mV*-potential steps as in the experiment. The following must be done if we want that larger potential steps, let's say *5 mV*, are used in the course of data fitting.

4. Click on Data Fitting->Modify Selected Target Files and enter ***0.005*** in the input filed labelled as ***Potential steps (V)*** as shown below.



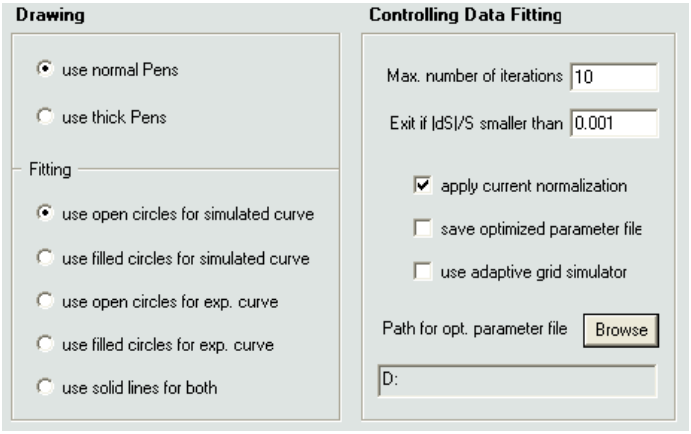
Note that the entered value applies only to the simulations executed during data fitting for reproducing the experimental CV indicated in the dialog box's title. That means, the value of ***Potential steps (V)*** needs not to be the same for each file. This option provides a high flexibility. In the present case (where the same value is used for each file) it is somewhat tedious. Click on the **Next File** button to activate the data referring to the next file and enter ***0.005*** again.

Click on **OK** if all files are done.

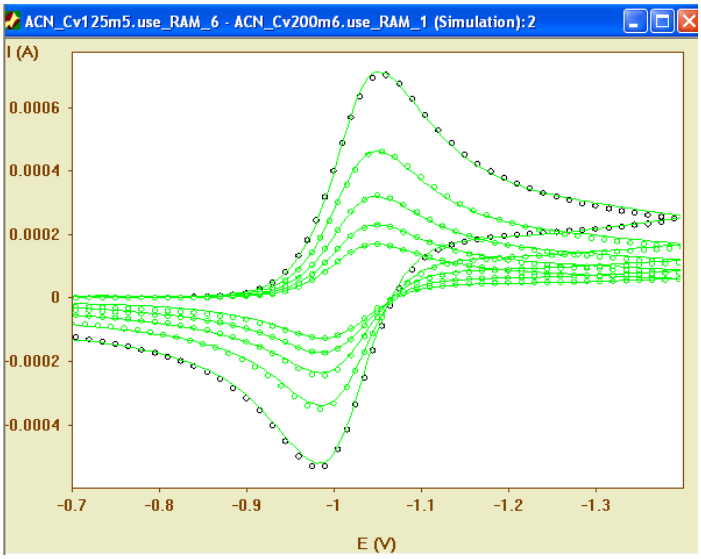
Remark:

- The modifications entered in the above dialog box do not affect the RAM-DISK files. Thus when re-selecting these files (as described in 2.) all modifications must be entered again.
- The modification of the potential steps can be done only once. After having replaced *Potential steps (V) =0.001* with *Potential steps (V)=0.005* it is not possible to undo this modification by applying the Data Fitting->Modify Selected Target Files command again. In order to avoid the accumulation of rounding errors, the input field ***Potential steps (V)*** is disabled after each modification because the original current curve is replaced by an interpolated one. A new modification can be accomplished only by applying the Data Fitting -> Select Target Curves from RAM-Disk ( ) command twice: 1) remove all files from the List of Selected Files and leave with **OK**, 2) re-select the respective files.

5. Before starting data fitting with the Data Fitting->Run Data Fitting ( ) – command, click on View -> Preferences ( ) and select the following options for Drawing and Controlling Data Fitting



6. Use the commands in the Simulation -> Compare Simulation with Experiment – menu to see (summarized in a single window) how well experimental and simulated CVs agree.



Select the couple displayed on the screen by means of the Simulation -> Compare Simulation with Experiment -> Select Couple ( ) – command. Then click on Simulation -> Compare Simulation with Experiment -> Show Next Couple ( ) and select ( ) this couple, too. (Note that a selection can be undone by means of the Simulation -> Compare Simulation with Experiment -> Clear Selection ( )-command). If all couples have been selected in this way, click on Simulation -> Compare Simulation with Experiment -> Show all Selected Couples. It makes that all selected couples are displayed in a new window as shown in the picture. After closing this window, the Fitting Menu and the associated splitter window is reactivated again.

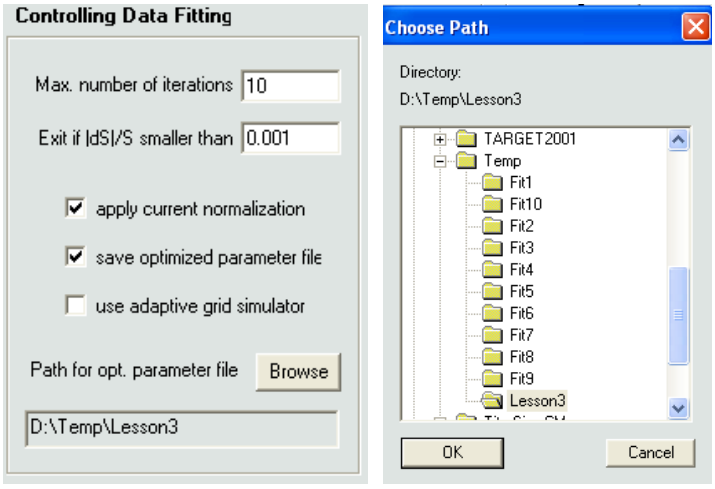
The time saving effected by using higher potential steps is not very impressive for this example because only 6 files are involved in the fitting project and the simulations are extremely fast for a mechanism containing only two species. For this reason, the procedure is repeated now for a more sophisticated fitting example.

Fitting all experimental CVs on the basis of a square scheme

7. Close all open child windows (or quit *DigiElch* but make sure that the RAM-DISK has been saved before as described in IV. If you want to continue later, restart *DigiElch* and load the "Data.rmd" RAM-DISK file. Note that the commands File -> Load RAM-Disk and Document -> Load RAM-Disk are enabled only if the RAM-DISK is empty.)

8. Open the "Start.cvs" file included in the "Lesson 3.zip archive. This file contains a template for a square scheme mechanism formulated with the required species names *NiL* and *DP*. It also contains sensible starting parameters and parameters selected for being optimized by the fitting procedure. What still remains to be done is the selection of the target CVs. Make sure that the experimental CVs are stored in the RAM-DISK, click on Data Fitting -> Prepare Fitting Project examine the proposed mechanism and starting parameters. Close the dialog and select the target CVs as described in 2. but select the entire set of experimental CVs not only the ones measured in acetonitrile in the absence of DP.

9. Click on View -> Preferences ( ), activate the option save optimized parameter file as shown below and select a path for this file by clicking on the Browse



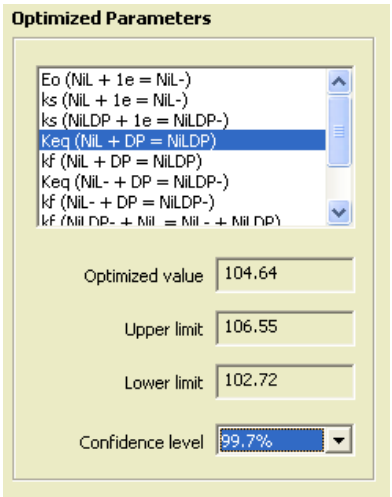
Selecting save optimized parameter file makes that a file named "optimal.cvs" containing the parameter set of the "best fit" is stored in the directory which is D:\Temp\Lesson 3 in the example shown on the left.

10. Start data fitting for the unmodified files by clicking on Data Fitting->Run Data Fitting ( ). The fitting is executed now using the original potential steps of *1mV*. Even on a fast computer it may take 10 or more minutes before the fitting procedure has found the "best fit parameters". Note that a sensible mechanism and starting parameter are usually not known. It is therefore rather unlikely that satisfactory results are already obtained with the first trial. It makes therefore sense to speed up the fitting procedure by using larger potential steps.

11. Deselect the option save optimized parameter file (see 9.) in order to ensure that the parameter set of the best fit obtained with *1 mV* potential steps is not overwritten when restarting the data fitting.

12. Modify all experimental target CVs as described above in 4. in order to accomplish that potential steps of *5 mV* are used in all simulations executed by the fitting procedure.

13. Restart data fitting for the modified files by clicking on Data Fitting->Run Data Fitting ( ). The procedure is about five times faster yielding virtually in the same optimized parameter set. The latter becomes visible by comparing the optimized values regained for each parameter using *5mV* steps with those stored in the optimal.cvs file referring to *1mV*.



Remark:
The approximation of the time derivatives implemented into *DigiElch* is 4th order accurate. Using potential steps of *5* or even *10 mV* has therefore a relatively small effect on the accuracy of the simulations but the experimental data are diluted. For this reason we consider potential steps of *5 mV* the optimal choice for balancing speed and accuracy of the fitting process in most cases.