User Manual

for

Frequency Response Analysis (FRA)
for Windows
version 4.9

Eco Chemie B.V.
P.O. Box 85163
3508 AD Utrecht
The Netherlands

1. Principles of operation

1.1 Preface

Autolab and the Frequency Response Analysis system software (FRA) provide fully computer controlled electrochemical impedance spectroscopy.

This powerful technique can be used in the study of, for example, electrode kinetics, electro deposition, corrosion, and membranes.

The instrument is controlled by a personal computer. The Autolab configurations supported by FRA are:
- Autolab with potentiostat/galvanostat PGSTAT10 and FRA modules
- Autolab with potentiostat/galvanostat PGSTAT12 and FRA modules
- Autolab with potentiostat/galvanostat PGSTAT20 and FRA modules
- Autolab with potentiostat/galvanostat PGSTAT30 and FRA modules
- Autolab with potentiostat/galvanostat PGSTAT100 and FRA modules.

The FRA combines the measurement of data and its subsequent analysis. The "Installation and Diagnostics" guide describes its installation.
The user should be familiar with MS-Windows.
The FRA program consists of two distinct parts, i.e.:
- The user-interface, graphics and data-analysis software.
- The routines that perform all the communication with the Autolab instrument.

Familiarisation with FRA is best obtained by experimenting. The on-line help within the program provides most of the required help, which may be necessary to perform the measurements and the data analysis.

This manual concentrates more on explaining the general concepts and backgrounds than on guiding the user through the program. Moreover, this manual tries to explain the possibilities of FRA. Please keep this manual together with the "Installation and Diagnostics" guide. The latter guide explains the installation.

1.2 The concept

The FRA screen consists of several windows: one for manual control over the potentiostat/galvanostat, one for data presentation and manipulation, one for entering the experiment parameters, one for viewing the FRA settings, and one for controlling the FRA modules. Surrounding windows, menu options, and tool bars give extra facilities like cell-diagnosis, accessory control, Autolab configuration, access, and data transfer to programs like Excel and MS-Word.

The MS-Windows related terminology used in this manual is in agreement with the standard as described in the book "The GUI Guide - international terminology for Windows Interface" (Microsoft Press, Washington ISBN 1-55615-538-7).

The following mouse conventions are used:

- Quickly pressing and releasing the mouse button is called "clicking". A click of the left mouse button on a menu option, a button, an input item on the screen, etcetera will result in an action.
- Clicking and holding down the left mouse button is called "dragging" and is used for several purposes. You can focus on an item on the screen without an action. You can drag a window when the mouse pointer is in its title bar. It can be used to shrink or to enlarge a window when the mouse pointer is on the border of a window. Finally, you can drag a scroll bar, a slider, or a zoom-panel.
- A double-click of the left mouse button is used to perform particular actions. Except for the standard uses in window actions, it is used to edit the graph in the Data presentation window.
- A click of the right mouse button is used to open a zoom panel in the Data presentation window, or to shrink or enlarge the Graphics panel in the Print menu window. This panel appears after selecting Print from the File option in the FRA Manager window

The following keyboard functions are supported:

- RETURN/ENTER key:
  jump to next data input field;
  select menu option; or
  click button with focus.
- left and right arrow key:
  move cursor in data input field.
- up and down arrow:
  move up and down in a menu.
- ALT:
  puts focus on the menu bar of the window with the focus;
  typing a subsequent underlined character will move the cursor to the corresponding menu item; and
  a RETURN/ENTER will select the menu item.
- ESC: aborts the execution of the measurement procedure.
- F1: access Help.
- F4: plot rescale.
- F5: starts the execution of the measurement procedure.
- F6 and shift F6: change focus to the next window.

This manual does not describe the background of electrochemical impedance spectroscopy. We would like to refer to some excellent textbooks:

- C.M.A. Brett and A.M.O. Oliveira Brett,
  Electrochemistry
  Oxford science publications ISBN 0-19-855388-9

- Allen J. Bard and Larry R. Faulkner,
  Electrochemical Methods: Fundamentals and Applications
  J. Wiley & Sons ISBN 0-471-05542-5

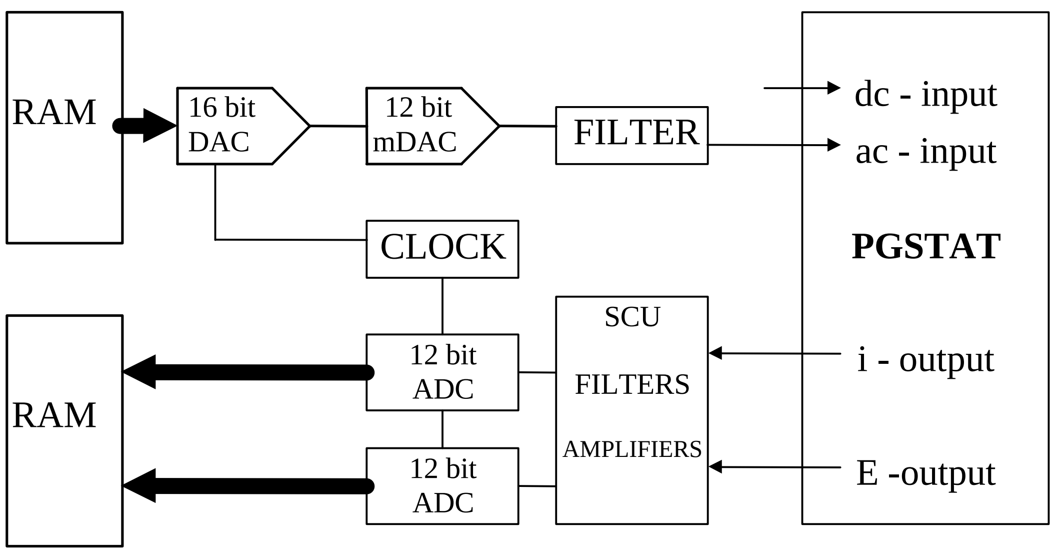
- R. Greef, R. Peat, L.M. Peter, D. Pletcher and J. Robinson,
  Instrumental Methods in Electrochemistry
  Ellis Horwood Limited ISBN 0-13-472093-8.

- John R. Scully, David C. Silverman and Martin W. Kendig,
  Electrochemical Impedance: Analysis and Interpretation
  STP 1188 ASTM ISBN 0-8031-1861-9

1.3 The instrument and hardware description

The FRA-hardware consists of a digital signal generator (DSG), a signal conditioning unit (SCU), and a fast analog to digital converter with two channels (ADC).
The DSG consists of a large digital memory, which is loaded with the digital representation of the applied signal and a fast settling 16-bit digital to analog converter. A multiplying digital to analog converter controls the signal amplitude. This architecture ensures accurate signal generation.
The time dependent potential and current signals from the potentiostat are filtered and amplified by the SCU and recorded by means of the ADC. The acquired signals are stored in the digital memory on the ADC board. This digital memory allows time domain averaging of up to 4096 repetitive measurement cycles.
Each cycle can consist of 4096 points. This feature provides high accuracy and reproducibility. Since a cycle can consist of 4096 points and a measurement can consist of 4096 repetitive cycles, a single impedance measurement can take 4096 x 4096 AD-conversions for each channel.

Fig. 1 *Scheme of the FRA instrument*



The analysis of the time-domain measurements is done by means of the 'Fast Fourier Transform' method. Both the potential signal e(t) and current signal i(t) are transformed to E(f), I(f) and their complex conjugated E°(f) and I°(f).
The cell impedance Z is calculated from the equation:

$$Z=(E(f)\ E°(f))/(I(f)\ E°(f))$$

The older FRA-module allows measurements in the range of 0.1 mHz to 50 kHz. The newer FRA2-module allows measurements in the range of 0.01 mHz to 1 Mhz. The module can be used in two different modes:

- single sine, i.e. a signal with a single frequency is applied,
- multiple sines, i.e. a signal with more than one frequency is applied.

The 'single sine' mode offers highest accuracy at higher frequencies, e.g. higher than 50 Hz. However, at low frequencies, the time of measurement of a complete frequency scan can cause a problem. The 'multiple sines' mode provides the opportunity of measuring 5 frequencies within one decade or even 15 frequencies within two decades in a single measurement cycle. This method saves a lot of time, thus allowing the measurement of more reliable impedance data in case the behaviour of the electrochemical cell is time dependent.

Each of the two parts, FRA-DSG and FRA-ADC, consists of two boards.
The 64 kB RAM of the digital signal generator (DSG), is loaded from the computer. While loading, the LED marked 'load DSG' is on. The memory is loaded with the digital representation of the signal to be applied. The 16-bits words are loaded from the hard disk drive.

The 12 bit multiplying DAC is used to control the amplitude of the output signal of the DSG. The maximum amplitude of the DSG peak to peak equals 3.5 V (FRA2) or 10 V (FRA). This mDAC makes it possible to set the output of the DSG with a resolution of 1 in 4096. Since the signal is divided by ten inside the potentiostat/galvanostat, the maximum amplitude peak to peak equals 0.35 V (FRA2) or 1 V (FRA). The resolution of the applied signal is better than 0.1 mV..

The output of the DSG is available at the BNC plug 'dsg out' or 'signal out'. As long as the contents of the RAM are used to set the 16 bit DAC, the LED 'signal on' will be on.

The output signals of the potentiostat, I (current output) and E (potential output), are filtered and amplified.
The two identical amplifiers have software programmable gains of 1, 2, 4, 8, 16, 32, 64, 128, 256, and 512. The filter is a programmable 8th order Butterworth low-pass filter.

The two-channel simultaneous-sample-and-hold analog to digital converters are 12 bits wide. The maximum conversion rate is 200 kHz for the older FRA and 800 kHz for the current FRA2. The results of the conversions are stored in two memories each with 4096 words of 24-bits wide. Thus each memory location can contain the sum of up to 4096 conversions.

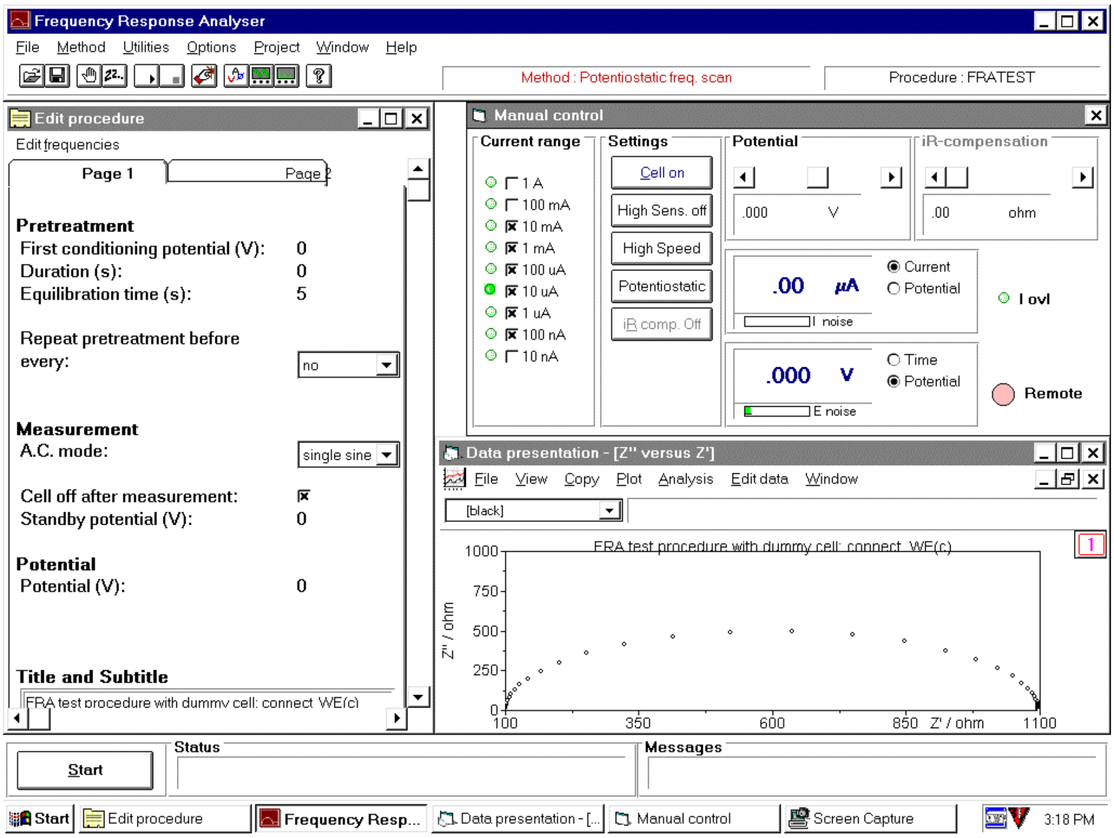
The DSG and the ADC's are synchronised by using one clock crystal for both modules.

2. Getting started with FRA

Connect the dummy cell box, which is delivered with Autolab. The red lead should be connected to WE(c). Switch the instrument on.

To start the program, double-click the FRA icon in the program manager. The factory default windows of FRA appear.

Fig. 2 *Factory default layout of the FRA windows*



The screen consists of the following parts:

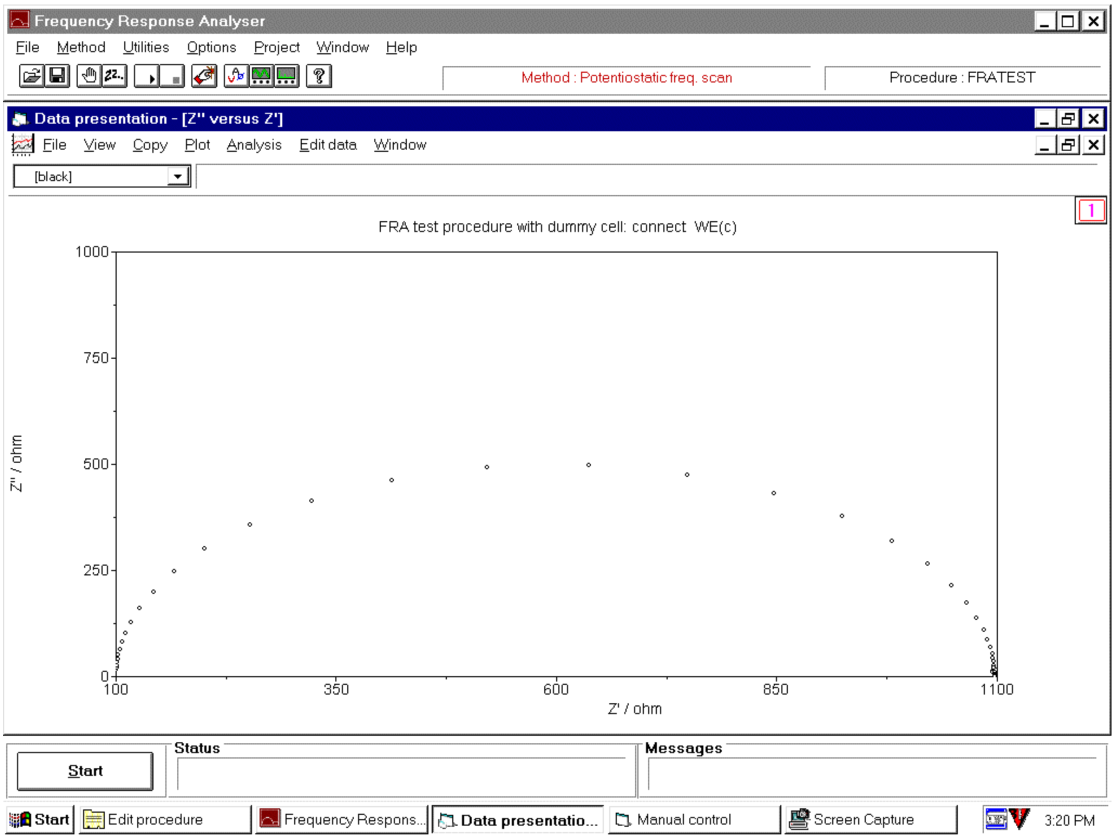
- The FRA Manager window with a title bar and a tool bar.
- The Manual control window. This window is used to control all potentiostat/galvanostat settings.
- The Edit procedure window. This window is used to modify experimental parameters. When using FRA for the first time the default parameters are the "factory" settings. Changed parameters are saved automatically at exit and appear as default parameters on the next occasion.
- The Data presentation window. This window gives a graphical display of the measured data and provides the entries to analyse and modify the data.
- The Status window. This window is used to start and stop a measurement procedure and to display system messages.

These windows are explained in detail in the next chapter. The rest of this chapter is used to walk through a number of examples that come with the FRA program. These examples give you an idea of the possibilities of the program. Please follow the instruction per example in detail. It is assumed that you have experience with the GPES program. Otherwise, please first read the chapter "Getting started with GPES" of the corresponding manual.

2.1 Recording an Impedance spectrum

1. Click the Method option in the upper left corner of the screen.
2. Click Potentiostatic.
3. Click Single potential.
4. Click File option in the upper left corner of the screen.
5. Click Open procedure...
6. Type \Autolab\testdata\fratest.pfr. Press ENTER.
7. Click View on the Data presentation window.
8. Click Z" versus Z'.
9. Click the upper right button of the Z" versus Z' window.
10. Click the upper right button of the Data presentation window.
11. Connect the dummy cell. The red lead should be connected to WE(c).
12. Click the Start button in the lower left corner of the screen.
13. Click during the measurements on the Plot option of the Data presentation window.
14. Click Automatic. The graph rescales.
15. Click during the measurements on both greenish toolbar buttons. They allow you to inspect the ac sine waves and their frequency spectrum.
16. After the measurement a semi-circle is displayed.

Fig. 3 *Semi-circle in impedance plot*



17 Click View again. Select Y'' versus Y'. Now the admittance plot appears

18 Click Window on the Data presentation window. Select the Tile option. Now the impedance and admittance plot are both presented.

19 Close the Admittance plot window.

20 Click Window on the Frequency response

2.2 Manual control

1 Connect the dummy cell. The red lead should be connected to WE(c).

2 Click Window on the Frequency Response Analyser manager window. Select FRA manual control and FRA settings.

3 Click the green led of the 1 mA current range. Make sure that the check box of 1 mA is checked.

4 Apply 1 V by moving the slider in the potential panel.

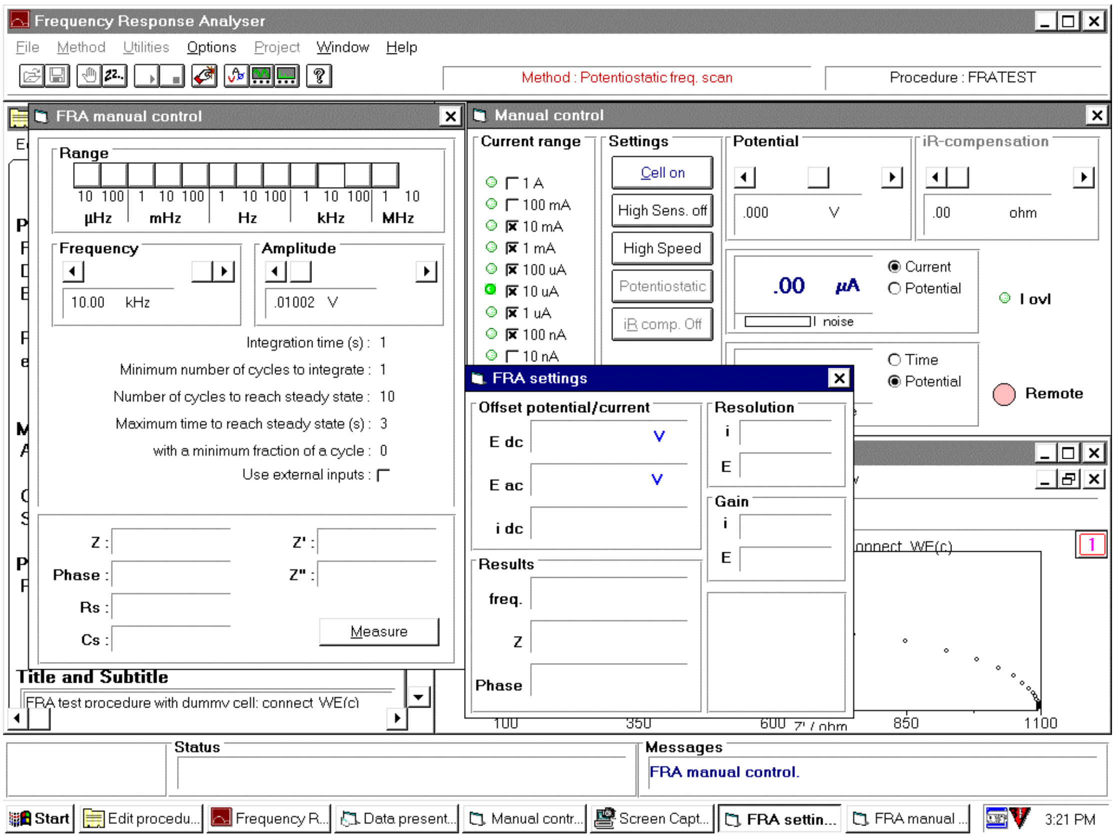
5 Click the Cell on. The current should be about 0.91 mA.

6 Click the 1 kHz button of the Range panel in the FRA manual control window.

7 Apply an amplitude of 0.01 V rms by moving the slider in the Amplitude panel.

8 Click the Measure button on the FRA manual control window. Inspect all the data presented on the active windows.

Fig. 4 *FRA manual control*

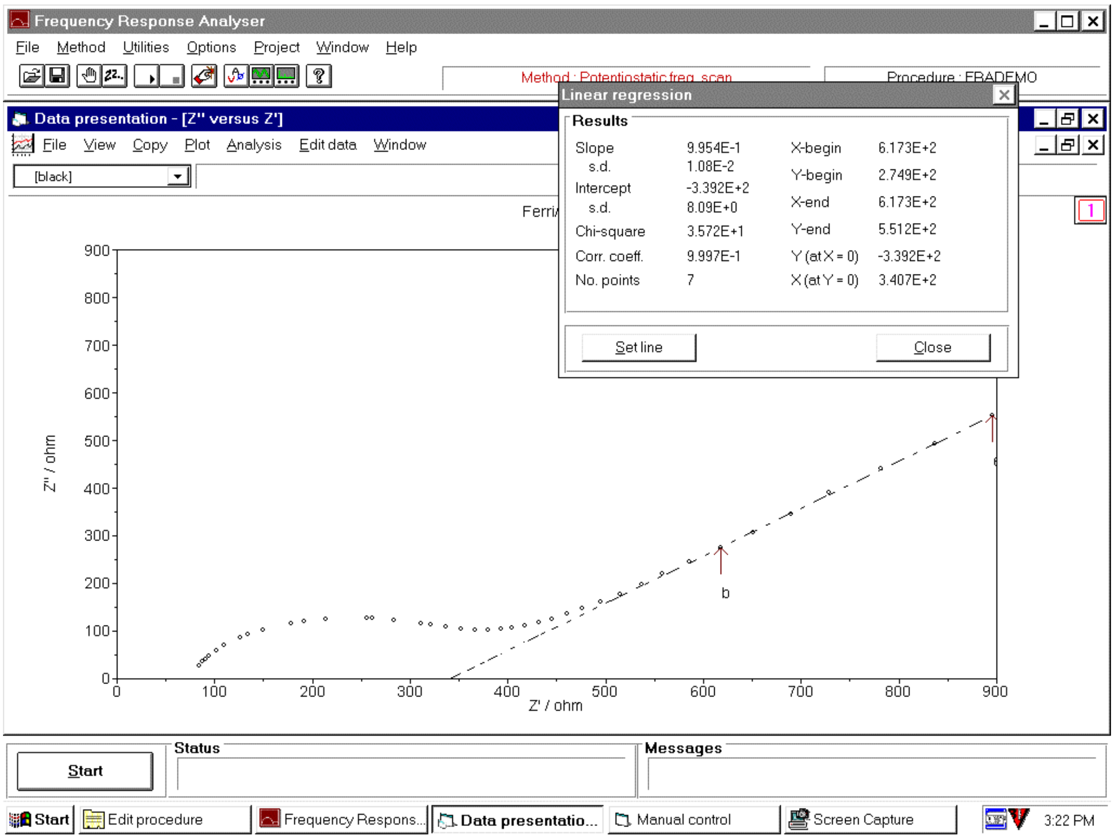


9 Click the greenish buttons on the toolbar to activate Oscilloscope windows.
10 Click the Stop button on the FRA manual control window.
11 Change the frequency to a lower value using the slider in the Frequency panel.
12 Click Measure again.
13 At the end click Stop and close the FRA manual control window.

2.3 Data manipulation with FRADEMO

1 Click the File option in the upper left corner of the screen.
2 Click Load data
3 Type \AUTOLAB\testdata\frademo.dfr. Press ENTER.
4 Click the upper right button of the Data presentation window. The Data presentation window will fill almost the whole screen.
5 Click the View option. Select Z" versus Z'.
6 Click now the upper right button of the Z" versus Z' window. The Z" versus Z' plot will now fill almost the whole screen. It is also possible to drag the borders of the window in such a way that the window is maximised or that the window looks like a square. Now you should see a semi-circle which, at the right side, becomes a straight rising line.
7 Click Analysis on the Data presentation window. Select the Linear regression option.

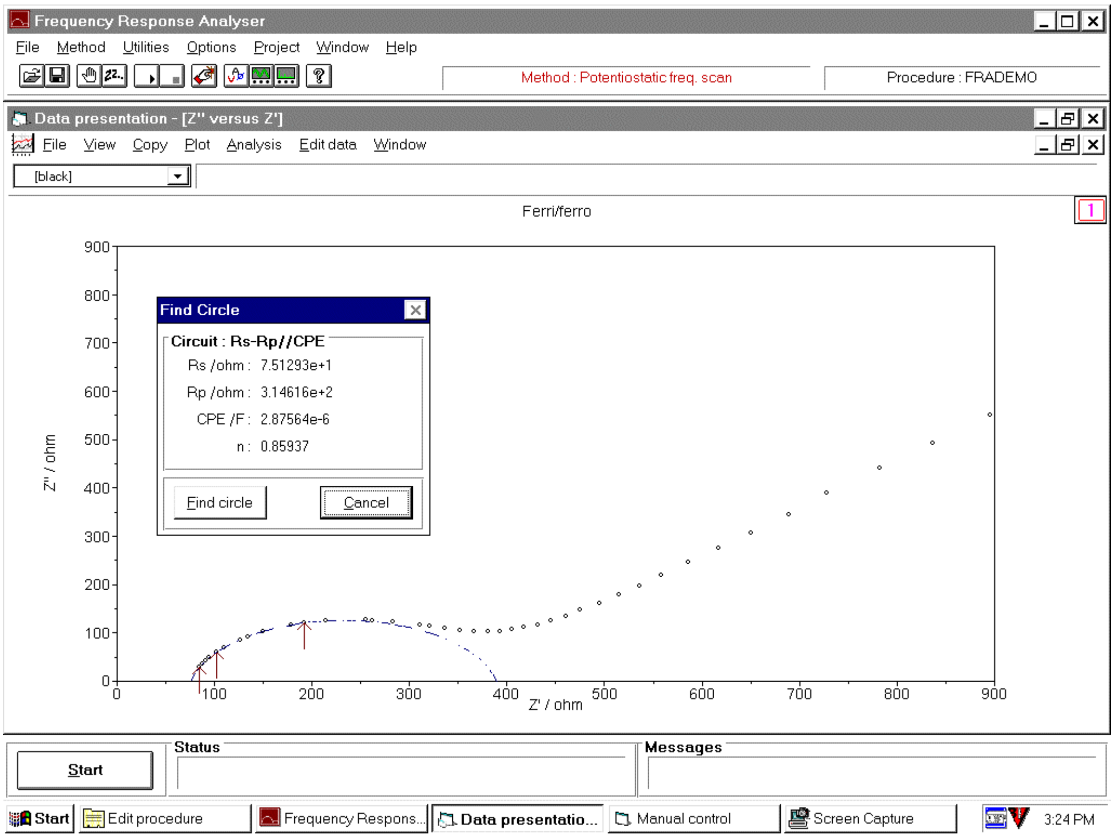
Fig. 5 *Straight line analysis*



8 Mark two points on the straight line part of the impedance plot by clicking them. After a data point has been clicked, the frequency at which the data point is measured is displayed in red in the top of the Z'' versus Z 'window.
9 Click OK on the Marker window.
10 A slope of nearly 1.00 should be printed in the Linear regression window.
11 Otherwise click the Set line option in this window to try it again.
12 Click Close on the Linear regression window
13 Click Window on the Frequency Response Analyser manager window. Select the Analysis results option to obtain a printed copy of the results.
14 Close the Analysis results window.
15 Click Analysis on the Data presentation window and select the option Find circle.
16 Mark three points on the semi-circle part of the impedance spectrum and subsequently click OK on the Marker window. The results are displayed in the Find circle window. Click Cancel to stop or Find circle to try again.

17 Click Edit data and select Correct for Ohmic drop. Type a value of 74 on the displayed window and click OK. Now the so called electrode impedance is displayed.

Fig. 6 *Semi-circle analysis*



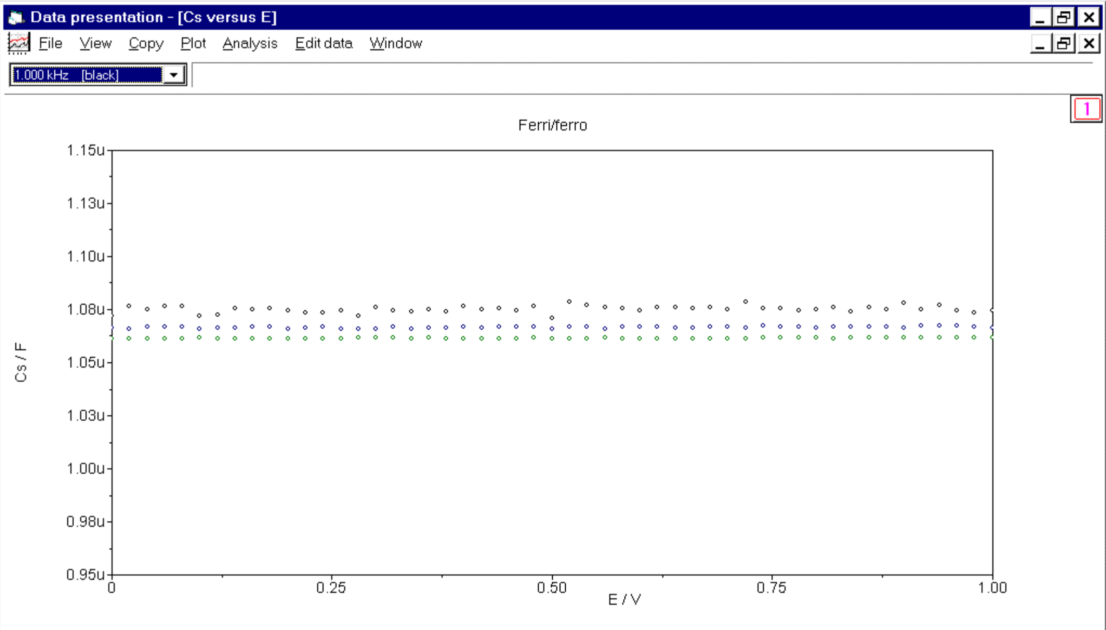
18 Close the Z'' versus Z' window.
19 Click Plot and select Change axis text.
20 Change for the Z'' versus Z' plot the Horizontal-axis and Main vertical axis text so that they indicate that electrode impedance is shown.
21 Click View and select the Z'' versus Z'. Now the axis text has been changed.
22 If the precision of the axis annotation is not sufficient, double-click the axis annotation and specify a new value for the precision and click OK.

2.4 Measuring double layer capacitance as a function of potential.

1 Click Window. Select the Tile option.
2 Click Method on the Title bar and select Potentiostatic: Potential scan.
3 Specify the next values in the Edit procedure screen:
Start potential (V): 0 V
End potential (V): -1 V
Step potential (V): 0.02 V
4 Connect the working electrode lead to WE(d).
5 Click 'Edit frequencies' in the Edit procedure screen.

6 Specify:
Begin frequency: 1000 Hz
End frequency: 100
Number of frequencies: 3
Amplitude: .005 V
Select a logarithmic frequency distribution.

Fig. 7 *Double layer capacitance measurements*



7 Click Calculate and then OK.
8 Select View in the Data presentation window. Click Potential scan plot and Cs vs E.
9 Click the upper right button of the Cs versus E window as well as of the Data presentation window.
10 Click Start and wait until the measurement is ready. During the measurement the plot can be re-scaled by pressing F4.
11 Select View and click Potential scan plot.
12 Click Select frequency and click in the part 'Frequencies not displayed' those frequencies to be shown and click the upper button to bring the selected frequency to the part 'Frequencies selected'. Now click the OK button. The selected frequencies are shown on the screen.
13 Click Edit data: Change all points. Select Cs/F and specify a value of 2.
14 Click the Multiply button. All capacitance values of the black coloured points are multiplied now. This option can be used to correct for the surface area. Click Close.
15 Select Plot and click Resume as well as Automatic. Now the original measured data are shown again.
16 Select View again followed by clicking Potential scan plot and Y''/w versus E plot.
17 Select Window in the Data presentation window and click Tile. The two plots are shown now.

18 Double-click the upper left button of the Y''/w versus E plot. This time the screen only shows the capacitance plot.

19 Select File from the upper left corner and select Save data as. Enter a filename and make sure that the Directory is \Autolab\DATA and press OK.

20 Now select File again and click Convert to ASCII. Select the data file created above and click Convert. Select the required file format and click Convert again. The data are stored as an ASCII file with the specified format. (For explanation of File extensions, see Appendix 1). If a potential scan is loaded, a potential value should be selected before the file can be converted. For each potential, a file is created with an extension as explained in Appendix 1.

21 Click in the upper left corner of the screen and exit the Frequency Response Analyser program.

3. The FRA windows

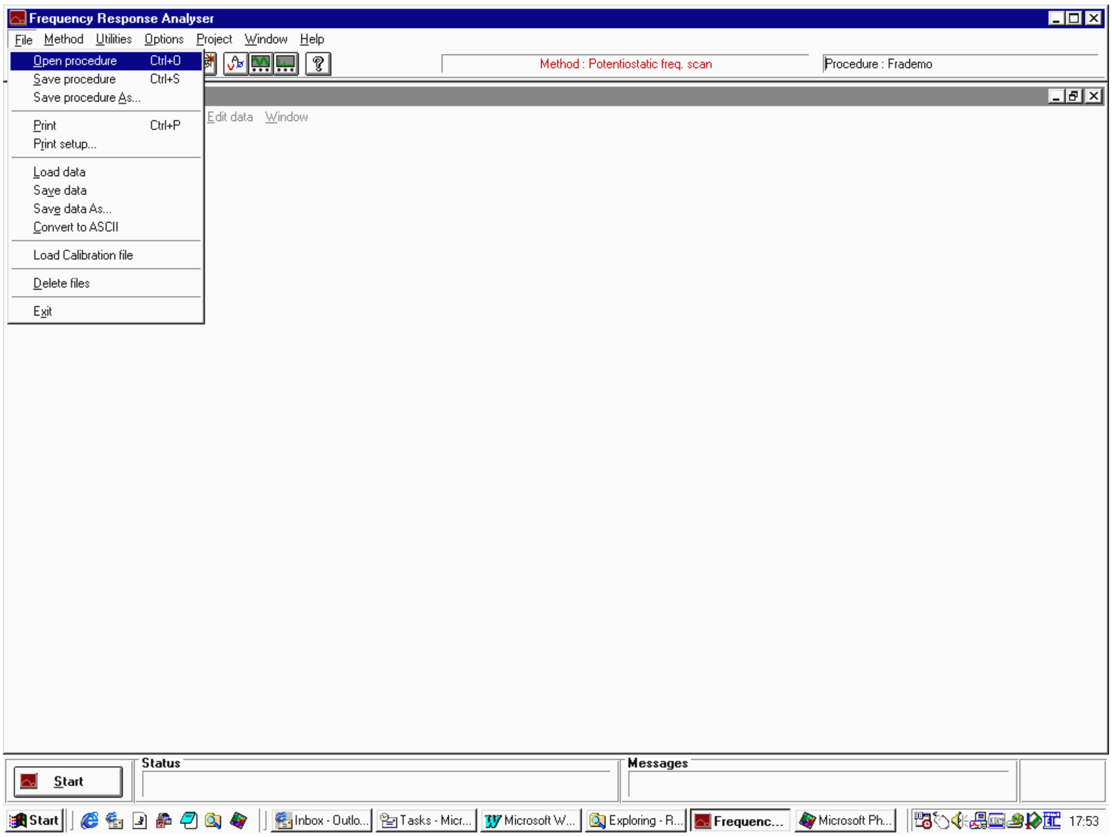
3.1 FRA Manager window

The title bar of the FRA Manager window contains several options, i.e. File, Method, Utilities, Project, Window, Help.

File menu

This menu contains options that are usually present in Windows programs.

Fig. 8 *The File menu*



Open procedure

A procedure is a file containing all the experiment parameters. It contains measurement parameters, potentiostat/galvanostat settings, and graphics display values. The extension of the file, which is mentioned in the "File name" field, should not be changed.

The directory in which the procedure file is stored, is called the procedure directory. When the directory in the Open procedure window is changed and a procedure file is successfully loaded from this new directory, this new directory becomes the new default procedure directory.

It is also possible to load procedure files from the DOS version of FRA. If this is required, click the "List Files of Type" drop down button and select the proper option.

Save procedure

This option will save a procedure under its current name in the procedure directory.

Save procedure as

The Save procedure option allows storage of a procedure on disk in the procedure directory with a different name as the current one. Please use the default file extension as mentioned in "File name" field or omit the extension. In the latter case the correct extension will be added.

Print

The Print menu window appears. The Print select panel makes it possible to choose between the print-out of the measured data, the experiment parameters, or a dump of the data presentation window. The type of data or the window can be selected from a neighbouring window. The Print Preview button allows you to preview the print-out of data.

Print setup...

This option gives access to the standard window for printer setup and control.

Load data

The Load data option allows load of previously measured data from disk. It is also possible to load data files from the DOS version of FRA. If this is required click the "List Files of Type" drop down button and select the proper option.

Save data

Store the most recent measured data under the current procedure name on disk. The data are stored in the so-called data directory, together with the corresponding procedure parameters.

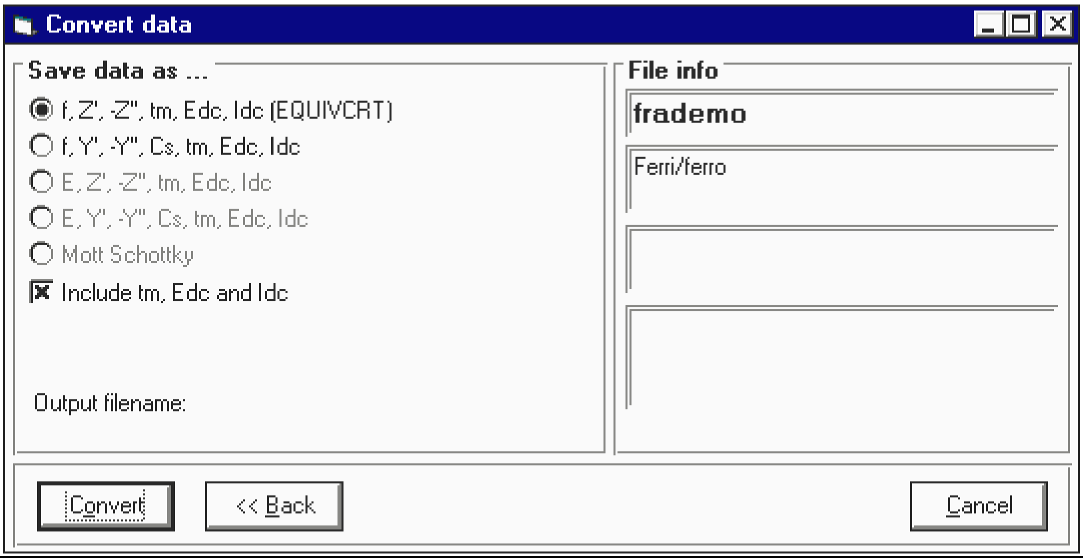
Save data as

The Save data as option is similar to the previous option, but the name of the file name containing the data can be specified.

Convert to ASCII

This option allows conversion of the FRA data files to readable ASCII files.
These files can be read by any spreadsheet program, but also by third party data analysis programs.

Fig. 8a *Convert data*



First a FRA output data file has to be selected. After clicking on a file in the list box some file info is given. To proceed the ‘Convert’ button has to be clicked. Subsequently, the following columned ASCII or text files can be created:
- Frequency value, Z’ and Z” value, time of measurement, Edc and Idc at the time of measurement
- Frequency value, Y’ and Y” value, serial capacitance value, time of measurement, Edc and Idc at the time of measurement.
- Potential value (or current value), Z’ and Z” value, time of measurement, Edc and Idc at the time of measurement.
- Potential value (or current value), Y’ and Y” value, serial capacitance value, time of measurement, Edc and Idc at the time of measurement.

The tm, Edc and Idc can be left out of the file by unchecking the ‘Include tm, Edc and Idc’ check box.

Depending on the type, the required ASCII file format, one or more frequency, potential or current value has to selected from the list box. For each frequency, potential or current a file is created. The name of the file is the same as the data file name. The files are stored in the same directory as the data file resides. The extension depends on the type of file (see Appendix).

A special type is the Mott-Schottky-file. It contains a matrix of values for $(\omega Z”)^2$-values for all frequencies and potentials. The extension of this file is .MOT. Please note that data sets created before FRA version 2.4 will not contain any data for time, Idc and Edc.

Load calibration file

This option allows to change the calibration values to optimise performance for specific FRA2 modules. This option is useful when different Autolab instruments are connected to a single computer.
Since the calibration files are instrument dependent, they should be kept together. The indicated number when starting up the FRA software should match the serial number on the instrument. If one exchanges instruments on one computer, the “Load calibration file” can be used to adjust the calibration file to the new situation. Please note that the new calibration file does not have to be in the Autolab root folder.
It is advisable to be cautious with this command and only use it for the situation described above. If you keep the computer and instrument as a pair after the initial software installation, this option may never be necessary.

Delete files

This option allows deletion of procedures and measured data files. The File window only shows the procedure files. A selected procedure will be deleted from disk together with corresponding data files. A delete action cannot be undone.

Exit

The FRA window will be closed and the program is exited. The program settings are stored on disk.

Method

The type of measurement can be selected with the Method menu. The experiment parameters in the Edit procedure window will change depending on the selected type of measurement.

The following methods are available:

Potentiostatic single potential

A frequency scan is measured at a single dc-potential value.

Potentiostatic potential scan

A frequency scan is measured at a set of dc-potentials.

Potentiostatic time scan

A frequency scan is made at a fixed potential at regular time intervals.

Galvanostatic single current

A frequency scan is measured at a single dc-current value.

Galvanostatic current scan

A frequency scan is measured at a set of dc-current values.

Galvanostatic time scan

A frequency scan is made at a fixed current at regular time intervals.

Utilities

The Utilities menu allows the user to select electrode control, burette control, RDE control and sleep mode.

Electrode control

The Electrode control option allows the user to operate a static mercury drop electrode which is connected via an IME-interface to the Autolab. The stirrer can be switched on and off, the purge valve can be opened and closed, and a mercury drop can be created.
The Reset button will reset the digital I/O port of the Autolab instrument. The Purge and Stirrer will be switched off. This option is not accessible when no static mercury drop electrode is connected to the Autolab.

Burette control

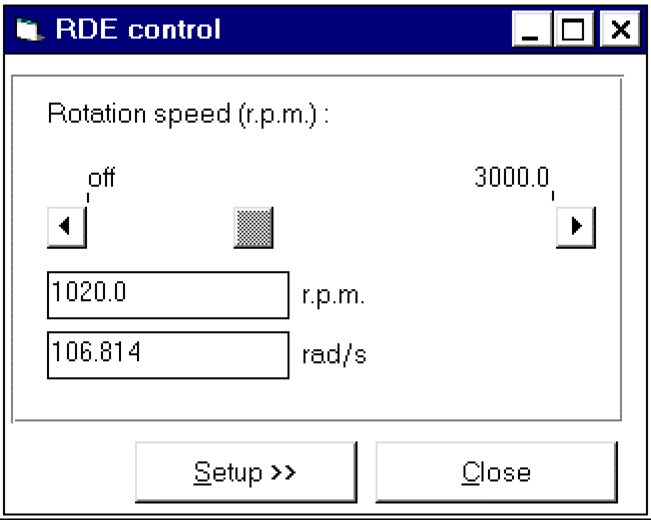
The burette control option allows the user to control motorburettes connected to Autolab via the DIO48 module. Consult the "Installation and Diagnostics" guide about the type of burettes that can be connected. First click the Setup button. Then select the burette.

The displayed Burette setup window gives the possibility to define the connected burette. Please consult the manual of your burette for the parameters.
The ‘Maximum time to check for Ready’ is the maximum time for the software waiting to receive a "ready" signal from the burette.
The DIO port used is shown on your Autolab front.
The Dose button will dose the amount specified above. The dosed volume is displayed.
The Dose on button will dose with the speed displayed above.
The Reset button will give a ‘reset’-command to the burette and sets the dosed volume to zero.

RDE-control

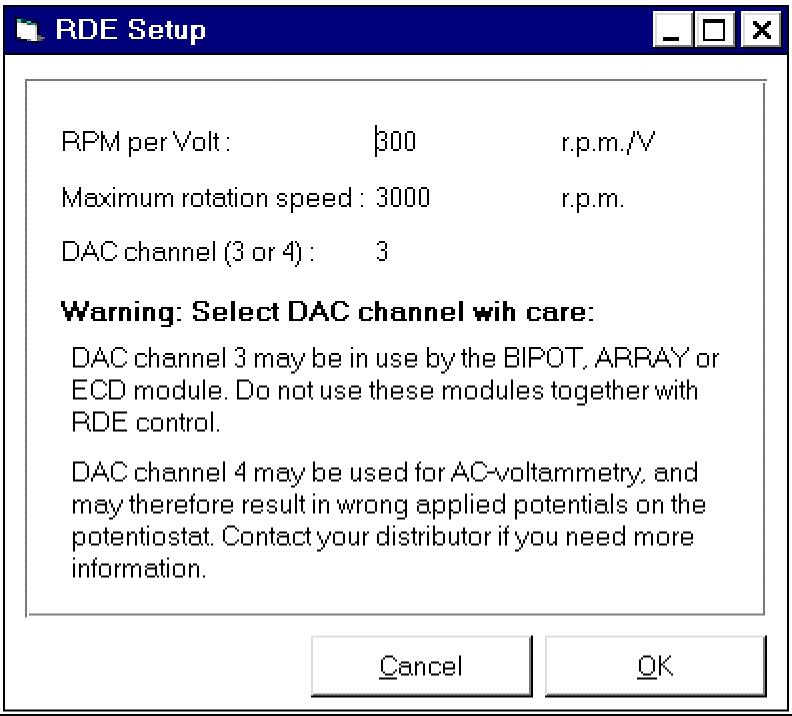
In order to control an external Rotating Disk Electrode (RDE), an option is available in the Utilities menu of the GPES manager. In the hardware configuration an external RDE should be specified. After selecting the RDE control item the following window appears:

Fig. 9 *The RDE control window*



With the scroll bar it is possible to control the rotation speed of the RDE. You can also enter the number of rotations per second by changing the r.p.m. edit field or enter the rotation speed in rad per second in the rad/s edit field.
After pressing the Setup button the RDE setup window appears:

Fig. 10 *The RDE setup window*



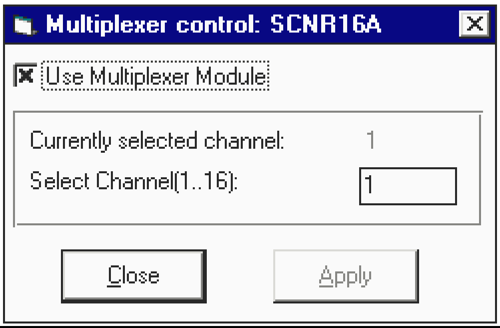
In this screen you can configure the RDE.

MUX control

The channel number of the SCNR16A, SCNR8A or MULTI4 module can be selected manually by the operator before starting the measurement procedure:

1. Open the MUX control dialog by selecting MUX control from the Utility menu. The dialog screen shown in the figure below will pop up.
2. Enable the checkbox “Use Multiplexer Module”.
3. Choose the desired channel.
4. Pressing <Apply> or closing the dialog screen will set the selected channel.
5. The active channel number will be indicated in the Manual control window.

Fig. 11 *The MUX control window*



If you want to return to direct connections, you can disable the “Use Multiplexer Module” checkbox.

Options

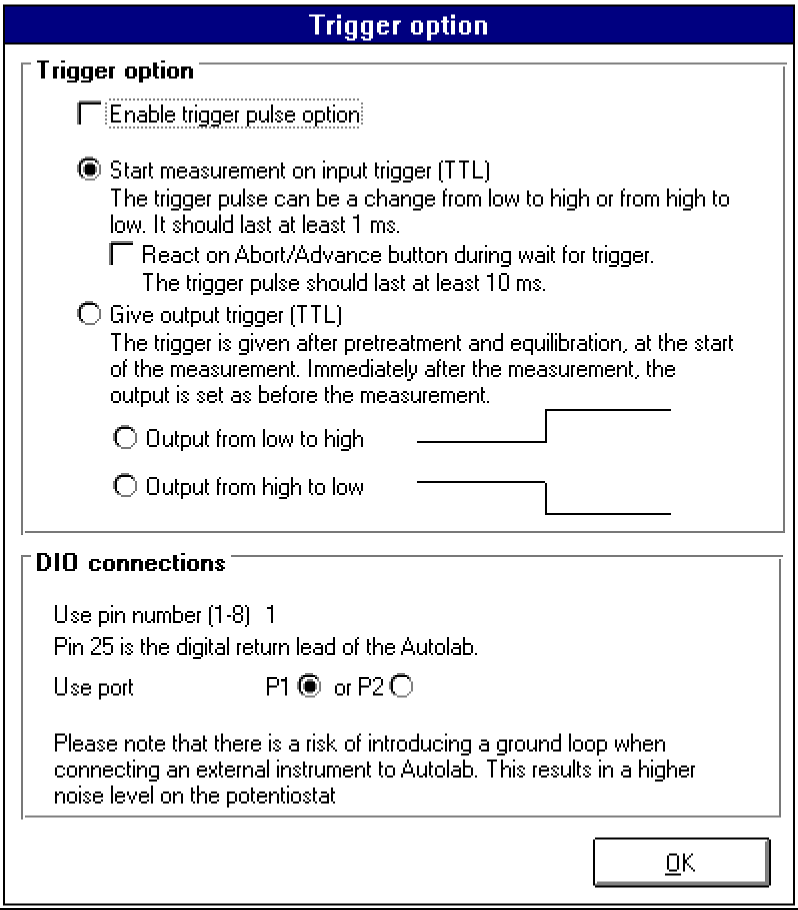
Several options for data presentation can be specified:
Rescale after measurement: perform autoscale and replot data when measurement has finished.
Rescale during measurement: rescale and replot when necessary, also during the measurement.
Procedure name in Data presentation: displays filename and path of the result file in graph.

Trigger

Under this item the option Trigger is present. After selecting this option the following window appears. In this window the trigger pulse can be configured.

After enabling the trigger pulse option, the 'Start' button has to be clicked. The program will go through pretreatment and equilibration and will then wait for the trigger-signal.

Fig. 11a *The Trigger option window*



Project

The Project option allows the execution of a large number of electrochemical experiments unattended. A project encompasses a number of tasks which have to be executed sequentially.
Sometimes this is called batch mode processing. A measurement procedure is normally activated by clicking the Start button in the lower left corner. It is also possible to start a procedure by creating and subsequently executing a project.
A project can be created by selecting the Project edit option. First you have to indicate whether a new project should be made (New option) or an existing project file should

be opened (Open option). An example of a project is delivered with the FRA2 program in the testdata directory.
After editing a Project it can be stored on disk under its current name (Save option) or under a new name (Save as option).
When Edit is selected the Edit project window appears with two options on the main menu bar. The Check option checks whether there are syntax errors in the project commands. The Edit option provides the standard Cut, Copy, and Paste option.
Below you will find the Project script language definitions and rules.

Project command rules

- Both upper and lower case characters can be used in command lines.
- Space characters are ignored.
- If during the execution an error occurs the project continues with the next line.
- An error message will be printed in the Results window.
- One line per command.

- The following commands are allowed:

; <string>	:	comment
rem <string>	:	comment
Procedure!Open("<filename>")	:	open a procedure file
Procedure!Start	:	start the execution of the procedure
Procedure!SaveAs(“<filename>”)	:	save a procedure file
Dataset!Open("<filename>")	:	open a previously measured data file
Dataset!SaveAs("<filename>")	:	save the measured data
Dataset!AutoNum = <n>	:	enable auto-numbered files names, starting with number <n>
Dataset!AutoReplace	:	specify the string which should be
("<string>")	:	replaced by a number in the <filename> for auto-numbered files.
System!Run("<filename>")	:	execute an other program.
System!Beep	:	give a beep
Print!Procedure	:	make a hardcopy of the experiment parameter
Print!PLOTZZ	:	print a hardcopy of the plot of Z" versus Z'
Print!PLOTYY	:	print a hardcopy of the plot of Y" versus Y'
Print!PLOTBODE	:	print a hardcopy of the Bode plot
Print!DATA	:	print a hardcopy of the measured data

Utility!Channel = <n>	:	sets the active channel to <n>. The MUX will be automatically enabled when necessary.
Utility!NextChannel	:	increase the active channel number with one. If the channel is not available, the active channel number is set to 1.

Please note:
The last 2 commands are available in the GPES and FRA programs. However, for FRA projects that are called from within GPES projects, all channel switching commands in the FRA project scripts are ignored. In such cases, the GPES project will have exclusive control over the channel selection.

Utility!Delay = <n>	:	hold the project for <n> seconds.
Repeat (<n>) EndRepeat	:	With these commands you can repeat an enclosed sequence of instructions multiple times. You can nest loops maximal 5 times.
Message ("string")	:	Give a message and wait for click on OK
ForAllChannels("<filename>")	:	executes the active measurement procedure for all available MUX-channels and store the results in the <filename> adding 3 characters to the filename as channel number counter, for example: fname001, fname002, etc. .
DIO!SetMode("<Connector>", "<Port>","<Mode>")	:	set the mode of a port of the DIO.
DIO!SetBit("<Connector>","<Port>", "<n>","<Bit>")	:	set a single pin of the DIO on or off.
DIO!SetByte("<Connector>","<Port>" ,"<n>")	:	set a port of the DIO to the specified value.
DIO!WaitBit("<Connector>","<Port>", "<n>","<Bit>")	:	wait until a single pin of the DIO is set on or off.
DIO!WaitByte("<Connector>","<Port>", "<n>")	:	wait until a port of the DIO is set to the specified value.

Burette!DoseVolume (<Burette number>
,<Dose volume>) : dose a specified volume to the specified burette.
Burette!Fill (<Burette number>) : Fill the burette.
Burette!Flush (<Burette number>
,<Number of flushes>) : flush the burette.
Burette!Reset (<Burette number>) : Will give a 'reset'-command to the burette.

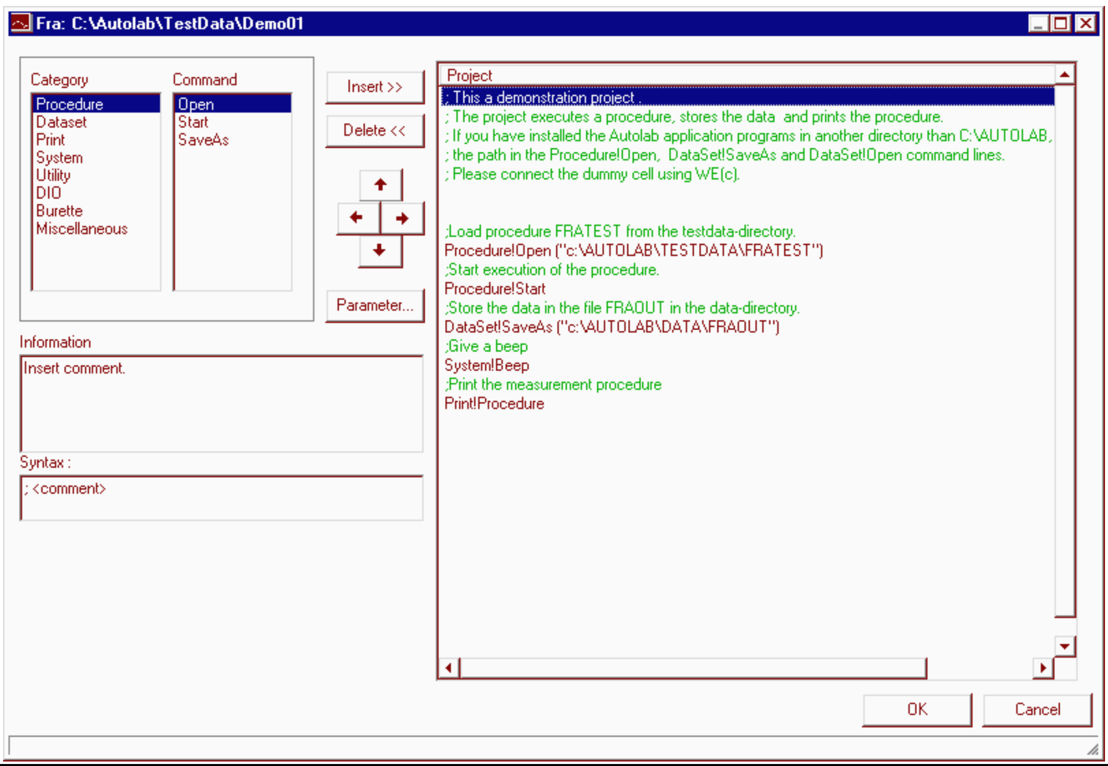
<string> : line of text
<filename> : a filename without extension, but including a directory name

A special case occurs when the measurements are done with respect to the open circuit potential. Normally the user is asked to click the Accept button, but in automatic mode the program continues by itself.

Project wizard

The Project wizard provides an easy way of editing and/or defining a project. This option allows the user to pick project command lines from a list of all commands, insert them in a project and define the parameters. The window below gives a project Wizard overview.

Fig. 12 *An example of a project inside the Project wizard*



Every project command can be inserted in the project, deleted or moved to another place. A short description of the command is given in the information and syntax box.

Using the parameter button one can define the parameters that belong to that specific command.

Project example

<u>Example 1 Record frequency scan on all available MUX-channels.</u>

This example script will record a frequency scan on all available MUX-channels, and store the results automatically as “fra scanner test_001”, “fra scanner test_002”, etc. until the last available channel is reached:

```
Procedure!Open("c:\autolab\testdata\fratest")
ForAllChannels("c:\autolab\data\fra scanner test_")
```

Window

The Window option allows selection of windows which should be shown on the screen. The Tile option gives the default partitioning of the screen.
The Close all option will delete all the FRA windows except for the status bar and the FRA Manager window.

Help

The Help option is the top entry point in the help structure. For most topics on the screen Help is available. By pressing F1 the specific information about the part of the screen on which has been focused is given.

Tool bar

The tool bar contains a list of buttons, the current electrochemical method, and the name of the current measurement procedure.
The buttons give short cuts to various menu options which are frequently used. Place the mouse pointer on top of a button. Its meaning will appear in yellow, if pressing the button is allowed.

The two greenish buttons require some extra explanation. They can be pressed during impedance measurements. They allow the user to inspect the ac potential and ac current signal in real time domain and in the frequency domain. When one or both buttons are pressed monitor plots appear. The vertical axis in the time domain plot represents the potential or current as a percentage of the full input range.

The vertical axis in the frequency domain plot is an arbitrary log scale of the amplitude of the ac signals.
This plot can be used in order to check whether second harmonic effects occur. In case of a single sine signal and low frequency (< 200 Hz) the applied sine wave has the index n=1. At higher frequencies, the index of the applied signal is equal to the number of sines present within a single cycle. When the multiple sine mode is used,

the number of applied frequencies is equal to 5 or 15. The frequency domain clearly shows high amplitudes for the applied frequencies.

The horizontal axis is an arbitrary time scale.

3.2 Status bar

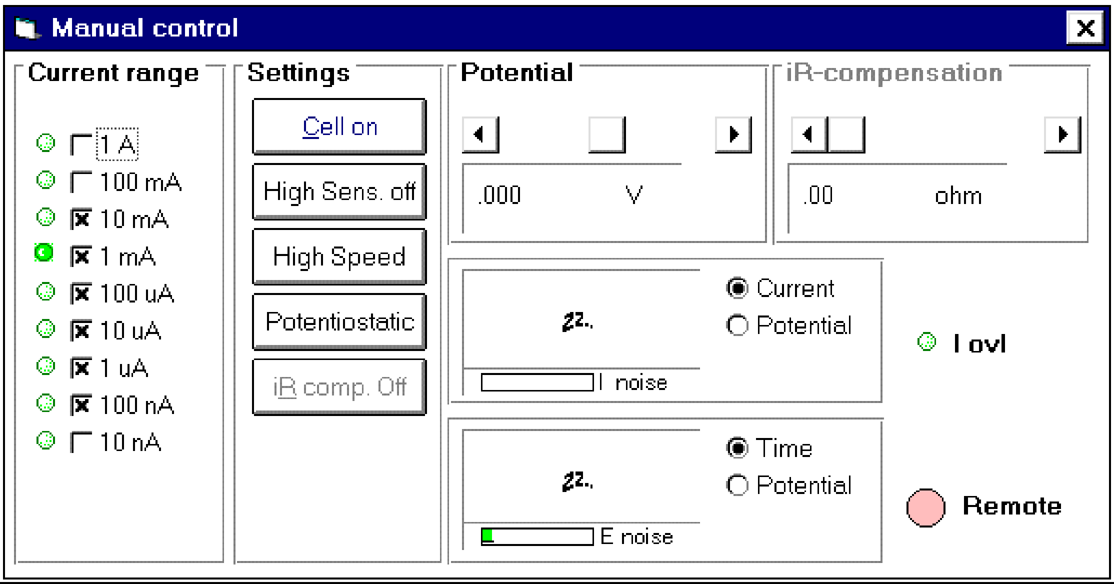
The lowest part of the screen is reserved for the status bar. The Start button starts the execution of a measurement procedure. After clicking this button, other buttons appear which make it possible to advance to a next stage or to abort a measurement procedure. The Status and Message panel give important control information. A measurement can be temporarily suspended by pressing the <Hold> button. More information on the sequence of events after starting the measurements is given in a separate chapter.

3.3 Autolab manual control window

The Manual control window gives full control over the potentiostat/galvanostat of the Autolab instrument.

Note, that some of the presented Autolab settings are part of the measurement procedure. The Manual control window consists of several panels.

Fig. 13 *Autolab manual control window*



Current range

In the Current range panel the green 'LED' indicates the actual current range. A mark in the neighbouring check box indicates whether the current range can be selected.

Only a joined column of selectable current ranges is allowed. The software always checks whether the row is closed. If a range separated from another range is checked, the intermediate ranges are checked automatically. When a check box is clicked again, the check disappears. The allowed current ranges are stored on disk as part of the procedure. The highest applicable current range for autoranging during potentiostatic measurements: the advised highest current range depends on the lowest measured impedance of the cell. In general the lowest measured impedance must be higher than 0.2/(current range), e.g. 20 ohm with a current range of 10 mA. In normal application the highest current range can be 1 A with the PGSTAT20/30, 100mA with PGSTAT12/100 or 10 mA with the PGSTAT10.

Settings

With the buttons in the settings panel the PGSTAT can be controlled.
The text on the button represents the current situation. The following buttons might appear (depending on the type of potentiostat/galvanostat):
<u>Cell on/off</u>: allows to switch cell on or off. In the 'off' position the connection of the potentiostat with the potentiostat/galvanostat is broken, so no current can flow between the counter and working electrode.
<u>High Sens off/on</u>: This button has limited functionality in the FRA-software. With High Sens on the displayed value of the dc current is improved with a factor of 10 compared to High Sens off. However, in most cases the button position is not relevant .
<u>High Stability/High Speed</u>: in High stability mode the PGSTAT is less susceptible to oscillations but its bandwidth is narrower.
It is advised to switch the potentiostat into 'High stability' mode before the measurements start in case you work with an electrochemical cell with a high capacitive load, i.e. in most cases a high electrode surface area. High stability mode offers the potentiostat a better protection for oscillation. Oscillations of the potentiostat might destroy your electrode.
If the applied frequency is too high for high stability the program will automatically switch the potentiostat into High speed mode.
<u>Potentiostat/Galvanostat</u>: allows to switch from potentiostatic to galvanostatic. It is highly recommended to switch the cell off before switching from one mode to another. In case of Potentiostatic control, the output of the DAC module corresponds to an applied potential level. In case of galvanostatic control, an output of the DAC module corresponds to an applied current.
<u>iR-compensation on/off</u>: Switches iR-compensation 'on' or 'off'. For impedance measurements iR-compensation should be switched off, therefore this button cannot be clicked in the FRA-program.

Noise meters

The noise levels for current and potential signals are visualised by 2 noise meters at the signal panels. When these VU-meters are active, the first green LED or a grey background is shown.
The VU-meter for the current signal is only active when the cell is switched on. The VU meter for the potential signal is also active when the cell is switched off i.e. no

current can flow. During the execution of the procedure (except for pre-treatment stage) the VU-meters are inactive.
In case more than 4 LED's of the VU-meter are on, it is advised to take precautions. You can select a higher current range or minimise the noise of your electrochemical cell. High voltage noise levels are often caused by the reference electrode.

Potential

The Potential panel contains a slider and a text box. With these tools the applied potential can be specified. The slider box can be dragged to change the value. A click on the arrows and slider bar changes the value by a distinct increment. The increment is different for the arrows and for the bar.
In the two panels below the measured current, potential and time can be displayed, depending on the option button selected.

iR-compensation (not yet possible)

The iR-compensation panel appears only when the Autolab is equipped with a PGSTAT12/20/30/100 potentiostat/galvanostat. In order to perform iR-compensation the iR-compensation button on the Settings panel should be switched to "iR-comp. on". Subsequently the ohmic resistance can be specified by using the slider or by typing in the textbox. Note that when the iR-compensation is switched on, automatic current ranging is no longer possible. The only checked current range box becomes the actual current range.

3.4 FRA Settings window

The parameters printed in this window give information about the measurements.
In the ‘Offset potential/current’ panel the values with which the potential and current are compensated to remove the DC component from the signal. Also the amplitude of the AC-signal is given.
In the Results panel the applied frequency (or base frequencies in case a multi-sine is used as modulation), the measured impedance and phase-shift are displayed.
In the Resolution panel the resolution of the actual measurement of the AC-current and -potential are displayed, the maximum value is 100%. A low resolution (say <0.5%) yields a poor accuracy of the results .
The resolution of the measurement depends on the applied current range and the gains of the amplifier. In case the resolution is too low and the gain of the amplifier is at its maximum, a lower current range can be used. However, the applicable lowest current range depends on the applied frequency, since the bandwidth decreases with lower current ranges. If the resolution is 100%, the measurement is done in an (almost) overload situation. The highest allowed current range has to be increased. See the Autolab manual control window.
The Gain panel indicates the gains which are used to amplify the I and E signal. The maximum gain is 128.

3.5 FRA manual control window

The FRA manual control window makes it possible to apply an ac signal to the electrochemical cell. It consists of several panels.

In the range panel a frequency range can be selected. With the Frequency and Amplitude panel below, the frequency and amplitude of the ac-signal can be selected. Both panels contain a slider and a text box. The slider box can be dragged to change the value. A click on the arrows or on the slider bar itself changes the value by a distinct increment. The increment is different for the arrows and for the bar. The input fields below determine how the measurements are done. They require some extra explanation.

The integration time

The minimum period during which the signals are measured. The longer this period, the more accurate the result will be. The minimum time of measurement is equal to one cycle of the (in case of multi-sine lowest) frequency. Thus, if the cycle time is longer than the sampling time, the sampling time will automatically set to the time of one cycle. A generally suitable value equals one second. If the time to measure the minimum number of cycles (see below) is larger than the specified integration time, the actual integration time will be determined by the minimum number of cycles.

The minimum number of cycles to integrate

The minimum number of ac signal periods during which the signals are measured. The more periods, the more accurate the result will be. One cycle is the minimum.

Number of cycles to reach steady state

The period between applying the ac-signal and start of the measurements. This time is often needed to measure stationary state behaviour. A standard value can be 10.

Maximum time to reach steady state

The maximum time between applying the ac-signal and the measurements. When the applied frequency is low, the time of the specified number of cycles to reach steady state, can be too high. As soon as the previous criterion or this criterion is found to be true, the measurement starts.

With a minimum fraction of cycle

In case the ‘Maximum time to reach steady state’ is shorter than the time equivalent to the duration of the ‘minimum fraction of cycle’, the latter value is used to wait for steady state.

The effective time to wait for steady state now depends on four parameters:
- f (frequency)
- Number of cycles to reach steady state: n_{cycles}
- Maximum time to reach steady state: t_{max}
- with a minimum fraction of a cycle: $X_{fraction}$

The time to wait for steady state t_{wait} is:
$t_{wait} = n_{cycles} / f$
if $t_{wait} \geq t_{max}$ then $t_{wait} = t_{max}$
if $t_{wait} \geq t_{max}$ then if $t_{wait} < X_{fraction} / f$ then $t_{wait} = X_{fraction} / f$

These parameters are also stored as part of the measurement procedure, so they might change when a procedure is loaded from disk.

In the panel below the results of the measurement can be observed after the Measure button has been clicked.

It is advised that during the 'manual' impedance measurements, the FRA Settings window is opened as well via the Window menu on the FRA manager window.

Use external inputs

When this box is checked, the FRA2 module does not determine the impedance by measuring the current and potential signals from the potentiostat/galvanostat. Instead, the signals applied to the BNC connectors X and Y are measured. It is possible that X or Y is connected to the BNC connector Eout or Iout respectively at the rear of the Autolab instrument (see also Appendix XI on Hydrodynamic Impedance Measurements).

3.6 Data presentation window

The Data presentation window serves several functions:
- display of data
- data analysis
- data manipulation
- communication with other programs like Paintbrush, Excel or MS-Word.

The window consists of a menu bar, a graphical display, and a message line.
As mentioned earlier the measured data are kept in a shared data memory block with the data acquisition software. During the measurement the measured data points are also copied to the memory block of the Data presentation window. After the measurements the data in this memory block can be modified by options in the Data presentation window. However, it is always possible to resume the measured data. Note that the save options of the File menu of the FRA Manager window always save the measured data. The data, which can be modified in the Data presentation window, are called work data and can be stored from the File menu of the Data presentation window in a work data file. This file cannot be distinguished from the files with measured data. Both types of files have the same format and layout.
On the message line at the bottom of the graphical display important text about the required user actions during analysis of editing data appears. If no message is displayed, the currently measured potential and current are displayed.

Copy

The Copy option allows to copy the graph to clipboard or to dump the graph in a bitmap file (.BMP) or a Windows meta file (.WMF). These files can be read by programs like Paintbrush, Excel, or MS-Word. These programs allow editing of the graphs. Please note that the size of the axis annotations etc. in the meta file depend on the size of the Data presentation window. Moreover, the sizes in the meta file may be somewhat different from what is displayed in the Data presentation window.
The best way to copy the graph to MS-Word is to make a .WMF file using the Copy to option. The best result is obtained by doing this from a maximised Data presentation window. By default FRA only draws dots. It is sometimes better to draw lines. This can be achieved by double-clicking the data points in the graph. For further information, see the paragraph on Editing graphical items.

File

The File option allows saving the data presented in the Data presentation window and allows merging of previously measured data with the current data.

Save work data

Allows saving of edited or merged data as previously discussed.

Merge

This option allows merging of two frequency scans at single potential or current.
The merged scans can subsequently be stored on disk using the "Save work data" option. However, conflicts may occur in the procedure parameters of the two merged data files. The procedure parameters of the already loaded data are dominant. This option is useful to obtain a full frequency scan from two or more separately measured scans. For example, in order to save time, the low frequency part of a scan is measured using the multi-sine mode and the high frequency part is measured using the single-sine mode. After a subsequent merge a full scan is obtained.

View

The View option makes it possible to inspect one or more graphical presentations of the measured impedance data. A maximum of 4 plot windows can be opened at the same time.

When the measurements are performed at one single potential or current a selection can be made from the following items:

Z" versus Z'

Draw a plot of the quadrature impedance versus in-phase impedance.

Y" versus Y'

Draw a plot of the quadrature admittance versus in-phase admittance.

Bode plot

Draw a plot of the logarithm of the impedance and the phase angle versus the logarithm of the frequency.

Z', Z" versus f

Draw in-phase and quadrature impedance versus the frequency.

Z versusÖw

Draw in-phase and quadrature impedance versus square root of 2πf.

Z versus 1/Öw

Draw in-phase and quadrature impedance versus one over square root of 2πf.

Y versus Öw)

Draw in-phase and quadrature admittance versus square root of 2πf.

Y versus 1/Öw

Draw in-phase and quadrature admittance versus one over square root of 2πf.

Y"/w versus Y'/w

Draw quadrature admittance over 2πf versus in-phase admittance over 2πf.

Epsilon plot

Draw quadrature versus in-phase permittivity, after specifying the geometric capacitance being the capacitance of the empty cell. The permittivity is defined as epsilon = Y/iωC = epsilon' + i*epsilon".

Z' versus wZ"

Draw in-phase versus 2πf times quadrature impedance.

Z' versus Z"/w

Draw in-phase versus quadrature impedance over 2πf.

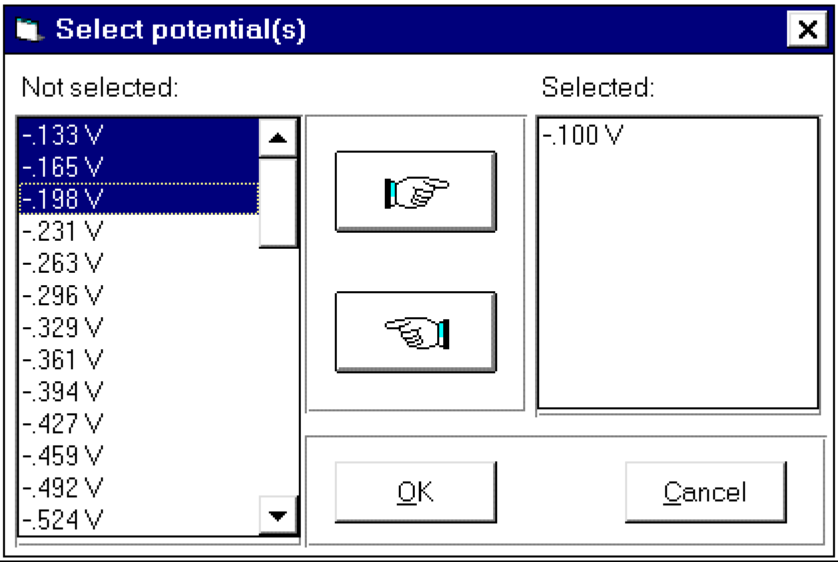
wZ'versus wZ"

Draw 2πf times in-phase versus 2πf times quadrature impedance.

Select potential or currents

When a potential or current scan has been performed, the option 'Select potential' or 'Select current can be chosen. A window appears from which one or more potentials or currents can be selected or deselected.
The frequency scans measured at the selected potentials or currents will be shown.

Fig. 14 *Select potentials window*



The data measured at the selected potentials or currents are plotted in different colours in one or more of the plot available types. The potential or current values at which the frequency scans are displayed, are shown in a drop down menu in the upper left corner of each graphical window. The value selected from the drop down menu is the so called work data set. All Edit and Analysis action are performed on this data set.

A maximum of four plot types can be displayed at the same time. Each plot in a separate window.

In case a potential or current scan has been performed one or more of the following potential scan plots can also be selected:

Z' versus E

Draw a plot of the in-phase impedance versus the potential (or current).

Z" versus E

Draw a plot of the quadrature impedance versus the potential (or current).

Y' versus E

Draw a plot of the in-phase admittance versus the potential (or current).

Y" versus E

Draw a plot of the quadrature admittance versus the potential (or current).

Cs versus E

Draw a plot of the substituted serial capacitance versus the potential (or current).

wZ' versus E

Draw a plot of the in-phase impedance * 2πf versus the potential (or current).

wZ" versus E

Draw a plot of the quadrature impedance * 2πf versus the potential (or current).

Mott-Schottky

Two types of Mott-Schottky plots are available:
Rs-Cs: the experimental capacitance is calculated from a Rs-Cs circuit in series.
Rs-Cp/Rp: the capacitance is calculated assuming that a resistance Rs is in series with a capacitor Cp.

Select frequency

The impedance/admittance plots can be drawn at one or more frequencies.
A window appears from which one or more frequencies can be selected or deselected.
The potential scans measured at the frequencies will be shown.

The data measured at the selected frequencies are plotted in different colours in one or more of the plot available types. The frequency values at which the frequency scans are displayed, are shown in a drop down menu in the upper left corner of each graphical window. The value selected from the drop down menu is the so called work data set. All Edit and Analysis action are performed on this data set.

A maximum of four plot types can be displayed at the same time. Each plot in a separate window.

When a time scan has been performed one or more of the following time scan plots can be selected:

Z' versus t

Draw a plot of the in-phase impedance versus time.

Z" versus t

Draw a plot of the quadrature impedance versus time.

Y' versus t

Draw a plot of the in-phase admittance versus time.

Y" versus t

Draw a plot of the quadrature admittance versus time.

Cs versus t

Draw a plot of the substituted serial capacitance versus time.

wZ' versus t

Draw a plot of the in-phase impedance * 2πf versus time.

wZ" versus t

Draw a plot of the quadrature impedance * 2πf versus time.

Z', Z" versus t

Draw in-phase and quadrature impedance versus time.

Z, Phi versus t

Draw impedance and Phase shift versus time.

Y', Y" versus t

Draw in-phase and quadrature admittance as a function of time.

A maximum of four plot types can be displayed at the same time. Each plot in a separate window.

Plot

The Plot option contains all kind of possibilities to manipulate the graph like plot refresh, automatic scaling, zooming, or display of a previously measured signal. Sometimes, not all options are selectable because they are not applicable or intervene with current active data analysis options. Also when the execution of a procedure is going on, not all options are selectable.

Some sub-options require explanation.

Automatic

The plot will be scaled automatically. Some plots i.e. Z'' versus Z' and Y'' versus Y' will be scaled in such a way that both axes have a similar division, so that a semi-circle can be displayed correctly.

Resume

The Resume option makes a fresh copy of the measured data into the Data presentation window.

Zoom

Clicking the Zoom option has the same effect as pressing the right mouse button. When this option is activated a magnifying glass appears. When subsequently the left mouse button is clicked and held down, a Zoom window can be created.

Set window

This option allows to select part of the data set for further editing of data or data analysis. Only the selected range of data-points remains visible on the plot. The removal will be done in all loaded plots. With the Resume option on the Plot menu the originally measured data will be reloaded. The Save work data option on the File menu can be used to save the selection of the data set.

Load overlay file

This option allows the making of an overlay of one or more previously measured data sets. The overlay data will appear in all open graphs. The legends of these overlay files are selectable with the overlay legends dropdown box. This dropdown box overrules the standard dropdown box where the different potentials/currents/frequencies are shown. A maximum of 5 overlays can be made. In case the overlay file contains a potential or current scan, a window appears to select a potential, current or frequency value, depending on the active plot type,. After clicking the Resume option (see above) the overlays will disappear.

Enter text

When this option is clicked the "Additional text" appears in the top left corner of the graph. This text can be dragged over the graph. After double-clicking the field, the text itself as well as the format can be modified. The first text line of the Paste buffer can be inserted on the text field as well. Thus a line of text from the Analysis results window can be copied to the Paste buffer and subsequently inserted there. Please note that the text cannot be stored.

Change axis text

A window appears in which the axis description of all plot types can be edited.
After clicking OK, all future plots will appear with the updated axis text.
The modified axis description will be stored on disk when the FRA program has been exited in a regular way. This options offers also the possibility to specify an Isotropic plot. The plot will be shown isotropic the next time you open the plot.

Fig. 14a *Change axis text window*

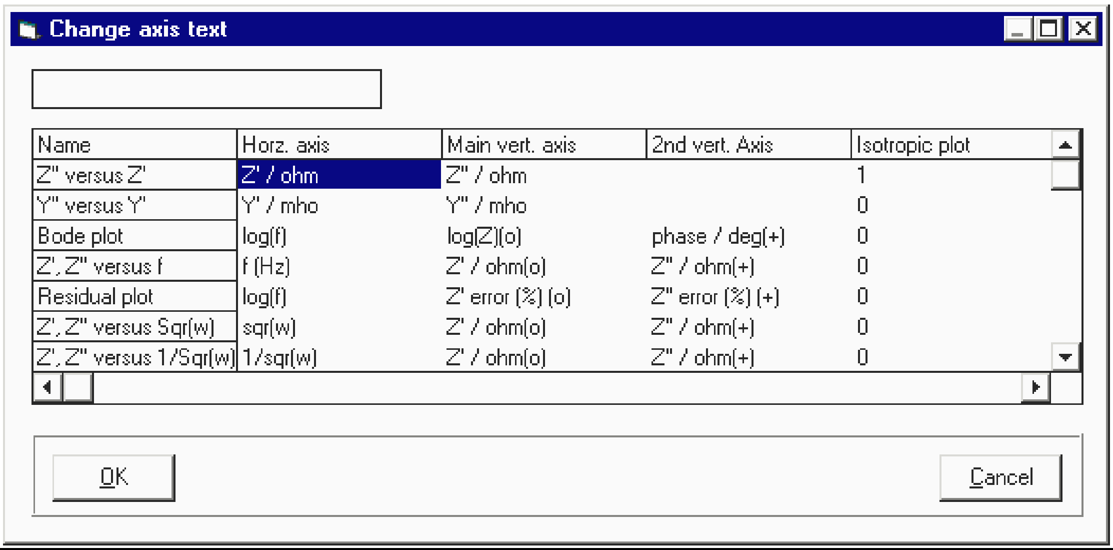
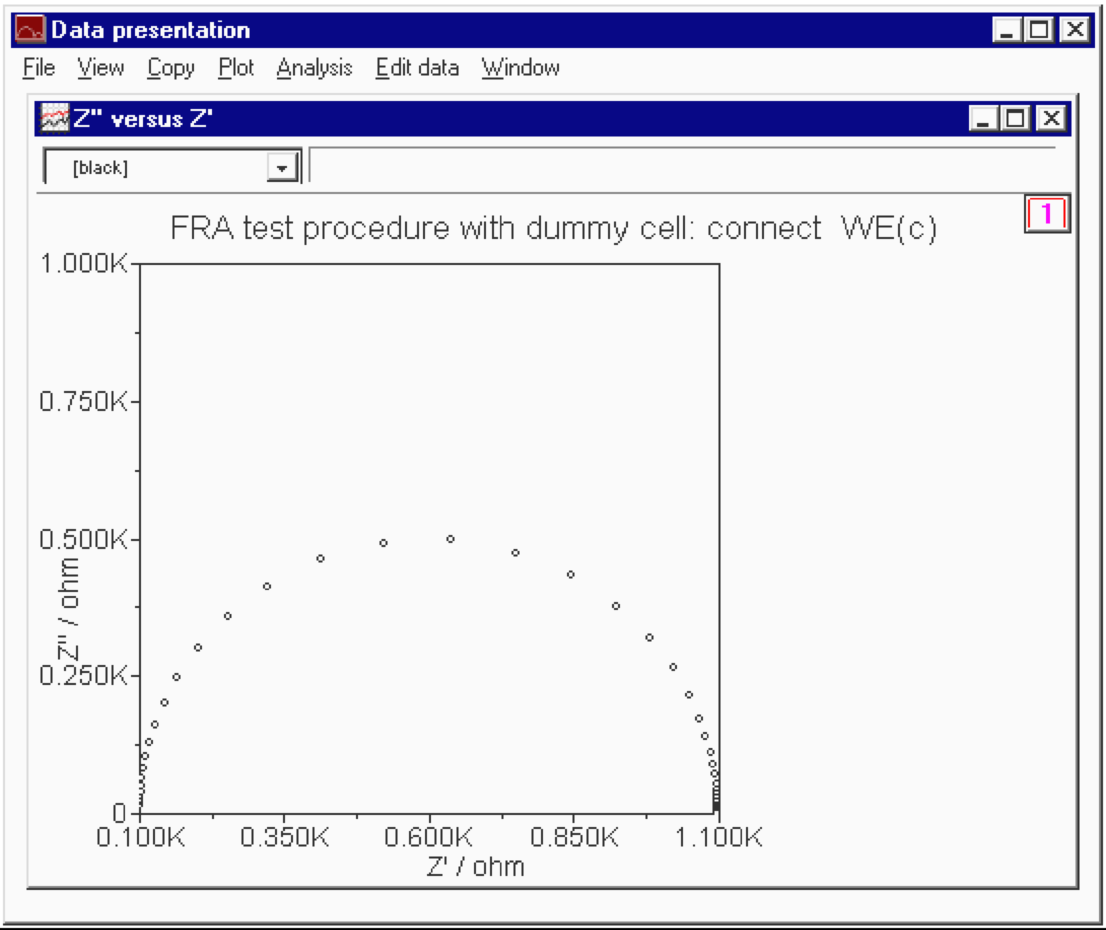


Fig 14b. *Example of an Isotropic Z', Z'' plot*



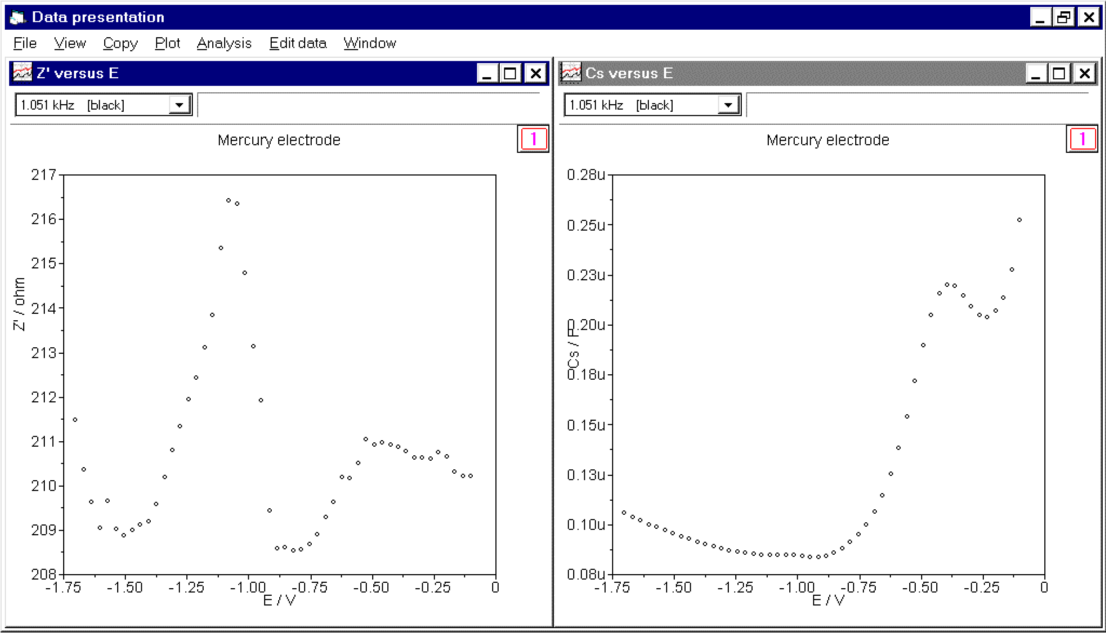
Save graphical settings

The presentation of the graphs is determined by many parameters like the marker type of each displayed data set, the format of the axis indices, the colours, etc. All these parameters can be modified (see below). The modified settings can be saved by selecting this option. Only one set of graphics parameters can be saved, so any new plot type subsequently created will use the newly saved graphical settings as default. The graphical settings are stored on disk when the program is exited in a regular way.

Default graphical settings

All parameters which determine the presentation of the graph will be set to their default i.e. as they were when the graphical settings were saved the last time.

Fig. 15 *Two potential scan plots*



Analysis

The analysis menu has four options. Selection of these options opens a specific window to perform the operation and to display the results. The results are printed in the Analysis results window as well. This window can be made visible from the Window option on the FRA manager menu bar.

Linear regression

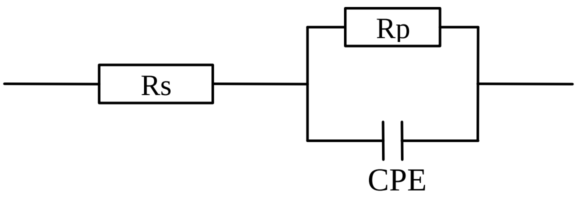
The Linear regression option makes it possible to fit a straight line through a part of the measured curve. When the option is selected, two windows appear. One is the Linear regression window and the other is the Markers window. When the begin and end point of the line have been marked on the measured curve and the OK button on the Markers window has been clicked, a line is drawn in such a way that the sum of squares of the differences between measured data points and calculated line is minimum. The slope of the line (dY/dX), the intercepts i.e. Y(at X=0) and X(at Y=0), and several other helpful data are given. More lines can be fitted when the Set line button is clicked.
In case the plot type is such that a left as well as a right hand Y-axis is displayed, an extra panel is added to the Linear regression window where the user can select on which data the linear regression should take place.

Find Circle

The Find circle option makes it possible to fit a semi-circle through a part of the measured curve. When the option is selected, two windows appear. One is the Find circle window and the other is the Markers window. When the begin, centre, and end point of the circle have been marked on the measured curve and OK is clicked on the Markers window, a semi-circle is drawn through the marked points. The slope of the

line (dY/dX), the intercepts i.e. Y(at X=0) and X(at Y=0), and several other helpful data. More semi-circles can be drawn when the Find circle button is clicked.
If the Find circle option is not appropriate for a certain plot type, it can not be selected.
For the plot type Z'' vs Z', the program calculates the values of Rs, Rp and CPE assuming an equivalent circuit with a CPE parallel to a resistance Rp and a resistor in series with this combination. The impedance of the CPE is $Z = 1/(i\omega CPE)^n$

Fig. 16 *The Rs-Rp//CPE equivalent circuit*



For the plot Y'' vs Y', the program calculates the values of Rs, Rp and r
where r is the radius of the semi-circle.

Find minimum and maximum

The Find minimum and maximum option shows the minimum and maximum Y-value(s) with their corresponding X-values.

Interpolate

The Interpolate option allows to calculate one or more X-values or Y-values which correspond to a given value on the axis. A linear interpolation is used to calculate intermediate values.

Data info

this option sets a marker in the presently loaded curve and gives the corresponding frequency and X,Y values.

The Kramers-Kronig (K-K) test

This test can be used to check whether the measured data comply with the assumptions of Kramers-Kronig transformation. These assumptions are: (1) the response is only related to the excitation signal, (2) the response is linear (or the perturbation is small, e.g. <10 mV, for non-linear systems), (3) the system does not change with time and (4) the system is finite for all values of ω, including zero and infinity. If the investigated system changes with time due to e.g. ageing, temperature change, non-equilibrium initial state etc., the test fails. Failure of K-K test usually means that no good fit can be obtained using the equivalent circuits method. This option is based on the work of Dr. B.A. Boukamp as published in J. Electrochem. Soc., Vol 142, 6 (June 1995) and coded in the program RCNTRANS by the same author.
Please refer to the Appendix for more information about this option.

Fit and Simulation

This option allows you to simulate responses of equivalent circuit and to fit the circuit parameters to the measured data, using the non-linear least squares method. The equivalent circuits can be defined by the user (using Circuit Description Code). It is possible to define elements with fixed values as well as constraints for values of fitted parameters. This option is based on the work of Dr. B.A. Boukamp as first published in Solid State Ionics, 20 (1986) 31-44 and coded in the program EQUIVCRT by the same author.
Please refer to the Appendix for more information about this option.

Edit data

Change all points

All the data displayed in the focused plot window can be changed; however, the change only effects the displayed data, not the work data. This means that the changed data cannot be saved and also newly created plots will be based on the unchanged work data.

Correct for ohmic drop

All data points can be changed using this option. A value for either Z', Z'' or the potential, current or time can be given. Subsequently all loaded plots will be updated with newly calculated values. With the Resume option of the Plot menu the originally measured data will be reloaded. The Save work data option of the File menu can be used to save the modified data set.

Delete points

An option is available to remove points from the plot. This option can be used to remove spikes from the measured data. The removal will be activated in all loaded plots. With the Resume option from the Plot menu the original data set will be plots. The Save work data option from the File menu can be used to save the adjusted data-set.

Element subtraction

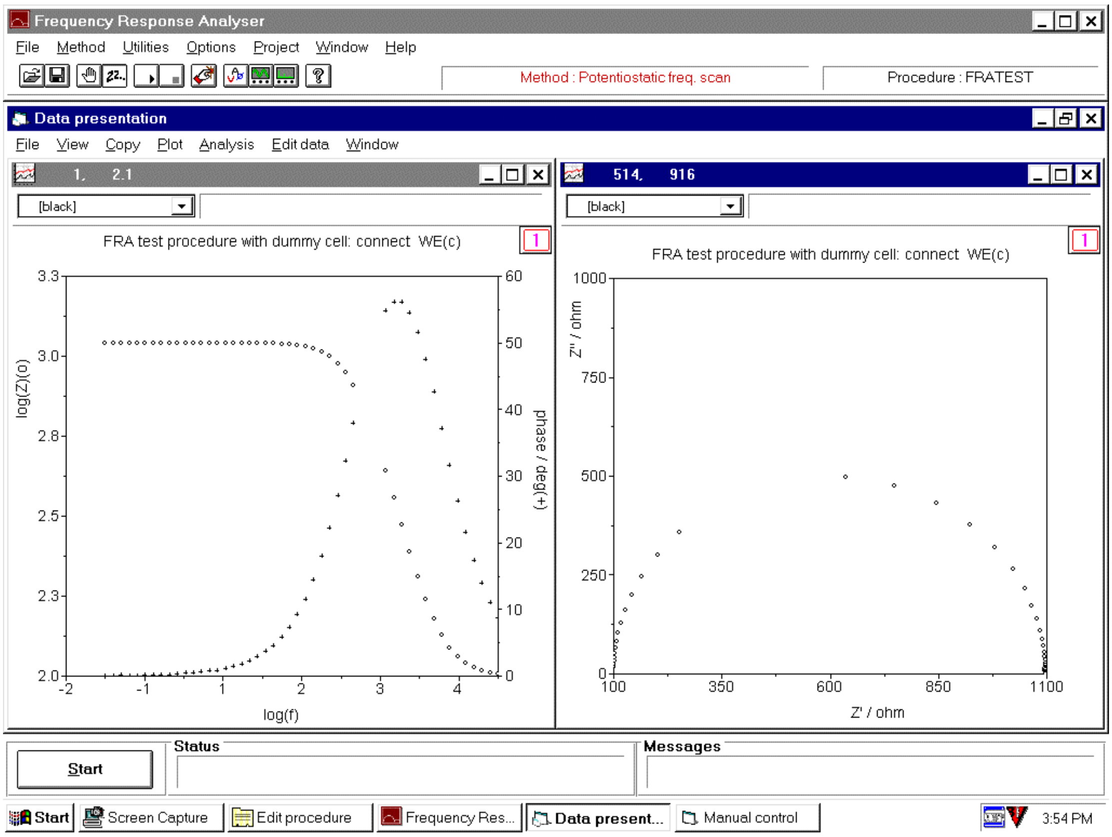
The influence of a circuit elements can be subtracted from the measured data. This can simplify the analysis of the data. All elements which can be used in the Fit and simulation option can also be subtracted. The element can either be subtracted from impedance data or from admittance data. The impedance data should be used in case the element is supposed to be in series with the remaining circuit; the admittance data should be used if the element is parallel with the remaining circuit.
A description of the available circuit elements can be found in the appendix on Fit and simulation.

Dispersion functions for elements

The table below defines the dispersion functions for the elements in both impedance and admittance representation ($\omega = 2\pi f$).

CDC	**element**	**impedance**	**admittance**	**parameters**
R	resistance	R	$1/R$	R
C	capacitance	$-j/(\omega C)$	$j\omega C$	C
L	inductance	$j\omega L$	$-j/(\omega L)$	L
W	Warburg impedance	$1/\left(\mathrm{Y}_0\sqrt{\mathrm{jw}}\right)$	$Y_0\sqrt{j\omega}$	Y_0
Q	constant phase element	$\left(Y_0 j\omega\right)^{-n}$	$\left(Y_0 j\omega\right)^{n}$	$Y_0,\ n$
T	hyperbolic tangent element	$\left(Y_0\sqrt{j\omega}\right)^{-1}\coth\left(B\sqrt{j\omega}\right)$	$\left(Y_0\sqrt{j\omega}\right)\tanh\left(B\sqrt{j\omega}\right)$	$Y_0,\ B$
O	hyperbolic cotangent element	$\left(Y_0\sqrt{j\omega}\right)^{-1}\tanh\left(B\sqrt{j\omega}\right)$	$\left(Y_0\sqrt{j\omega}\right)\coth\left(B\sqrt{j\omega}\right)$	$Y_0,\ B$
G	Gerischer impedance	$\left(Y_0\right)^{-1}\Big/\sqrt{K_a + j\omega}$	$Y_0\sqrt{K_a + j\omega}$	$Y_0,\ K_\mathrm{a}$

(Please note that the definition of the Q element differs from the EQUIVCRT program fig. 16b *The marked points have been removed from the data-set*



Editing graphical items and viewing data

Except for the available options, items of the graph can be edited by double-clicking them. The following items can be double-clicked:

- the axis labels
- the axis itself
- the axis description
- the plot title and subtitle
- the data.

Colours, sizes, marker types, text, formats, axis position: all these things can be changed. Please take some care with changes in Colours. E.g. do not make the data colour the same as its background colour.

By double-clicking the data points a window appears, which among the standard graphical operations also gives the possibility to view the data values itself and to edit them. Moreover, the data can be copied to clipboard and subsequently be entered into e.g. a spreadsheet program. The format of the data is similar to the format of the axis labels.

Double-clicking the axis itself allows scaling and positioning of the axis and selection of the axis function. Data can be displayed, among others, as linear inverse, ^{10}log, natural log, square root, inverse square root. Except for the linear and ^{10}log, the value

of the presented data is modified in real. So all subsequent operations are really performed on e.g. the square root of the data.
In case of the ^{10}log, not the values but the axis is changed to a logarithmic axis. Sometimes it is necessary to perform automatic scaling after changing the axis, press F4.

Double clicking the axis labels allows specification of the format of the axis labels. It is very important that the correct precision of the labels is specified.

When the button "| 1 |" in the upper right corner is clicked, the Graph parameter window appears. This window allows modification of the relative scale parameters of the so called graph and plotting area, and their background colours.

All changes made to colour and sizes are stored in the default graphics display file. Other changes are kept in the procedure file.

Fig. 17 *Window which appears after double clicking horizontal axis*

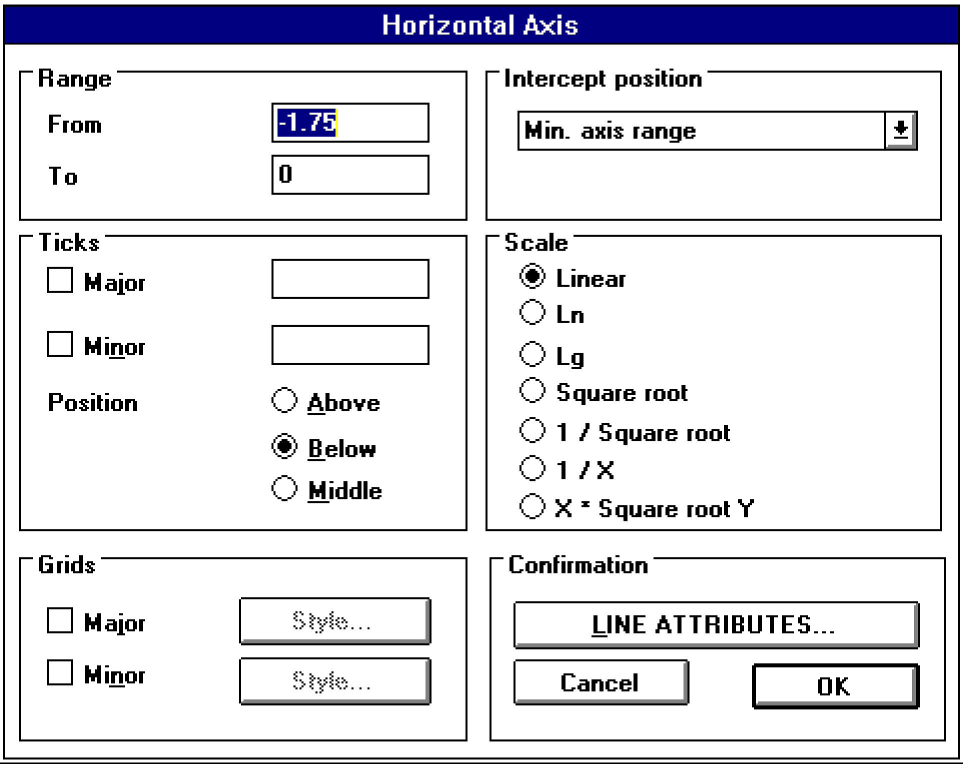


Fig. 18 *Window which appears after double clicking the axis labels*

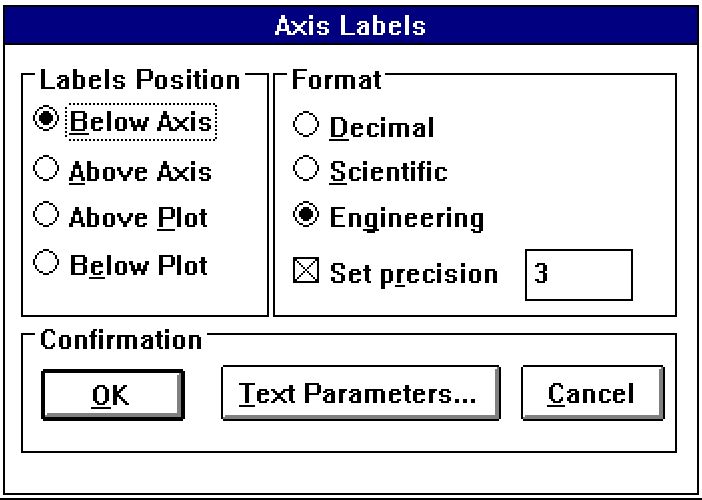
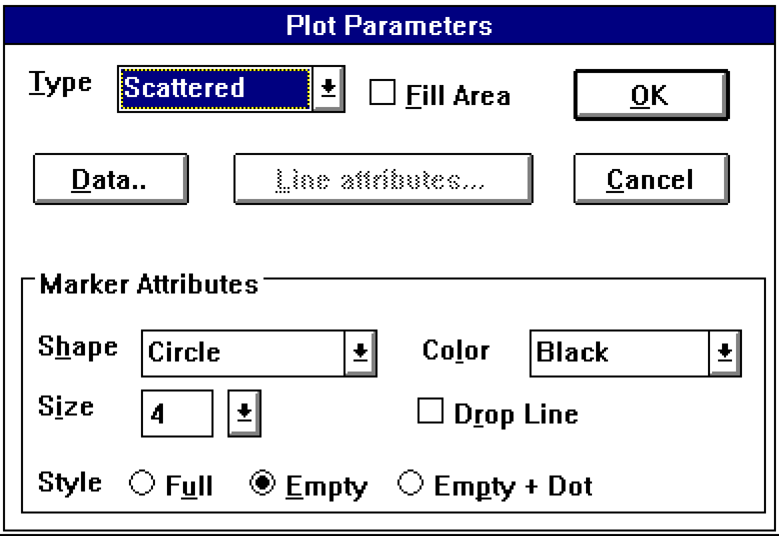


Fig. 19 *Window which appears after double clicking the data*



3.7 Edit procedure window

The edit procedure window consists of two pages. On page 1 the most common parameters can be specified. Page 2 contains the other parameters.
The parameters are divided in several sections i.e. pre-treatment, measurement, potential, comment, title, and subtitle. A full list of the definition is found in the appendix.

The FRA data can be saved directly to disk while the measurement is in progress by specifying a direct output name. The data will be written with the extension ".DFR".

This option is useful for long duration scans and prevents data loss due to a failure of the power supply. If no path is included, the default data directory is used.

Please note that next to the parameter in this window, the current ranges of the Autolab manual control window and the four parameters of the FRA manual control window will be stored as part of the procedure as well and will influence the measurements.

Pre-treatment

The pre-treatment facility allows conditioning of the electrochemical cell at specified potentials or currents, during a specified time. This pre-treatment can be performed before each applied ac frequency or before each new applied dc potential or current. If this facility is not to be used, specify all times as zero.

Edit frequencies

The frequencies can be edited from a separate window which can be opened by clicking on Edit frequency option just below the top window bar.

The frequencies to be applied can be calculated according to the parameters in the Parameter panel.

The exact applied frequencies and their amplitude can be changed in the second input screen.

A complete frequency scan can be divided in up to five sub-scans.
This facility makes it possible to measure for instance from 50 kHz down up to 10 Hz with an amplitude of 0.005 V first and after that from 10 Hz down to 1 mHz at 0.05 V.

Begin and end frequency : The (sub-)scan is performed from the begin to the end frequency. It is strongly advised to perform a frequency scan from high to low frequencies. The frequency limits are 50 kHz down to 0.1 mHz (FRA) or 1 MHz down to 0.01 mHz (FRA2).

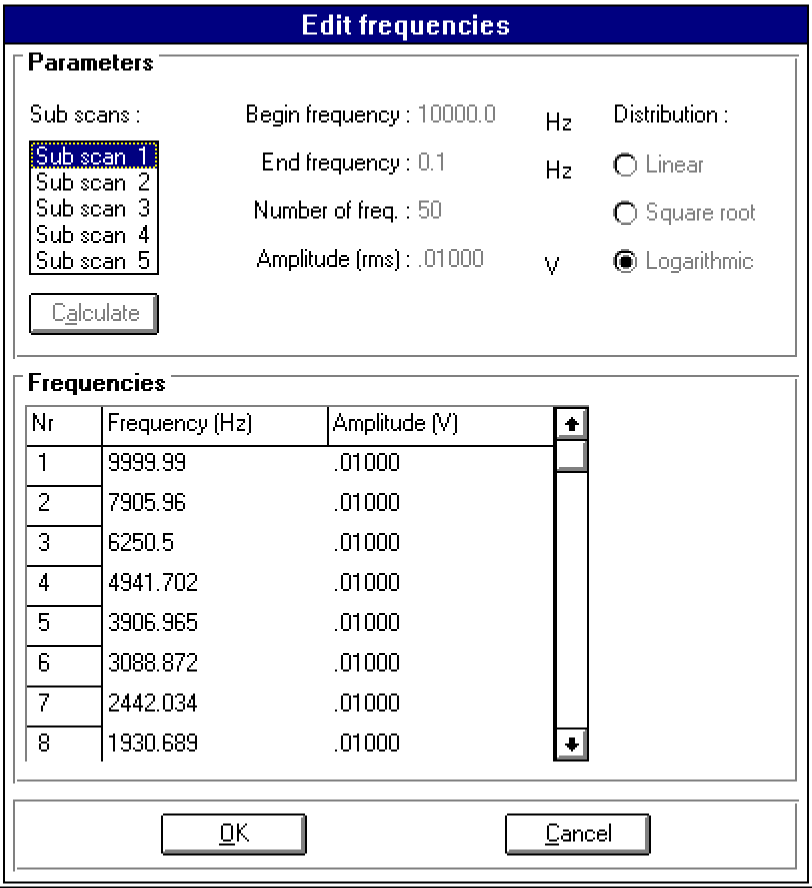
Number of points: The number of frequencies in the (sub-)scan.

Frequency distribution : The distribution of the frequencies from the begin to the end frequency can be either linear, square root-linear, or logarithmic.

The amplitude (rms value) of the ac signal. In case of potentiostatic measurements, a general applicable value equals 0.01 V. The value should be so low that non-linear effects are avoided. Amplitude limits are normally 0.0002 V and 0.35 V.
In case of galvanostatic measurements, the ac current amplitude should cause a potential response at which, again, no second harmonic effects are found. However some specific measurements, e.g. in case of very high impedance’s, require increased ac signals.

In case it is unknown at which amplitudes non-linear effects occur, some measurements can be performed, while monitoring the frequency domain plot. Non-linear effects will give higher amplitudes at frequencies higher than the applied frequencies. The software provides the button ‘Show/hide FFT spectrum’ in order to monitor the amplitude as a function of frequency.

Fig. 20 *Edit frequency window*



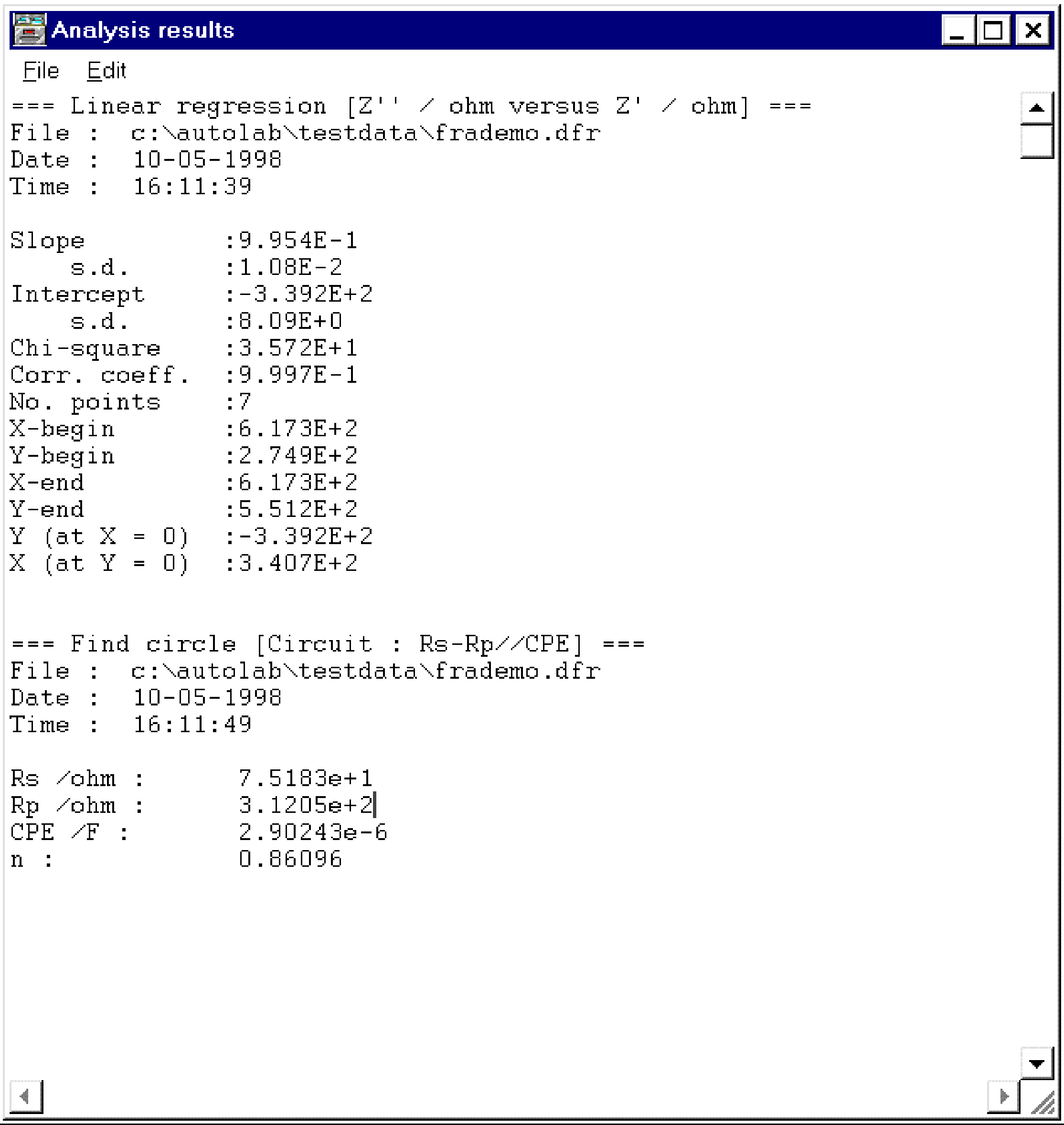
3.8 Analysis results window

The Analysis option of the Data presentation window allows the making of an analysis of the data. In some cases the results are displayed in a special window which differs per analysis technique. In all cases an analysis report is printed in the Analysis results window.

The Analysis results window contains all the results of the analysis of the data. Only when the FRA Manager window is closed, the Analysis results window is cleared. The File option of this window allows the user to clear, save, or print the content of the window. The Edit option allows the user to remove (Cut) the selected part of the text. Text can be selected by keeping the left mouse button pressed and moving it over the window. The Copy option copies the content of the window to the paste buffer. The Paste option will include text from the paste buffer.

It is possible to copy the analysis results to the data presentation graph in this manner.

Fig. 21 *Analysis results window*



4. Measurements

4.1 Advice on measurements

It is advised to switch the potentiostat into ‘High stability’ mode before the measurements start in case you work with an electrochemical cell with a high capacitive load, i.e. in most cases a high electrode surface area. High stability mode offers the potentiostat a better protection for oscillation. Oscillations of the potentiostat might destroy your electrode.
If the applied frequency is too high for high stability the program will automatically switch the potentiostat into High speed mode.
It is better to start with higher frequencies and then go to lower frequencies. It can save time. The FRA module will settle at the first applied frequency. At very low frequencies this might take quite a long time.

4.2 Internal / External measurements

The FRA2-modules allow doing impedance measurements by passing the built-in potentiostat/galvanostat. The external inputs X and Y can be seen on the front of the module. The program supports recording the impedance with respect to an external applied ac-signal instead of the applied ac-potential. For this purpose the applied ac-signal should be connected from an external source to the X-input. Furthermore, the checkbox ‘Use external inputs’ should be clicked on the FRA manual control window. Now the current response with respect to this external source is measured. The current signal from the rear of the Autolab instrument (connector I_{out}) should be connected to ‘Y’ using a BNC cable. This software option is only available for instruments delivered after September 1997. Please consult Eco Chemie in case of problems.

4.3 Time, potential and current measurements

After each impedance measurement the time, dc-current and dc-potential are recorded. The time is recorded from the start of the equilibration stage.

4.4 Time scan

It is possible to perform frequency scan of impedance measurements at a specified interval time at a fixed potential or current.
For this purpose the Method menu on the FRA-manager window contains the option ‘Time scan’ for both the potentiostatic as well as the galvanostatic mode.

The minimum interval time is at least two seconds, but will depend on factors like the number of frequencies to be measured, the frequency itself, the ‘minimum cycles to integrate’ and the ‘maximum time to reach steady state’ (see the FRA manual control window). In case the interval time exceeds the specified value, a message will be given but the measurements will continue.
The time at which a measurement is done is stored in memory for every single frequency, but on the graphical window the whole frequency scan is plotted at the time at which the latest frequency in the scan is measured.

The time at which each single frequency is measured can be viewed in ASCII-files which can be created. (See the paragraph on ‘Convert to ASCII')

4.5 Single and Multiple Sine-waves

The applied AC perturbation on top of a DC potential or current can either be a single sine, a superposition of five carefully selected sines of different frequencies over one decade or fifteen sines over three decades of frequencies. It is advised for common use to choose the single sine wave as perturbation, because it gives the best signal to noise ratio. The multi-sine capabilities can be of use in two particular cases:
- to save time in the low frequency region.
- to record a frequency spectrum at an unstable electrode surface

The multiple sine mode can only be used in a limited frequency range. The maximum base frequency for the five sine perturbation is 3120 Hz and for fifteen sine perturbation is 312 Hz.
In both cases the maximum upper frequency is about 31200 Hz.

4.6 The measurement sequence

The execution of the measurement procedure is conducted through several stages:

1. The memory of the DSG is loaded using one of the signal files from disk, containing the proper ac-signal, but is not switched on yet.
2. A new drop signal is generated if the hardware configuration shows the presence of a mercury drop electrode (see Hardware configuration program).
3. The pre-treatment starts if one or more conditioning times are unequal to zero and the pre-treatment has to be performed before every frequency.
4. The dc-potential or dc-current is applied and the filter is set to the proper cut-off frequency. The ac-signal is applied. The timer is set to the equilibration time and waits until the timer is ready. If the measurement is synchronised, the timer is set to the equilibration time minus 1 second, but the program continues without waiting for end of timer.
5. The gains of both amplifiers are set. The current range is set. In case of the first measurement, the 'Highest current range'. In all other cases according to calculated optimal current range, depending on last measured results. If the measurement is synchronised, the program holds until end of timer is found. Now the timer is set to one second.
6. At higher frequencies (higher than the minimum frequency for autoranging, see Appendix I), the gains of both channels are increased until an overload is found and then decreased with a factor of 2. At lower frequencies, the gains are set according to the previous measurement.
7. If the measurement is synchronised, the program waits for end of timer and waits the specified time, needed to reach steady state of the ac-response.
8. The measurement is performed and results are calculated. If an overload is found, the gains and if necessary the current range are corrected and measurement is repeated at step 2. If the resolution of the measurement is too poor, the measurement is repeated if a more optimal setting is possible.

9 The impedance is calculated. If the applied current range does not match the measured impedance, the new 'best' current range is determined and if applicable, the measurement is performed again from step 2.
10 The results are graphically displayed.

The pre-treatment as well as the measurements can be aborted by clicking the Abort button or by pressing the <ESC> key. If the FRA-settings window is opened, it will show whether the measurements are done properly. If the greenish button on the tool bar is clicked, the monitor plots appear. They also give an indication about the quality of the measurement. The results of the measurements are plotted in the data presentation window. When no plot is loaded, the measurements will automatically be presented in a Z” versus Z’ plot. See the View option on the data presentation window for other plot types.
After the measurement the data are now always sorted on frequency. Data files measured with older versions of the FRA software (version 2.1) are not sorted.
A sorted data-set can be obtained after saving a loaded data file, using the option “Save work data” from the Data presentation window.

4.7 Technical background

This paragraph explains step by step the measurement sequence which is conducted during the execution of a procedure. However, more dedicated this time towards the software and hardware internals.

1. Load the memory (RAM) of the digital signal generator (DSG).

   The data to fill the memory of the DSG is read from the disk. On the disk several files, each representing a specific signal type, must be present in the signal directory:

   - W_SIN01.F01 (FRA) or W_SGNL01.F12 and .F22 (FRA2)
     : a single sine
   - W_SIN02.F01 (FRA) or W_SGNL05.F12 and .F22
     : five superimposed sine waves
   - W_SIN03.F01 (FRA) or W)_SGNL15.F12 and .F22 (FRA2)
     : fifteen superimposed sine waves.

   The datafile contains 16384 (FRA) or 32728 (FRA2) words of 16 bits wide, representing the specified signal. The content of this file is downloaded in the memory of the DSG. The 16 bit DAC is set with a maximum frequency of 3.23 MHz (FRA) or 32 MHz (FRA2). The number of points or DA conversions per sine wave depends on the frequency. With the FRA module, a single sine is generated with 16384 points when the frequency is below 197 Hz. When the frequency is below 976 Hz, the FRA2 generates it with 32768 points.

2. The amplitude of the signal is controlled by setting the 12 bit multiplying DAC, providing a amplitude setting with a resolution of 1 in 4096. The output of the DSG is filtered with a RC-filter.

3. If the measurements have to be performed by using the autoranging facility, the optimal current range is set, according to the specified input parameters. The selected current range during autoranging depends on the value of the impedance Z. The measured value at the selected current must be between FACTOR1/(current range) and FACTOR2/(current range). The default values for FACTOR1 and FACTOR2 are 0.2 and 5. Thus a current range of 1 mA is selected for impedance's between 200 ohm and 5000 ohm. The selected current range depends on the applied frequency. This is due to the fact that lower current ranges have a lower bandwidth (See Appendix).

4. The filter is set to a cut-off frequency of the frequency to be measured multiplied by a user-specified factor. In case a multiple sine is applied, the cut-off frequency equals the highest frequency to be measured multiplied by this user-specified multiplication factor. However, the highest cut-off frequency is limited to 140 kHz (FRA) or 160 kHz (FRA2). However, with the FRA2 modules a fixed filter is used when the applied frequency is higher than 19 kHz. The lowest applied cut-off frequency is limited by software. The default frequency limit is 10 Hz. A cut-off frequency close to the applied frequency (factor for filter frequency close to unity), cause significant attenuation of the signal as well as a severe phase shift. Since both filters do not exactly match, a systematic error will be found. A reasonable minimum value for this filter factor is 32.

5. The conversion rate of the two simultaneous sampling ADC's is set. This is done by using the same crystal as used for the 16 bit DAC, and by dividing its frequency by an integer number.

   The default number of points for one cycle of ADC's equals 1024. For lower frequencies the FRA2 also measures 2048 or 4096 points per sine wave. At frequencies higher than 200 Hz (FRA) or 488 Hz (FRA2) more than one sine wave is measured with 1024 points. The oscilloscope windows will show more than one sine wave.

   Each memory location is 24 bits wide. Since the ADC's are 12 bits, the maximum number of conversions per memory location equals 4096. Thus, a frequency of for instance 200 Hz is sampled with 200 kHz conversion rate. Measurement of one cycle takes 1/200 s = 0.005 s. Up to 4096 cycles can be measured and averaged. The maximum time of measurement or integration time equals 1/200 Hz x 4096 = 20 s.
   When the frequency of the applied sine wave is so low that the time between two samples of the ADC allows more than one conversion per point, multiple conversions are added within the same memory location. So, the conversion rate of the ADC is always as high as possible, in order to perform as many measurements as possible. The actual integration will never be shorter than the specified integration time, and the time needed to complete the specified minimum number of integration cycles (see FRA manual control window).

During conversions, the software checks the overload indicators. As soon as an overload is detected, the measurement is aborted, the gain of the corresponding amplifier is lowered, and the measurement is performed again.

6. After completing the measurement, the data from the memory of the two ADC's are read by the computer. A Fast Fourier Transform method is applied to calculate the frequency spectra of both potential and current. These spectra are used to calculate the in-phase and quadrature components of the impedance. The software allows the user to view the data read from the memory; the 'time domain plot' as well as the FFT processed signal; the 'frequency domain plot'.

For more information about the basics of the approach of this instrument, see:
R.J. Schwall, A.M. Bond, R.J. Loyd, J.G. Larsen and D.E. Smith, Analytical Chemistry, Vol. 49, no.12, October 1977, p.1797-1805 and p.1805-1812.

4.8 Measurements using an Automatic mercury drop electrode

The Autolab instrument supports several mercury drop electrode configurations. The IME or IME663 interface for mercury drop electrode provides an interface. The FRA measurements can be done at a static as well as at a mercury drop electrode.
A new drop is created when "New drop" has been checked on page 2 of the Edit procedure window and the presence of an automatic electrode is indicated in the hardware configuration. In the sequence of events a new drop is created, just after the first conditioning potential, or current stage has finished (if any):

- In the Edit screen called 'Pre-treatment', 'Yes' is specified behind 'New drop'.
- 'Second conditioning time' is greater than zero. This means that a new drop is created at this 'Second conditioning potential', after which the specified conditioning time is included.
- If 'Repeat pre-treatment before every frequency' is 'Yes' then every measurement is performed at a new drop. In case it is 'No', but 'Yes' is specified for 'Repeat pre-treatment before every potential', a new drop is created for each frequency scan at a new dc-potential or dc-current.

4.9 Sequence of measurements in case of synchronised measurements

The sequence of measurements in case of synchronised measurements is as follows:

1. If the duration of the first conditioning potential or current is larger than zero, the first conditioning potential or current is applied.

2. If 'New drop' is checked on Page 2 of the Edit procedure window, New drop signals are generated.

3. If the duration of the second conditioning potential or current is larger than zero, the second conditioning potential or current is applied.

4. If the duration of the third conditioning potential or current is larger than zero, the third conditioning potential or current is applied.

5. The measurement potential or current is applied.

6. The equilibration period starts with the ac-signal applied and the instrument settings are controlled.

7. Immediately perform the measurements without controlling the settings. This assures accurate timed or synchronised measurements, after applying the dc-potential or current.

8. If the measurement is incorrect i.e. an overload occurred or less accurate measurements were recorded, the measurement sequence is repeated.

9. Depending on whether a repeat of the pre-treatment is required, the program continues with point 1 or 5.

4.10 Measurements at open circuit potential

In case the frequency scan is to be measured at open circuit potential (OCP), the equilibration stage is to be used to apply a potential where the measured current is as low as possible.
The OCP, measured with the cell switched off, is applied at the start of the equilibration stage. During this stage, the potential is continuously adjusted to a value where the current is minimal.
In case the pre-treatment is repeated before each frequency, the applied potential may vary from frequency to frequency. This feature is enabled with the option Repeat pre-treatment before every scan or frequency.

The algorithm that minimises the current is as follows:
Ecoarse = 1.5 (in mV)
Efine = .15 (in mV)
Ncount = 15 Number of times Efine is used before return to Ecoarse

E = E_{OCP} (first measured Open circuit potential)
Estep = Ecoarse
Read Current
PreviousCurrent = Current
iTel = 0
Repeat
  E = E + Estep
  Apply E
  Read Current
  if Sign (Current) <> Sign (PreviousCurrent) then Estep = Efine
  if Estep = Efine then iTel = iTel + 1
  if iTel > Ncount then iTel = 0: Estep = Ecoarse
  PreviousCurrent = Current
Until Equilibration Stage is finished

Appendix I FRA Data Files

The following types of files are used by FRA

File	Description	Directory
*.PFR	Experiment parameters	Default procedure directory
*.DFR	Measured data	Default data directory
*.FMA	Project	Default data directory
*.TXT	Analysis results	Default data directory
*.P??	Frequency, Z' and Z"/ File format for EQUIVCRT program (?? = potential no.)	Default data directory
*.C??	Frequency, Y' and Y" (?? = potential no.)	Default data directory
*.F??	Potential, Z' and Z" (?? = frequency no.)	Default data directory
*.E??	Potential, Y', Y" and Cs (?? = frequency no.)	Default data directory
*.MOT	Mott Schottky data	Default data directory
SYSDEF40.INP	System definition parameters	Autolab directory
SYSDEF40.TXT	Description of SYSDEF40.INP	Autolab directory
W_SIN*.*	Signal file for DSG (FRA)	Signals directory
W_SGNL*.*	Signal file for DSG (FRA2)	Signals directory
FRA.INI	FRA user settings	Autolab directory
FRA2CAL.INI	FRA2 calibration data	Autolab directory

Appendix II Bandwidth and Gains

The bandwidth of the current follower depends on which current range is used. In the system definition the highest applicable frequency for each current range is specified. When the autoranging facility is used, i.e. more than one current range is enabled in the Manual control window.
The optimal current range is determined by:

- the dc current, the current should be given an analog output signal within the linear range of the current to voltage converter (± 5 V),
- the cell impedance, the ac output signal should have an amplitude high enough to be measured accurately, but should also be within the linear range,
- the applied frequency, the frequency must be lower than the specified maximum frequency, so within the bandwidth of the current range.

The system default maximum frequency is 15Hz for the 100nA scale, 150Hz for the 1µA, 1500Hz for the 10µA and 10.000Hz for the 100µA. Higher current ranges are not frequency limited. In case you want to change them, please contact Eco Chemie. However, please note that they have been carefully chosen and wrong values can deteriorate measurements.

The allowed gains of the amplifiers are also in the system definition file.
Possible values of the gains range from 0 (gain=1) to 9 (gain=512). The system default for the maximum gain is 128 for all current ranges.
The minimum gain is 8 for all current ranges, except for the highest current range for which the gain is set to 1.

Appendix III Definition of procedure parameters

A.C. mode:
This is the most important measurement parameter. It determines whether the applied ac-signal is a sine with one frequency or whether it is a signal composed of 5 sines over one decade or 15 sines over two decades of frequencies. The multi-sine option is suitable for low frequencies, when the measurement time should be as short as possible.

Base frequency:
The lowest applied frequency in case the multi-sine mode is used. The applied signal is a super imposition the specified base frequency and 4 or 14 higher harmonics.

Cell off after measurement:
When a measurement is completed, the cell can either be switched off or left switched on at a potential or current specified as standby potential.

Comments:
A panel to type in several lines of text.

Current range:
Current range to be used for galvanostatic experiments.

Define potentials w.r.t. OCP:
The potential values specified under ‘Potential’ on page 1 are applied with respect to the open circuit potential which is measured before the impedance measurements are started. If the measurements have to be done at the open circuit potential, the value to be specified is 0.000V. Note that the potentials given under pre-treatment and as stand-by potential are not applied versus the open circuit potential.

Duration of measurement:
The total time the execution of the measurement should last, including the equilibration time, in case a potentiostatic or galvanostatic time scan is made.
Enable internal ac-input of PGSTAT

Enable internal ac-input of PGSTAT:
If external inputs are used, the DSG signal is also applied to the PGSTAT.

End potential or current:
The last potential or current of a potential or current scan. This input is only requested for the potential scan method.

Equilibration threshold level:
If enabled, the Equilibration stage will be aborted after reaching this specified current. The measurements will start as soon as this threshold is exceeded. This option is not available for galvanostatic measurements.

Equilibration time:
Time between applying the dc-potential or dc-current and actual impedance measurement. In case of synchronised measurements, the minimum time is 1 s.

First, second and third conditioning potential or current:
Before the actual ac-impedance measurement, a conditioning potential or current can be applied. When the duration is set to zero, the stage is discarded.

Interval time:
The time between frequency scans of impedance measurements in case a potentiostatic or galvanostatic time scan is made.
The minimum interval time is at least two seconds, but will depend on the ‘minimum cycles to integrate’ and the ‘maximum time to reach steady state’ (see the FRA manual control window). If the interval time is exceeded, a message will be given, but the measurements will continue.

*New drop***:**
If checked, a new mercury drop is created immediately after applying the first conditioning potential. This option is only applicable if an Automatic electrode is selected in the AUTOLAB hardware configuration program. Consult the proper Appendix in case a mercury drop electrode is applied.

Potential or current:
Potential or current at which the measurement has to be performed. This input is only requested for the single potential or current method.

Repeat pre-treatment before every:
The drop down menu appears from which the options 'no', 'frequency' and 'freq. scan' can be selected. The latter option only appears in case potential or current scan is made. 'no' means that the pre-treatment only takes place before the measurements.

Standby potential or current:
The potential or current applied as soon as the measurements have been performed.

Start potential or current:
The first potential or current of a potential or current scan. This input is only requested for the potential scan method.

Step potential or current:
The potential or current increment between two successive measurements. This input is only requested for the potential scan method.

Stirrer on during conditioning:
Switch on the stirrer during the different conditioning stages.

Synchronised measurement:
If checked, the impedance measurement is performed after a waiting period equal to the 'Equilibration time'. This allows measurement at a fixed time after applying the dc-potential or dc-current.
For more information, please read the chapter about the measurement sequence.

Stop equilibrium at threshold
Enable the option to abort the equilibration stage when the Equilibrium threshold level is reached.

Time to wait for OCP:
The time you want to wait for acceptance of the Open Circuit Potential. If this time has expired the program will continue using the OCP measured at that time. If this parameter is 0(zero), the program will not continue, unless the 'Accept' button is pressed. If 0(zero) is specified in a procedure that is used in a project, the program will wait for 1 second and will use the OCP measured at that moment.

Title and Subtitle:
Two lines of text to describe the experiment. These lines are the same as the ones displayed above the plot.

Appendix IV Combination of GPES and FRA

The FRA and GPES programs can be used at the same time. Moreover a FRA project file can be executed from GPES. The command FRA!Start(<"filename">) is available for this purpose.
However, in general it is important to note that both programs share the Autolab instrument and the graphics part of the software. Moreover, both programs require a considerable amount of the system resources. This means that when both programs are active, hardly any system resources are left.

Practical rules are:

- The computer should be equipped with 32 MB RAM
- It is not possible that both programs measure and control the Autolab instrument
- Before the FRA program starts measuring, the ‘sleep mode’ in GPES is automatically switched on. This means that the GPES screen is no longer updated.
- Do not use function keys when both programs are active, because they will cause actions in both programs.
- When a measurement procedure is being executed, user interaction with the programs should be avoided.
- Apart from GPES and FRA no other application should be active.

Appendix V Noise considerations

Some rules for preventing excessive noise are:

- Do not use unshielded cables and connections.
- Place the electrochemical cell as far as possible from electrical appliances.
- Place the cell inside a faraday cage.
- The Differential Electrometer Amplifier increases the noise. Do not use it if it is not required, i.e. a two or three (and not four) electrode cell is used and the dc-current does not exceed approximately 10 to 50 mA.
- Use the high stability mode where possible.

Appendix VI Specifications

	μAutolab type III /FRA2	**Autolab with PGSTAT12**	**Autolab with PGSTAT302N**	**Autolab with PGSTAT100**
maximum output current	± 80 mA	± 250 mA	± 2 A	± 250 mA
maximum output voltage	± 12 V	± 12 V	± 30 V	± 100 V
potentiostat	yes	yes	yes	yes
galvanostat	yes	yes	yes	yes
potential range	± 5 V	± 10 V	± 10 V	± 10 V
applied potential accuracy	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV
applied potential resolution	150 μV	150 μV	150 μV	150 μV
measured potential resolution	300 or 30 μV	300 or 30 μV	300 or 30 μV	300 or 30 μV
current ranges	10 nA to 10 mA in seven ranges	10 nA to 100 mA in eight ranges	10 nA to 1 A in nine ranges	10 nA to 100 mA in eight ranges
applied and measured current accuracy	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range
applied current resolution	0.015% of current range	0.015% of current range	0.015% of current range	0.015% of current range
measured current resolution	0.0003% of current range	0.0003% of current range	0.0003% of current range	0.0003% of current range
- at current range of 10 nA	30 fA	30 fA	30 fA	30 fA
potentiostat bandwidth (1)	500 kHz	500 kHz	>1 MHz	500 kHz
- potentiostat risetime/falltime (1 V step, 10-90%) (1)	1 μs	< 500 ns	< 250 ns (with external source)	< 500 ns
potentiostat modes	high speed/ high stability	high speed/ high stability	high speed/ high stability	high speed/ high stability
input impedance of electrometer	> 100 GΩ//< 8 pF	> 100 GΩ//< 8 pF	> 1 TΩ//< 8 pF	> 100 GΩ//< 8 pF
input bias current @25°C	< 1 pA	< 1 pA	< 1 pA	< 1 pA
bandwidth of electrometer	> 4 MHz	> 4 MHz	> 4 MHz	> 4 MHz
IR-compensation	n.a.	depending on selected range: 0Ω-200Ω at 100 mA range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available	depending on selected range: 0Ω-20Ω at 1 A range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available	depending on selected range: 0Ω-200Ω at 100 mA range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available
- resolution	n.a.	0.025%	0.025%	0.025%
four electrode control	no	yes	yes	yes
front panel meter	no	potential and current	potential and current	potential and current
Analog outputs (BNC connector)	potential and current	potential, current and optionally charge	potential, current and optionally charge	potential, current and optionally charge
control voltage input	no	yes	yes	yes
multichannel option	no	multipleWE option	multipleWE option	no

	µAutolab type III /FRA2	**Autolab with PGSTAT12**	**Autolab with PGSTAT302N**	**Autolab with PGSTAT100**
booster option	no	no	yes	on request BSTR10A only
analog integrator	yes	optionally available	optionally available	optionally available
- time constants	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s
interfacing	USB	USB	USB	USB
A/D converter	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100
auxiliary input channels	1	2	2	2
D/A converter	16-bit three channels	16-bit, four channels (optionally eight)	16-bit, four channels (optionally eight)	16-bit, four channels (optionally eight)
auxiliary output channel	1	1	1	1
digital I/O lines	48	48	48	48
(W x D x H)	26 x 26 x 10 cm^3	52 x 42 x 17 cm^3	51.5 x 41.6 x 16 cm^3	52 x 42 x 17 cm^3
weight	4.2kg / FRA2	18 kg	18 kg	21 kg
power requirements	144 W 100-240 V, 50/60 Hz	247 W 100-240 V, 50/60 Hz	247 W 100-240 V, 50/60 Hz	300 W 100-240 V, 50/60 Hz

Notes: (1) Measured at 1 mA current range, 1 kOhm impedance, high speed mode when applicable.
All specifications at 25°C.

Hardware specifications

FRA modules

• frequency range	0.1 mHz to 50 kHz
• applied amplitude	0.2 mV to 0.35 V(rms) with steps of 0.1 mV (potentiostatic mode) 0.0002 to 0.35 with steps of 0.0001 times applied current range (galvanostatic mode)
• resolution of DSG	1 in 65536 (16 bits)
• output impedance of DSG	50 Ohm
• resolution of dual channel ADC	1 in 4096 (12 bits)
• ADC input ranges	0.01 V to 5 V (10 ranges, software programmable)

FRA2 module

• frequency range	10 µHz to 1 MHz
• applied amplitude	0.2 mV to 0.35 V(rms) with steps of 0.1 mV (potentiostatic mode) 0.0002 to 0.35 with steps of 0.0001 times applied current range (galvanostatic mode)
• resolution of DSG	1 in 65536 (16 bits)
• output impedance of DSG	50 Ohm
• resolution of dual channel ADC	1 in 4096 (12 bits)
• ADC input ranges	0.01 V to 5 V (10 ranges, software programmable)

Software specifications

• maximum number of frequencies * maximum number of dc-potentials or dc-currents	20000 (not checked)
• measurement modes	single sine 5 superimposed sines (within one decade) 15 superimposed sines (within two decades)
• automatic current ranging	optional mode
• 1st, 2nd and 3rd conditioning time	0 - 30000 s
• 1st, 2nd and 3rd conditioning potential	± 10 V
• or conditioning current	± 1 A (PGSTAT12/20/30/100) or ± 50 mA (PGSTAT10)
• wait time before measurement	0 - 30000 s
• stand-by potential	± 10 V
• stand-by current	± 1 A (PGSTAT12/20/30/100) or ± 50 mA (PGSTAT10)
• potential scan measurement	
initial and final potential	± 5 V
• current scan measurement	
initial and final current	± 1 A (PGSTAT12/20/30/100) or ± 50 mA (PGSTAT10)
• time scan measurement	
end time	1 - 30000 s
interval time	1 - 30000 s
integration time	0.1 - 10000 s
• minimum number of cycles to be integrated	1 - 16
• minimum number of cycles to reach steady state	0 - 30000
• maximum time to reach steady state	0 - 30000 s
• With a minimum fraction of cycle	0 - 10
• repeat prepolarisation before each frequency scan	Y/N
• repeat prepolarisation before each frequency	Y/N
• synchronised measurement	Y/N
• cell off after measurement	Y/N
• potentials with respect to open circuit potential	Y/N

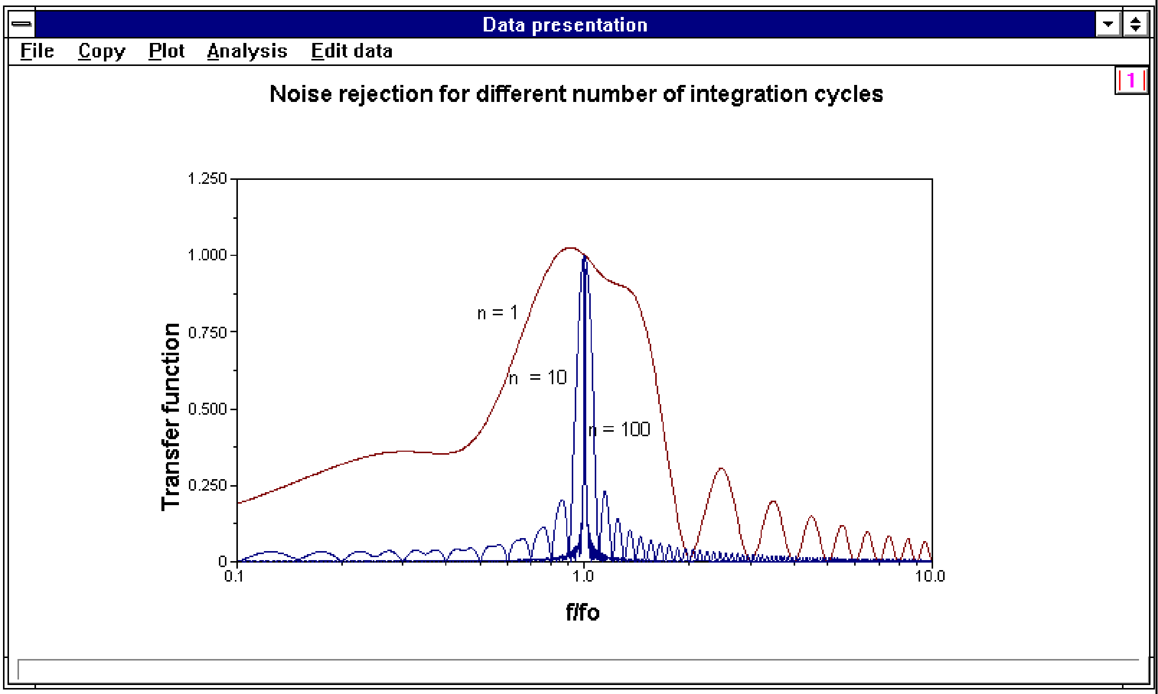
Appendix VII Theoretical considerations on the performance of FRA instrument

The performance of the FRA impedance analyser depends partly on the construction principles and partly on the setup parameters, i.e. the integration time, the number of integration cycles and the time to reach steady state. These parameters can be specified on the FRA manual control window.
In this appendix it is investigated how the measurement results depend on these parameters. Moreover, this appendix can be used to compare the measurement principle of the FRA with other impedance analysers.
All the data presented in this appendix result from numerical simulation.

Effect of integration time on noise rejection

The effect of integration time on noise rejection is determined by numerical simulation. The transfer function of the FRA module as a function of the frequency, normalised with respect to e.g. 1000Hz, for a different number of integrated cycles has been calculated. The transfer function is calculated by performing Fast Fourier Transformation on the signal generated with frequency f. The amplitude found at frequency f_0 gives the transfer function. Frequency f_0 is in fact the frequency at which the impedance should be measured. The transfer function shows the theoretical noise rejection ability.

Fig.22 *Transfer function of the FRA module as a function of the normalised frequency*



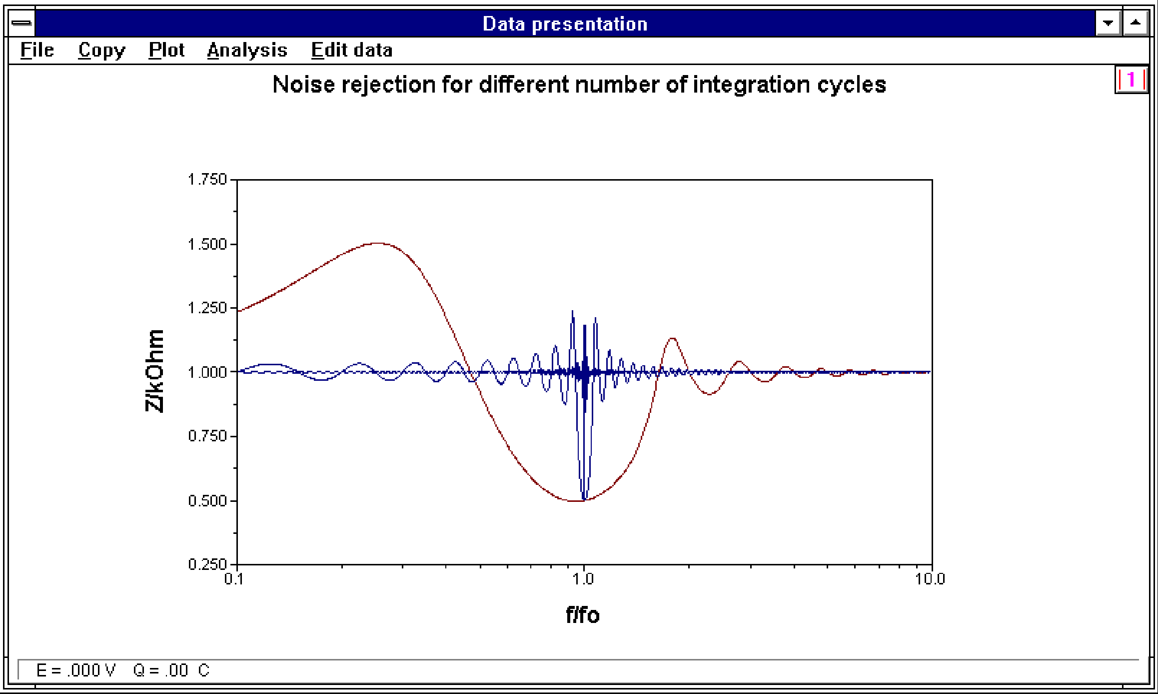
The transfer function, i.e. the impedance normalised with respect to f = f_0, is calculated for a different number of integration cycles. In case of e.g. 100 Hz, an integration time of 0.01 s gives one integration cycle. The default integration time of 1 s gives 100 integration cycles.
The transfer function resembles the calculated curve for a different FRA instrument based on correlation with synchronous reference signals (Ref. Impedance Spectroscopy by J. Ross Macdonald (Ed.), Wiley, New York, 1987).

Conclusion:
It is clearly shown that a larger number of integration cycles, and thus a longer integration time, significantly improves noise rejection.

Effect of noise on impedance measurements

The effect of noise on impedance measurements can also be simulated. This is done by adding noise with frequency f to a signal of interest at frequency f_0. The calculations are done using a sine wave for the potential and the current. Both have the same amplitude and frequency f_0. A sine wave with the same amplitude but different frequency f is superimposed on the potential and current perturbations.
The simulation is performed assuming a current range of 1 mA. The perfect impedance should therefore be 1.000 kOhm and the phase shift 0. When the frequency of the noise is f_0 as well, the amplitude of the current signal will be doubled. This yields an impedance of 500 ohm.

Fig. 23 *Effect of 'noise' with frequency f on the impedance measured at frequency f_0. The 'noise' amplitude is equal to the amplitude of the frequency of interest f*

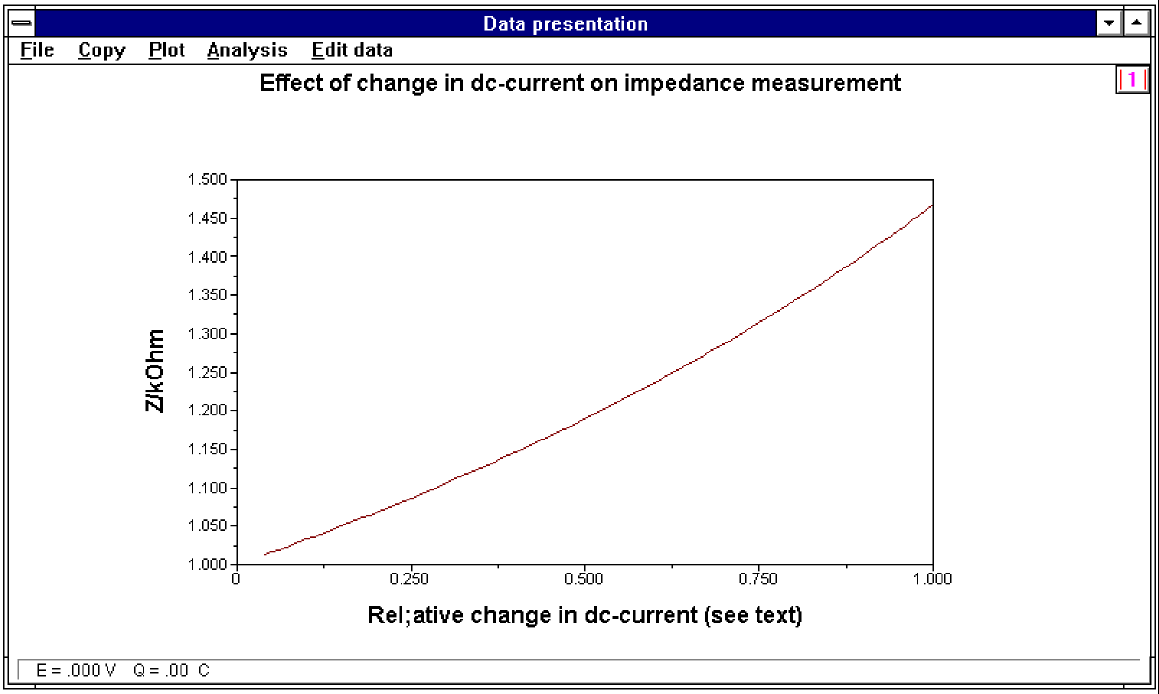


Conclusion:
A longer integration time will improve the result of the measurements.

Effect of non-stationary dc-current

Impedance measurements with a non-stationary dc-current are simulated by performing FFT calculations on a pure sine wave for the potential and sine wave with super-imposed dc-slope for the current.
The error in the calculated impedance Z as a function of the dc-component of the current has been investigated. In the simulation calculation it is assumed that the current range is 1 mA and the 'real' impedance is 1.000 ohm.

Fig. 24 *Effect of non-stationary dc-current on calculated impedance*



x is the relative change in dc-current, x= 0 corresponds to a perfect stationary current, for x= 1 the change in dc-level is equal to the peak amplitude after exactly one period of the sine.

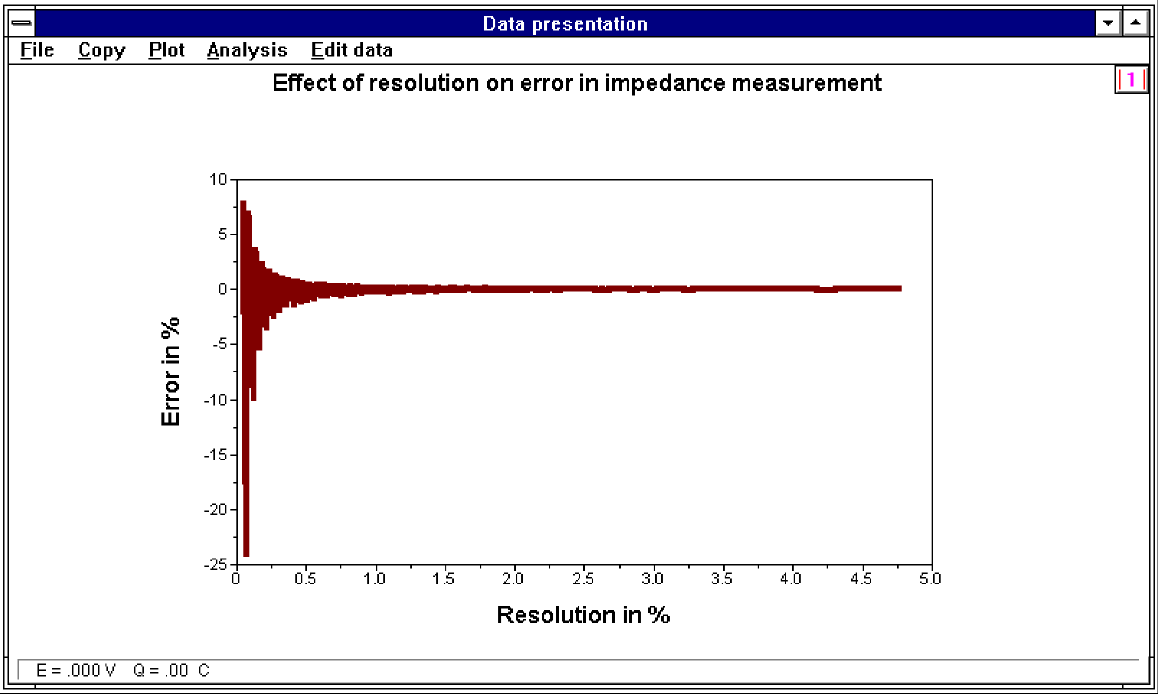
It shows that significant errors are found at low values of x. A small dc-ramp will give a significant error.

Conclusion:
Impedance measurements should be done under stationary conditions.
The dc-current for potentiostatic measurements should be constant and for galvanostatic measurements the dc-potential should not vary.

Effect of measurement resolution

The amplitude of the measured potential and current signals depends on the output of the potentiostat/galvanostat. The current range determines the amplitude for the current signal. The setting of the amplifiers of the FRA also determines the amplitude of the final measurement. The recorded amplitudes are shown in the 'FRA control' window, as well as in the 'Oscilloscope' windows. The maximum resolution is 100 %, however, a much lower amplitude is often found.
The effect of varying amplitude or resolution of the current signal on the calculated impedance has been investigated.

Fig. 25 *Percentage error in the impedance as a function of the resolution of the current measurement. The resolution is given in percentage.*



The curve is valid for a resolution of the potential of 50 %, normally found at an amplitude of 15 mV (rms). A resolution of 0.5 % is observed for a measurement of an impedance of 100.000 ohm, when the current range is 1 mA.

Conclusion:

A minimum resolution of 0.5% is required if the maximum impedance error should be better than 1%. A higher accuracy than 0.2% requires a minimum resolution of 1%.

Appendix VIII Fit and Simulation

The Fit and Simulation option in the program allows you to simulate responses of equivalent circuit and to fit the circuit parameters to the measured data, using the non-linear least squares method. The equivalent circuits can be defined by the user (using Circuit Description Code). It is possible to define elements with fixed values as well as constraints for values of fitted parameters. This option is based on the work of Dr. B.A. Boukamp as first published in Solid State Ionics, 20 (1986) 31-44 and coded in the program EQUIVCRT by the same author.

Circuit description code (cdc)

This is a code used for defining equivalent circuits. It consists of letters representing circuit elements and round and square brackets representing parallel or serial arrangement of elements. The table below shows the meaning of the letters:

letter	**element**	**letter**	**element**
R	resistance	Q	constant phase element (CPE)
C	capacitance	T	hyperbolic tangent element
L	inductance	O	hyperbolic cotangent element
W	Warburg impedance	G	Gerischer impedance

Square brackets mean that the elements enclosed in the brackets are arranged in series. Elements enclosed in round brackets are arranged in parallel. In order to simplify the notation it is assumed, that if CDC starts with letter instead of a bracket, the elements are arranged in series. Therefore, [R(CW)] and R(CW) are equivalent.
A number of examples of CDC together with the corresponding equivalent circuits are shown:

RCL

(RCL)

R(RQ)

R(C[RW])

R(C[R(C[RW])])Q

Dispersion functions for elements

The table below defines the dispersion functions for the elements in both impedance and admittance representation ($\omega = 2\pi f$).

CDC	element	impedance	admittance	parameters
R	resistance	R	$1/R$	R
C	capacitance	$-j/(\omega C)$	$j\omega C$	C
L	inductance	jwL	$-j/(\omega L)$	L
W	Warburg impedance	$1/\left(Y_0\sqrt{jw}\right)$	$Y_0\sqrt{j\omega}$	Y_0
Q	constant phase element	$1/\left(Y_0 jw\right)^n$	$\left(Y_0 jw\right)^n$	Y_0, n
T	hyperbolic tangent element	$\left(Y_0\sqrt{jw}\right)^{-1}\coth\left(B\sqrt{jw}\right)$	$\left(Y_0\sqrt{jw}\right)\tanh\left(B\sqrt{jw}\right)$	Y_0, B
O	hyperbolic cotangent element	$\left(Y_0\sqrt{jw}\right)^{-1}\tanh\left(B\sqrt{jw}\right)$	$\left(Y_0\sqrt{jw}\right)\coth\left(B\sqrt{jw}\right)$	Y_0, B
G	Gerischer impedance	$\left(Y_0\right)^{-1}/\sqrt{K_a + j\omega}$	$Y_0\sqrt{K_a + j\omega}$	Y_0, K_a

(Please note that the definition of the Q element differs from the EQUIVCRT program of Dr. B.A. Boukamp)

Fit and simulation window

When the Fit and Simulation window is opened, the settings are similar to the previously closed window. The window has a number of drop-down menus and a panel for equivalent circuit description (CDC) located at the top. A list of parameters of CDC elements and a panel for parameter editing are located at the middle of the window. The Fit panel and buttons for starting and stopping fit and simulation are located at the bottom of the window. The functions of these components are described below.

File menu

Load circuit

Loads the previously saved user-defined equivalent circuit from the disk.

Save circuit

Saves the currently used equivalent circuit to the disk.,

Copy to work data

The most recent calculated data, which result either from a simulation or from the fit, are turned into the so-called ‘work data’ and thus remain available after closing the Fit and simulation window. Normally, the fitted and simulated data sets are erased. The work data can be stored on disk using the File option on the Data presentation window.

Close

Closes the window and returns the focus back to the Data presentation window. The simulated and fitted data sets are lost, unless Copy to work data is used. Results of fitting are printed in the Analysis results window.

Edit menu

Circuit Description

Opens a window for entering or editing the Circuit Description Code (CDC). The CDC can be modified and also standard circuits can be inserted using the "Insert circuit" command in the toolbar. If the code contains syntax errors (like bracket mismatch), it will not be accepted. The Help button displays a list of available elements and shows examples of circuits and their CDC's.

Fit control parameters

Opens a window in which fitting-related parameters, like convergence criteria, iteration limit and the type of fit can be set:

- Maximum change in χ^2 (scaled): this is one of the convergence criteria. Fitting will not be finished until the absolute change in the chi-square parameter (including weight factors) will be lower than this value. The default value is 0.001.
- Maximum number of iterations: fitting will always stop if this number is exceeded. The default is 50.
- Number of iterations per fitting step: the fitting step, finished by displaying a new data set and update of the parameter set on the screen, can consist of a single or multiple iterations. This option is useful if the program is running on a relatively slow computer because update of the screen takes some time, so increasing the number of iterations per fitting step can result in a slight improvement of fitting speed.
- Maximum number of iterations giving no improvement: if during the fit there is no change in the specified number of consecutive iterations χ^2 value and other convergence criteria are still not satisfied, the program stops with an appropriate warning. It usually suggests that the model is not appropriate - no further improvement can be obtained while the χ^2 value is still too high. The recommended action is to change the CDC or - if the fitted curve differs very much from the examined data set - to try other starting values for fitted parameters.
- Use weighted fit: if this box is checked, each point is multiplied with a weight factor equal to the inverse of the square of the impedance modules,
i.e. $w=1/((Z')^2 +(Z'')^2)$. If this box is empty, weight factors for all points are equal to the inverse of square root of mean impedance modules.

It is important to note that in addition to the explicit convergence criteria (i.e., max. change in χ^2) there is an implicit criterion that the change in the parameter value during one iteration should not exceed 0.5%.

Options menu

The following items are available in this menu:

Select frequencies

Using this option one can select the frequencies used in simulation or fitting.

Use constraints

The fitting procedure uses internal (default) constraints for maximum and minimum values of parameters. If these limits should be changed, the Use constraints option should be activated. The limits can then be set manually in the parameter editing panel in the middle part of the Fit and Simulation window.

Show covariance matrix

This option displays a covariance matrix after a successful fit has been completed. In the covariance matrix the diagonal elements are unity, and off-diagonal terms are a measure of covariance (interdependence) of the parameters. In general, the off-diagonal values should be small compared to diagonal elements. If large off-diagonal elements are present, it suggests that the parameter corresponding to the row is not independent from the parameter corresponding to the column in the matrix. Fitting does not give correct results if parameters are not independent.
The absolute value of elements of the covariance matrix depend on the way the weighing factors are defined.

Show residual plot

Displays residual plot (i.e., difference between the fitted and the measured data) for both real and the imaginary part of impedance/admittance.

Circuit description panel

This panel displays the current Circuit Description Code (CDC). Each circuit element consist of a character describing its type, and a digit to distinguish between elements of the same type. To enter a new CDC or to modify the existing one, it is necessary to click the panel, to use Circuit description option of the Edit menu, or to press control-C. The Edit circuit description window appears, which allows to modify the CDC, or paste one of standard CDC. In this sub-window only letters, standing for elements, and the brackets should be entered - the digits are added automatically when the sub-window is closed. The Help button gives an overview of the codes and bracket uses. The Insert circuit menu at the top of the sub-window allows you to insert complete circuits.

List of CDC parameters

The list at the middle part of the Fit and Simulation window shows symbols of elements (as in the CDC string above), accompanied by current values of their parameters, the error estimate (appears after the successful fit) and the information whether the parameter is fitted or kept fixed. When CDC is modified, the values of element parameters are defaults used as start values.
If an element from the list is selected, its parameters and settings can be edited in the parameter editing panel directly below the element list.

Panel for parameters editing

In this panel the full description of the element selected in the list above is available and can be edited. The values of parameters can be changed, and the parameter can be made fitable or fixed. If the ‘Use constraints’ option (Option menu) is selected, the limiting values for the parameters can be adjusted (otherwise, internal defaults for maximal and minimal values are used).

Fit panel

This panel allows to choose whether fitting and simulation should use impedance or admittance representation of the data. In the lower part of the panel the status of fitting is displayed (iteration number, fit finish, error indication) together with the value of χ^2.

Fit/Simulation switch

Using this switch one can choose between the fitting function and the simulation function. When simulation is chosen, the buttons Simulate and Close will appear. When fitting is chosen, three buttons are available: Fit, Stop Fit and Close.

Using fit and simulation

Fitting of equivalent circuit to the measured data

1. Load data.
2. Choose Fit and Simulation from Analysis menu (Data presentation window).
3. Make sure that the switch Fit/Simulation (bottom part of the window) is in Fit position.
4. Load a previously saved Circuit Description Code (Load circuit option from File menu, Fit and Simulation window) or click the Circuit Description panel to open a sub-window to enter the CDC manually.
5. Either type in the circuit code, or insert one of the standard predefined circuits. The predefined circuit is inserted at the cursor position, so they can be combined with user-defined circuits.
6. Press OK in the sub-window to return to the Fit and Simulation window. The CDC is now displayed in the Circuit description panel, each element having an ordinal number added to the element's symbol.
7. Select elements (one by one) in the element list below the Circuit description panel. Enter the starting value of the parameter (or leave the default) and choose whether the parameter should be fitted or not. If special constraints for element values are necessary, change the minimum and maximum allowed values of parameters (this may require selecting option Use constraints from Option menu located in Fit and Simulation window).
8. Choose whether the fitting should take place in impedance or admittance representation. Element parameters are defined independently of the actual representation used.
9. Press the Fit button.
10. If the fit is not satisfactory, press the Fit button again (you can also increase the maximum number of iterations selecting Fit control parameters in Edit menu of Fit and Simulation window) in order to continue with fitting.
11. You may wish to change the fit settings (Edit menu, Fit and Simulation window) to fine-tune the fitting process. Or select points for fit (Select frequencies in Option menu, Fit and Simulation window).
12. Fit results are automatically copied to Analysis window.
13. Should an error message appear, consult the section on error conditions.

14. If the fit is finished, you may want to save the used CDC. To do this, use the ‘Save circuit’ option from the File menu (Fit and Simulation window)
15. If you want to use or save fitted data set, choose the option Copy to work data (File menu, Fit and Simulation window) to replace the actual data set with the fitted data.
16. Finish fitting by pressing Close button.

Simulation of equivalent circuit response

1. Load the data file FRADEMO from the \AUTOLAB\TESTDATA directory
2. Choose Fit and Simulation from Analysis menu (Data presentation window).
3. Make sure that the switch Fit/Simulation (bottom part of the window) is in Simulation position.
4. Open the File menu on the Fit and Simulation window. Load the Circuit Description Code file FRADEMO from the \AUTOLAB\TESTDATA directory. This circuit will fit rather well.
5. Click the Circuit Description panel to open a sub-window to enter the CDC manually.
6. Either type in the circuit code, or insert one of standard predefined circuits. The predefined circuit is inserted at the cursor position, so they can be combined with user-defined circuits.
7. Press OK in the sub-window to return to the Fit and Simulation window. The CDC is now displayed in the Circuit description panel, each element having an ordinal number added to the element's symbol.
8. Select elements (one by one) in the element list appearing below the Circuit description panel. Enter the value of the parameter.
9. Choose whether the simulation should take place in impedance or admittance representation (the displayed result is always in the same representation as the displayed data set). Element parameters are defined independently of the actual representation used.
10. Press Simulate button.
11. If the simulation is finished, you may want to save the used CDC. To do this, use option Save circuit option from File menu (Fit and Simulation window)
12. If you want to use or save simulation results, choose option Copy to work data (File menu, Fit and Simulation window) to replace the actual data set with the simulated data.
13. Finish simulation by pressing Close button.

Fit and simulation error messages

error -1: "xxxx"
Internal error of the fit and simulation module. String "xxxx" contains specific information about the problem. Please report “xxxx” and the circumstances under which this error appeared.

error 1: Not enough memory
There is not enough memory to carry out fit or simulation. Try to free some memory by closing other applications.

error 2: Overflow in numerical calculations
Value of parameters are so large or so small that overflow appears in numerical calculations. Check the values of element parameters and change them (or use constraints) to more moderate values.

error 51: GAUSSJ: Singular Matrix-1
Two or more parameters are dependent or nearly dependent. This error can also happen if some parameters have extreme values. Consider use of another CDC, change parameters to more moderated values or use constraints.

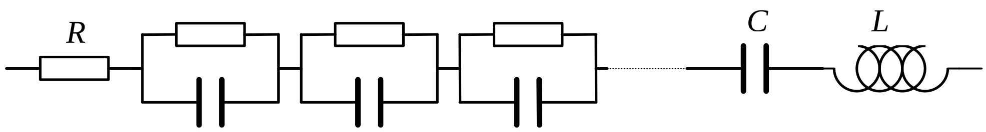
error 51: GAUSSJ: Singular Matrix-2
Two or more parameters are dependent or nearly dependent. This error can also occur if some parameters have extreme values. Consider using another CDC, change parameters to more moderated values or use constraints.

error 60: error in CDC
The entered CDC is not correct.

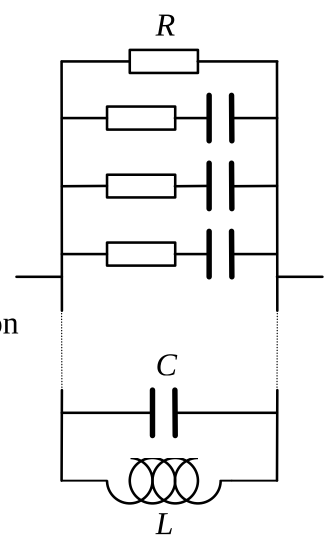
Appendix IX Kramers-Kronig test

The Kramers-Kronig test

The Kramers-Kronig (K-K) test can be used to check whether the measured system is stable in time and linear. Stability and linearity are a prerequisite for fitting equivalent circuits. If the system changes in time the data points measured on the beginning of the experiment do not agree with those measured at the end of the experiment. Stability problems are most likely to be observed in low frequency range.
In fact, the K-K test checks whether the measured data comply with the assumptions of Kramers-Kronig transformation. These assumptions are: (1) the response is only related to the excitation signal, (2) the response is linear (or the perturbation is small, e.g. <10 mV, for non-linear systems), (3) the system does not change with time and (4) the system is finite for all values of ω, including zero and infinity. If the investigated system changes with time due to e.g. ageing, temperature change, non-equilibrium initial state etc., the test fails.
The idea of K-K test is based on fitting a special model circuit (which always satisfies K-K assumptions) to the measured data points. If the measured data set can be represented with this circuit, then the data set should also satisfy Kramers-Kronig assumptions. The special circuit used in the test is a series of RC circuits (for impedance representation) or a ladder of serial RC arrangements (for admittance representation). These circuits are shown below:



circuit for impedance representation



circuit for admittance representation

By default, the number of RC circuits or RC serial arrangements is equal to the number of data points. If there is a chance that the measured signal was very noisy, the number of circuits may be reduced to avoid overfitting and - consequently - including the noise in the model.
The ‘Tau-range factor’ is a special parameter which is default set to 1. It is related to the distribution of RC-times in the circuits, which are kept fixed during the fit. In the ‘K-K’ fit is only done on the R-value of each RC-circuit. The parameter should not be modified unless the theory, as fully described in the article by
B.A. Boukamp, J. Electrochem. Soc. 142, 1885 (1995), is understood.
The result of the test is the value of pseudo χ^2, the sum of squares of the relative residuals. In each case the χ^2 for the real and the imaginary part is reported (overall χ^2 is a sum of real and imaginary χ^2). Large χ^2 value means bad fit, small value - good fit. What is actually large and small depends on the number and the value of data points. As a rule of thumb, values lower than 10^{-6} usually mean an excellent fit, reasonable between 10^{-5} and 10^{-6} , marginal between 10^{-4} and 10^{-5} and bad for even higher values. Moreover, the residuals should be small and randomly distributed around zero.
The test can be carried out on real part, imaginary part or both part of admittance/impedance (complex fit). In the case of fit on one part only, the second part of the measured data set is generated using Kramers-Kronig transformation (on the assumption that the system obeys K-K criteria) and then χ^2 for the second part is computed.

Definitions of pseudo χ^2

$$\chi_{ps}^2 = \sum_{i=1}^{N} \frac{\left[Z_{re,i} - Z_{re}(\omega_i)\right]^2 + \left[Z_{im,i} - Z_{im}(\omega_i)\right]^2}{\left|Z_{(\omega_i)}\right|^2}$$

$$\chi_{re}^2 = \sum_{i=1}^{N} \frac{\left[Z_{re,i} - Z_{re}(\omega_i)\right]^2}{\left|Z(\omega_i)\right|^2} \qquad \chi_{im}^2 = \sum_{i=1}^{N} \frac{\left[Z_{im,i} - Z_{im}(\omega_i)\right]^2}{\left|Z(\omega_i)\right|^2}$$

$Z_{re,i}$ and $Z_{im,i}$ are the experimental data.
$Z_{re(\omega i)}$ and $Z_{im(\omega i)}$ are the fitted, calculated values.
In addition to χ^2, the serial or parallel (depending on representation) R, L and C values are computed (see circuits). These values do not have any special meaning and they simply belong to the set of results of K-K test. In particular, they should not be associated with any serial or parallel elements present in the system or its equivalent circuit representation.
The detailed discussion of the Kramers-Kronig test, the theory underlying the choice of parameters, and a refined interpretation of the outcomes can be found in the previously mentioned article of Dr. B.A. Boukamp. It is advised to read this article before this option is used.

Using the Kramers-Kronig test

1. Load the data file FRADEMO from the \AUTOLAB\TESTDATA directory.
2. From the Analysis menu (Data presentation window) select Kramers-Kronig test.
3. Choose whether impedance or admittance representation of the tested data should be used.
4. Modify the number of subcircuits if necessary (default number of subcircuits is equal to the number of data points).
5. If necessary, change the number of frequencies per decade using the extension factor (default=1, i.e., the number of frequencies per decade is the same as in the measured data).
6. Choose the type of the test: complex, real or imaginary.
7. Press Start test button.
8. To leave the window, press Close button.

Appendix X Hydrodynamic Impedance Measurements

Autolab instruments equipped with the FRA2 module can be used for hydrodynamic impedance measurements.
The required external connections to the BNC connectors at the front panel of the FRA2 module are:
- 'signal out' to the input of the controller of the rotating disk electrode (RDE)
- 'Y' to the output of the controller of the RDE
- 'X' to the current output marked ‘Iout’ at the rear of Autolab

These connections have to be made using shielded BNC cables.

The 'signal out' of the FRA2 module is used to modulate the rotational speed of the RDE.

The impedance analyser part of the FRA2 measures the signal from the RDE controller and the current intensity from the potentiostat/galvanostat.

When signals coming from the X and Y external inputs on the front panel have to be measured, this can be specified in the FRA manual control window. The check box 'Use external inputs' in this window must be checked.

The message 'External inputs are used!' appears after the START button has been pressed.

Index