RelaxIS 3

Impedance Spectrum Analysis

USER'S MANUAL

Exclusively distributed by

rhd instruments
flexible cell solutions

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PREFACE

Thank you for using RelaxIS!

RelaxIS is a rich software suite that combines many tools used for the evaluation of spectra measured in Impedance Spectroscopy experiments. In RelaxIS, you can organize and evaluate your measurement results using powerful fitting algorithms with models of your choice. Furthermore, RelaxIS also offers advanced tools that allow further evaluation of the results, as well as exporting and reporting functionalities to allow the presentation of your findings.

This manual first shows the installation of RelaxIS. It then continues with an explanation of the main user interface and the basic data structure.

The manual then details aspects of the presentation layer, investigation of data quality, main fitting routines you can use to model your data and how you can investigate the quality of the results.

Afterwards, advanced tools for the further evaluation, presentation of data and automation of the evaluations are introduced.

We wish you a good time working with RelaxIS!

TABLE OF CONTENTS

1 INSTALLATION OF RELAXIS

1.1 INSTALLATION OF RELAXIS WITH THE INSTALLER

RelaxIS 3 requires the .NET Framework 4.7.2 or later and can therefore only be used on Microsoft Windows 7 SP1 (or newer).

⚠ Please note

As of December 31st, 2021 support for Windows 7, 8 and 8.1 has ceased. While RelaxIS may still function, it is not supported and can't be guaranteed. We recommend updating to Windows 10 to continue using new versions.

Please open the installer by double-clicking the **RelaxIS_3_0_xx_xxInstall.exe**. The location of the installer on your system depends on your chosen distribution system. If you have received a CD or flash-drive, the installer can also be started by using the Autostart feature of Microsoft Windows.

To use RelaxIS, you need to have the Microsoft .NET Framework 4.7.2 or later installed on your system. The installer checks if the framework is installed on your system. If it is not installed properly you will be prompted to download the installer from the web. If you have received a flash-drive or CD, you can also find the .NET Framework installer in the folder

CD-Drive:\.NET Framework\

If you received your copy of RelaxIS without the .NET Framework Installer please visit

https://dotnet.microsoft.com/download/dotnet-framework/net48

and download the .NET Framework Runtime installer. Run it and follow the instructions to install the .NET Framework. You can install the .NET Framework 4.8, as it is downwards compatible.

After the .NET Framework is installed, please perform the following steps in the RelaxIS installer:

1. Accept the RelaxIS program license

2. Select an installation path on your hard disk.
3. Choose if shortcuts for RelaxIS should be created.
4. Choose if you want to associate .EIS3 files (RelaxIS 3 project files) with RelaxIS. This allows you to open .EIS3 files with RelaxIS by double-clicking on them.
5. Begin the installation process

While installing RelaxIS, you will be prompted with the **CodeMeter Runtime** installer. This runtime is required for the hardware Dongle you received with RelaxIS to function properly. You can find further information in section 1.5. Please follow the installer's instructions, using the default settings to install the runtime. Once finished, the RelaxIS installation will continue.

Finally, you can either directly launch RelaxIS from the installer or use the shortcuts created in the Start Menu or on the Desktop.

1.2 RelaxIS With Online Access

If you have received account information for using RelaxIS with an online license (e.g. a Trial Version), please make sure that "Setup for Online Account" is selected in the feature selection during the installation.

If you have not received a link to download the installer, please contact rhd instruments.

After the installation, please launch RelaxIS from the installer or use the shortcuts created in the Start Menu or on the Desktop.

During start-up, you will be prompted for your account details. Please enter them exactly as received and click on the **Connect** button. This will start a client software, that will connect to the rhd instruments license server to validate and access the license.

RelaxIS should now start automatically. If the connection is successful, but RelaxIS does not start, please click **Retry**.

If you cannot start RelaxIS, please check

https://www.rhd-instruments.de/relaxis-online-guide

for further information and trouble-shooting instructions.

Here, note especially to run the tests provided by the trial client software. Find the trial client in the notification area (systray) and double-click the icon to show the window. Click Advanced → Run Tests. Please provide the test log to rhd instruments.

⚠ Please note

If RelaxIS is **very slow to start-up, or it takes a long time for functions to work**, it may be caused by high latency or slow speed of your network. RelaxIS needs to communicate with its license server multiple times, leading to delays.
For high latency, RelaxIS may take several minutes to start up.
We understand, that this is not really usable. If you experience poor performance, please contact rhd instruments. We may be able to provide you with a hardware dongle or custom solution, which allows you to use RelaxIS locally. **This applies to both the full version as well as the trial version!**

1.3 Portable Version of RelaxIS

In many restricted environments, a normal installation of RelaxIS is hardly possible. For this reason, a portable version of RelaxIS is also provided.

⚠ Please note

The portable version of RelaxIS is discontinued after version 3.0.15.

This version differs from the normal version in some ways:

- No installer is provided. The files need to be extracted from a .ZIP-archive to the desired program location by hand.
- You cannot update the program via the implemented update mechanism.
    - You can check online for a new version

    - You then need to contact the rhd instruments for more information on how to obtain the new version.
- All required user files are created directly in the directory that RelaxIS was extracted to. Therefore, **permanent read/write access** to the install directory must be provided (e.g. don't place the folder in the *Programs* directory, but in a directory like *C:\RelaxIS\Portable*)
- All settings are shared between all users of the particular installation. In order to use multiple settings, you need to copy RelaxIS Portable into multiple directories.
- O**nline access**, as described in 1.2, should work. If you experience any problems, please contact rhd instruments.

To install the portable version please follow these steps:

1. Open the installation medium in the Windows Explorer and locate the "RelaxIS Portable" directory.
2. Find the .ZIP file in this folder.
3. Use an extraction method of your choice, such as the one integrated into the Windows Explorer to extract the contents of the archive to a location of your choice.
4. Navigate to the extraction destination.
5. Start RelaxIS Portable by double-clicking "RelaxIS.exe".
6. Optional: Create a Desktop-shortcut by right-clicking "RelaxIS.exe" and choosing "Send to→Desktop (create shortcut)".

1.4 Possible Issues

- **Administrator privileges** are required for the installation. You may need to contact your system administrator if you do not have the necessary privileges on your user account.

⚠ Please note

If you experience any problems please check the following steps:

- Are any files or directories marked as read-only?
  - If so, unmark the read-only attribute.
  - Do you have unlimited access to the folder you copied RelaxIS to? If not, please move RelaxIS Portable to another location.
- Is it possible to read/write to the Windows registry (Current user)?
  - If not, please contact your system administrator for help.
- Are you using RelaxIS from a shared network folder?
  - It is possible to use a network-wide implementation of the Dongle.
  - Please contact rhd instruments for further details.

1.5 THE *CODEMETER* DONGLE

In order to use RelaxIS you need to connect the **CodeMeter Dongle** that was provided by rhd instruments to a free USB-Port on your computer. The CodeMeter Dongle is a product of the Wibu Systems AG and is used as a licensing tool for RelaxIS. In order for the Dongle to work, the **CodeMeter Runtime** must be running on your computer. The RelaxIS installer automatically installs this necessary, lightweight software. In case of the Portable version additional steps may be necessary (please see below in section 1.5.3). You can find further information about the CodeMeter system at http://www.wibu.com. You can also download additional software that allows more control and management services for your Dongle.

On every program start RelaxIS checks if the correct Dongle is connected to the computer, or *via* the online access. If the Dongle was not found, you will not be able to run RelaxIS or the Circuit Simulator.

⚠ Please note

If the Dongle is not accessible, RelaxIS ceases to function. Usually it is possible to resume the session by reconnecting the Dongle and clicking *Retry* in the warning dialog.
In some cases, e.g. after resuming Windows from Standby, or Hibernation it may **take up to a minute** for the warning dialog to appear, especially when an online license is used. Please be patient.
In rare cases you may experience problems, which cause RelaxIS to freeze permanently. **Please make sure to save your work frequently to avoid data loss.**

1.5.1 Upgrading the RelaxIS License

In order to upgrade your RelaxIS license from, for example, the trial version to the full version, it is not necessary to physically alter the Dongle you are already using. Usually rhd instruments will provide you with an update file that can be used by the **rhd instruments License Manager** to upgrade your Dongle.

The License Manager can be started from the Windows Start menu.

If you have already received the upgrade file (.WibuCmRaU) please perform the following steps to upgrade your Dongle:

1. Make sure the CodeMeter Dongle is correctly plugged into your computer.
2. Save the upgrade file you received on your computer's hard drive.
3. Open the rhd instruments License Manager.
4. Under the heading "Activate a new license" click the "…"-button and select the upgrade file.
5. Click the "Activate"-button.

The upgrade included in the upgrade file is then performed on your Dongle and you will be able to use the newly activated features immediately.

1.5.2 Requesting a License Upgrade

In some cases, rhd instruments will ask you for a so-called Context File before an upgrade can be provided for your Dongle. This Context File (.WibuCmRaC) contains information needed to create the upgrade file. The Context File can be easily created using the **rhd instruments License Manager**.

The License Manager can be started from the Windows Start menu.

To create a context file please perform the following steps:

1. Make sure the CodeMeter Dongle is correctly plugged into your computer.
2. Open the rhd instruments License Manager.
3. Under the heading “Create a license request” click the “…”-button and select the path where you wish to create the Context File.
4. Click the “Create”-button.
5. You will find a new file at the specified location, called “CmDongleUpdate20140423_0001.WibuCmRaC” or similar.
6. Send this file to rhd instruments to receive your Dongle upgrade file.

To upgrade your license afterwards please follow the steps explained above in chapter 1.5.1.

1.5.3 Special Notes for the Portable Version

In order for the portable version of RelaxIS to function properly the **CodeMeter service** needs to run on your system. Usually, this service is installed as a Windows service together with RelaxIS. However, since the portable version does not require an installer this is not the case here. The service should nevertheless be automatically started each time you launch RelaxIS. In some cases, this fails and **RelaxIS will prohibit the use of the software because it can’t properly communicate with the hardware Dongle**. In this case it is necessary to start the service manually. This can be done by manually launching the file “CodeMeter.exe” in the RelaxIS Portable directory. The

CodeMeter Runtime runs silently in the background and RelaxIS should start afterwards.

In order to avoid the manual launch of “CodeMeter.exe” after every reboot you can add a shortcut to the Windows Autostart folder. To do so please follow these steps:

1. Open the RelaxIS Portable directory in the Windows Explorer.
2. Right-click on the “CodeMeter.exe” and select “Create shortcut”
3. Right-click on the newly created shortcut and select “Copy”
4. Press WindowsKey+R or select “Run…” from the Start menu.
5. Type in %AppData% and press OK.
6. In the folder that is opened navigate to Microsoft\Windows\Start Menu\Programs\Startup (note that this folder may be called differently depending on your Windows localization)
7. Right-click in the explorer window and select “Paste”

Now the CodeMeter Runtime will be started automatically each time you start Windows.

2 IMPORTANT NOTES FOR USERS OF RELAXIS 2.X

RelaxIS 3 contains practically all functions of RelaxIS 2.x, sometimes however in slightly modified form. Some functions have changed as well.

Most importantly, the file format that RelaxIS data is saved in has changed. **Older .EIS files can not directly be loaded in RelaxIS**. They can however be easily converted to the new .EIS3 format. In RelaxIS 3 open the **File** menu in the top-left corner and select **Convert .EIS (2.0) files**. In the dialog click the **Select**… button and choose any .EIS files you wish to convert. Click the **Convert** button. RelaxIS will convert the files and place new .EIS3 files in the same directory as the source .EIS file.

Further important changes or redesigns in regard to RelaxIS 2.x are:

- **Arrhenius/VFT-Fits** are incorporated in the Further Result Evaluations functionality (see section 0).
- The **Circuit Element Designer** is replaced with plugins created using the RelaxIS SDK (see section 22). Existing user-created elements need to be redone in the new format.
- The **RC- and Cole-Cole-wizards** are currently not included but will be added in further patches (wizards can now also be created by yourself using the RelaxIS SDK).
- **Area** and **Thickness** parameters are now saved individually per spectrum and are used more extensively.
- The definitions (formulas) for the **Warburg Open** (Wo) and **Warburg Short** (Ws) circuit elements have changed. You can find the updated formulas in the appendices. The changes mean that you cannot directly compare parameter values for Wo- and Ws-elements between RelaxIS 2 and RelaxIS 3.

3 Behavior in Case of Program Crashes

On rare occasions RelaxIS might encounter a problem that necessitates a program restart. These problems are called *unhandled exceptions* because they occur at a point in the program and in a way, that was not anticipated during development.

After such a failure RelaxIS is in an **undefined state** because the program did not continue to run to a defined point and could have left program memory in an intermediary state which effects other parts of RelaxIS. Therefore, the correct functioning of other functions or calculations in future actions can not be foreseen. Hence, continuing using RelaxIS from such an undefined state can lead to a variety of obvious or hidden problems from wrong calculation results to data corruption when the current data is written back into the EIS3 database.

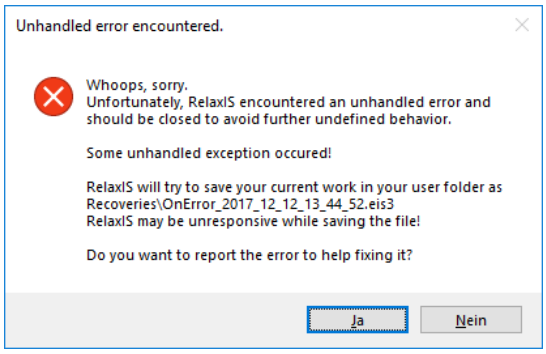
Up to version 3.0.7 the policy of RelaxIS when an unhandled exception occured was therefore to

1. Try to create a backup save of the current data in the UserData\Recoveries folder
2. Allow the user to send a bug report
3. Force an immediate shutdown of RelaxIS

From version 3.0.7 onwards this behavior is being changed to

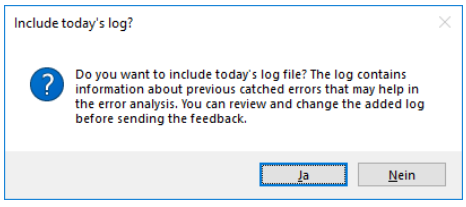
1. Create a backup save of the current data in the UserData\Recoveries folder
2. Allow the user to send a bug report
3. **Give the user the option to either shutdown RelaxIS immediate or continue using the program at own risk**

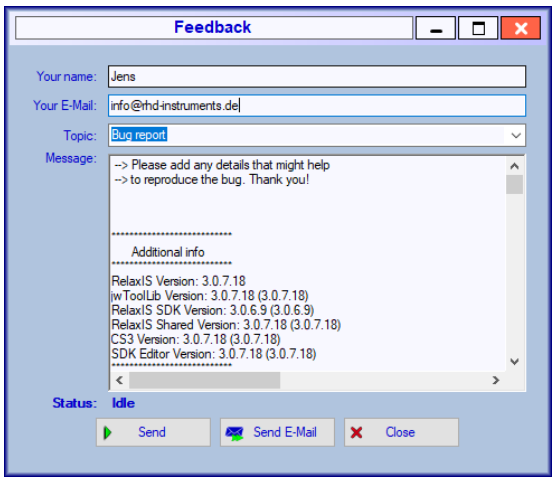
When an unhandled exception occurs a dialog pops up that informs you of the type of error encountered and the path of the recovery save.



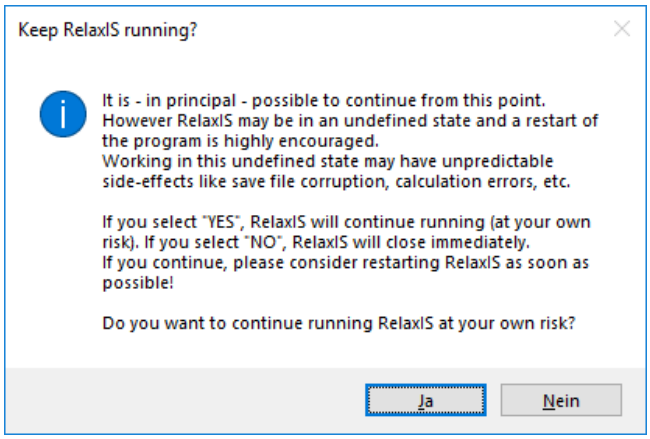
Sending a bug report is highly recommended because it allows us to know of the bug and fix it. If you like to receive feedback from us about the problem you have encountered or allow us to ask about further information please enter your mail address into the field. You are also asked if you would like to include todays log file, which may contain helpful details for us.

You can also enter additional information into the message field. Helpful information includes for instance a description under which circumstances you encountered the error (e.g. which component of RelaxIS you were using). The more details, the better. **Thank you!**





After sending (or not sending) the bug report, you will be asked if you would like to continue on from this point or if you want to close RelaxIS down now.



We **highly recommend** that even if you continue running RelaxIS you just use the time to save your work and then restart RelaxIS as soon as possible.

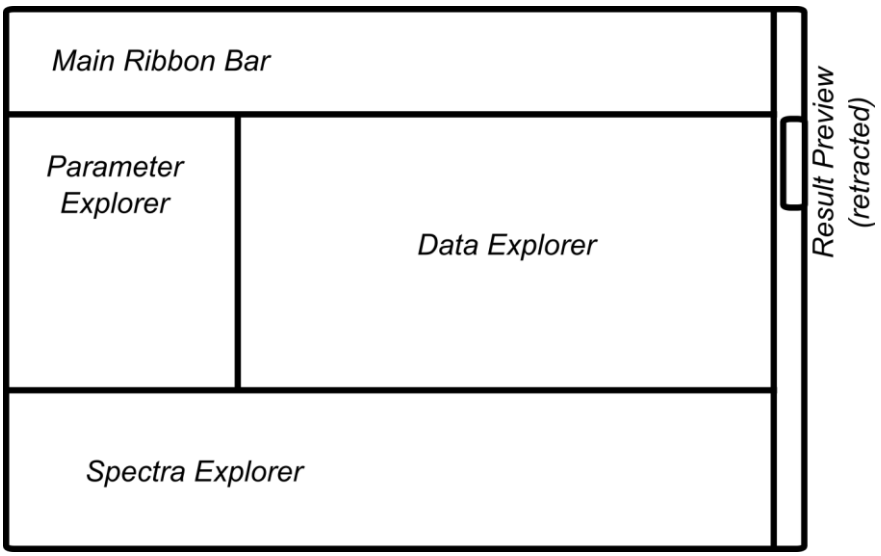
When you try to save data from an undefined state into the same project folder you will see a warning asking you if you want to continue. This is to avoid you overwriting “good” data with possibly corrupt data. Saving from an undefined state does not neccesarily lead to corrupt data, but the possibility can’t be excluded either.

A better option is to save the data as a new project folder under a different name and after restarting RelaxIS carefully checking if the data has been saved correctly.

4 THE MAIN USER INTERFACE

When you start RelaxIS you will be greeted by the Welcome Dialog. Here you can quickly create a new project folder, open an existing one or access the manual. If you don't want to see this dialog every time RelaxIS is opened, please mark the "Don't show this dialog again" box at the bottom right, and close the dialog. You can re-enable the Welcome Dialog using the "General Options" tab of the Settings dialog.

The main user interface of RelaxIS is – by default – divided into four parts.



1. The Ribbon Bar

   Grants access to **all functions** of RelaxIS through the various tabs. Not all functions are accessible at any time. This depends on loaded data, assigned models and so on. Unavailable items are grayed out.

   Some buttons are divided into a top and bottom half, where the bottom half usually grants quick access to default behaviors of the function.
2. The Parameter Explorer

   In this window, you manage parameter values of assigned models and can inspect fit results. It is also used for some helper functions.
3. The Data Explorer

   This is the main graph window that displays loaded data and fit curves. It is also used for advanced features like some initial parameter helpers or modification of the active frequency range.

4. The Spectra Explorer

   In this window, you manage the data of the current project. At the top, you can access a dropdown menu that lists all currently present models in the project, while the bottom table shows all spectra that are currently assigned to the active model. From this table, you select the currently active spectrum you want to work with.

   You can also **add data by drag & dropping files** onto the table.

You can **rearrange the windows** by clicking and dragging their title bars. You can leave the windows as floating windows, or dock them to other parts of the GUI. By clicking the needle icon in the title bar of the windows, it is also possible to retract the window into side bar. You can then show the window again by moving the mouse onto the flag at that side that represents the retracted window.

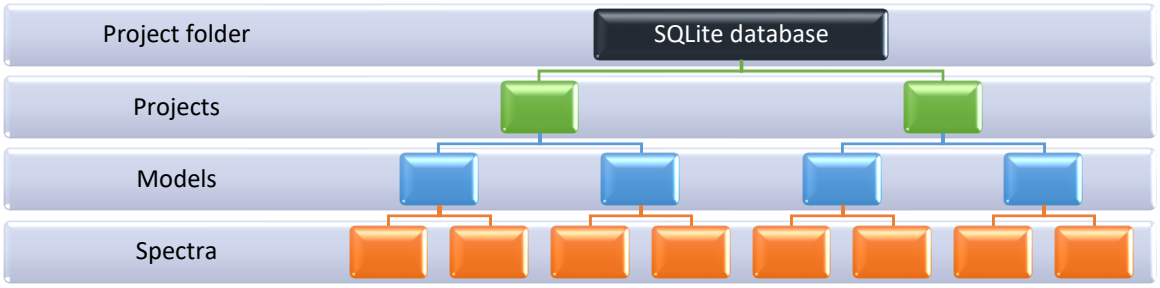
If you close one of the windows, you can **reopen** them using the button on the **Windows** tab of the main ribbon bar.

If any of the windows were moved into unreachable positions or are completely invisible you can **reset the window settings** by clicking the **Reset Window Positions** button on the **Windows** tab of the main ribbon bar.

This tab also allows you to enable the **Multi-Monitor Mode**. This button simply stretches the RelaxIS window automatically over all currently connected screens.

5 RelaxIS Data Structure

Data is stored and worked on as single spectra in RelaxIS. The general data structure can be visualized using a tree structure.



5.1 Spectra

Spectra contain information like raw impedance data as well as metadata. Metadata consists of secondary variables like temperature or DC bias that can be assigned in RelaxIS or read directly from the data source.

5.2 Models

Spectra are assigned to models. This allows working with more than one model at a time. Spectra can be moved between models or duplicated in order to try fitting the spectra with different models.

5.3 Projects

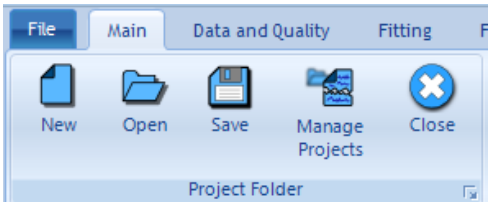
The models are themselves organized into projects. The projects may for example represent different dates, test series or similar. Projects also contain a Result Library, see section 15.

5.4 Project Folders

The projects are then stored in a project folder, which represents a **physical file on your hard drive**. These files are SQLite databases - a type of relational databases. SQLite is an open database format. It has the advantage of requiring no further configuration on the machine, while at the same time offering fast and reliable data storage capabilities. Project folders have the file ending .EIS3.

6 DATA MANAGEMENT

6.1 MANAGING PROJECTS

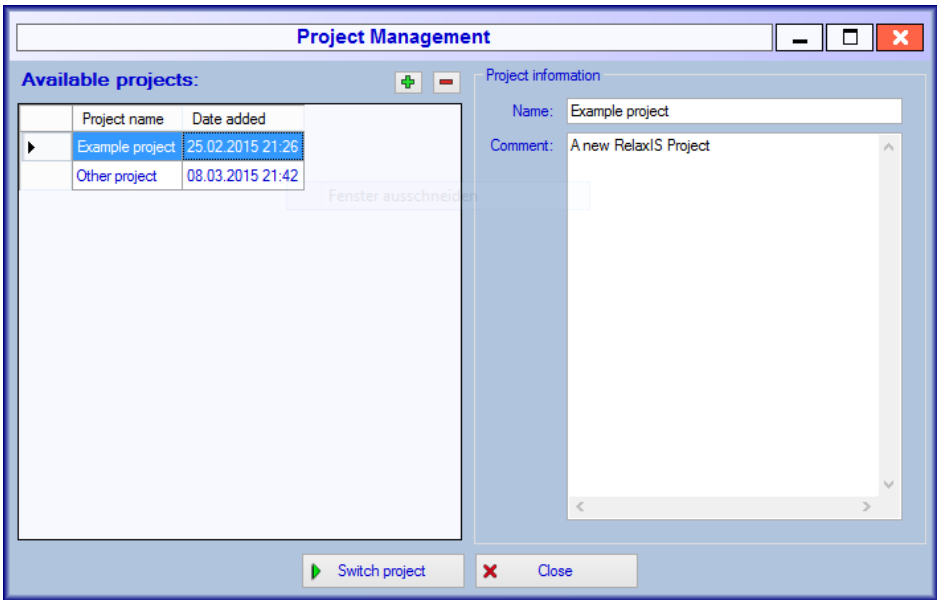


Use the buttons in the main ribbon bar's **Main** tab to create a **New** project folder, to **Open** an existing one or to **Save** the current project folder.

You can furthermore access the project management interface that allows you to add projects to your project folder, remove existing ones or switch between them by using the **Manage projects** button.

⚠ Please note

Before you can access the Project Management dialog, you have to save the project folder first. Only the currently active folder is held in memory, while the inactive ones are stored in the database. Therefore, you can't have more than one unsaved project opened at a time.



Use the + and – buttons to add or remove projects from the project folder. Select a project and click on **Switch project** to change the currently active project.

You can also edit the project names and comments through the respective interfaces.

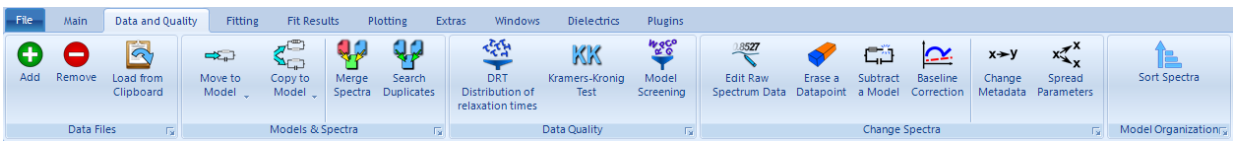
⚠ Please note (IMPORTANT)

The SQLite databases do not support concurrent access from multiple clients! You should **strictly avoid accessing the same database from multiple instances of RelaxIS**, or even from multiple computers using shared network-resources. Doing this can lead to data loss, since altered data in a project is stored in the computer's memory and not directly in the database. Saving the project again **will overwrite changes** made and saved by another client.

When a database is opened in RelaxIS, it will be flagged as opened and other users will receive a warning. If RelaxIS is not closed properly these **flags may persist** even after the database is not in use anymore. Therefore, the locks may be ignored, but please do so only after making sure no one else uses the database.

6.2 Adding Data to a Project

Most data management like adding, changing or removing data is performed using the buttons in the **Data and Quality** tab of the main ribbon bar.



You can add impedance spectra to RelaxIS by clicking the **Add** button from the **Data and Quality** tab, by copying text-based data into the Windows clipboard and selecting **Load from clipboard** after copying the data. You can also **Drag & Drop** files from the Windows Explorer or Outlook attachments onto the Spectra Explorer window.

⚠ Please note

When data is imported, from any source, RelaxIS checks if each datapoint is composed of valid numbers. The numbers can't be infinite or invalid, and must not be larger than a limit set under Main->Settings->Data and Import. In addition, frequencies must be larger than 1/limit (i.e. 1e-50 if the limit is 1e50). This is to avoid methods failing to perform suitable analysis of spectra with large numbers.

6.2.1 KNOWN DATA FILE FORMATS

RelaxIS supports several different data file formats, that can be read directly, sometimes including metadata. You can define additional formats using the **RelaxIS SDK**.

The supported formats are:

- Nova RelaxIS Export (Metrohm Autolab)
- .EPS (Novocontrol WinDETA binary data file) 3rd party
- .DCD (Novocontrol DETAchem binary data file) 3rd party
- Novocontrol WinDETA ASCII export file 3rd party
- .ISM (Zahner Zennium binary data file) 3rd party
- .MPR (BioLogic EC-Lab binary data file) 3rd party
- BioLogic EC-Lab© ASCII export file 3rd party
- hcDLL result files (rhd instruments GmbH & Co. KG)
- .NOX (Metrohm Autolab Nova) 3rd party, see note [1]
- .Z (Scribner ZView ASCII data file, Modulab ZView Export) 3rd party
- .DTA (Gamry instruments data file) 3rd party
- Digatron .CSV export files 3rd party
- .IDF, .IDS (Iviumstat) 3rd party
- .SPEC (Sciospec) 3rd party
- Solartron Versastudio ASCII export (Freq|Zre|-Zim or Zre|-Zim|Freq) 3rd party
- .psession (PalmSense data files) 3rd party

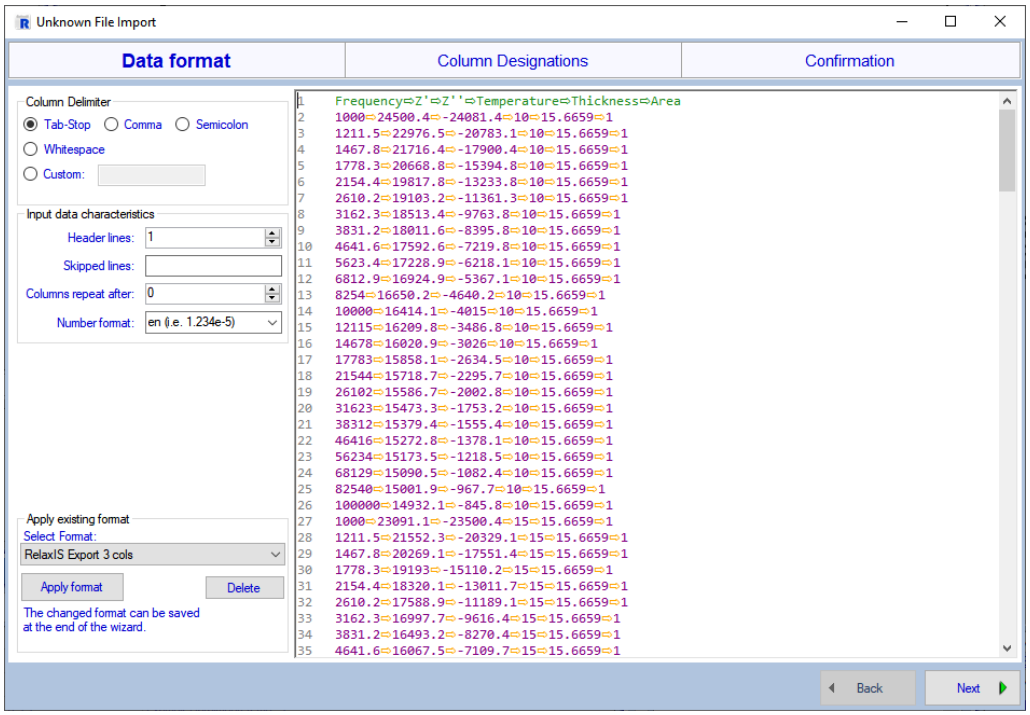
[1] Reading of NOX files can be improved by installing the Metrohm Nova software on the same PC as RelaxIS.

⚠ Please note

Not all file formats are officially specified by the respective manufacturer. Therefore, no guarantee can be given for the correct reading of all data files in every circumstance. **Please check the imported data carefully.** The formats are also subject to change when the manufacturer's software is updated, thus breaking the support. Please notify rhd instruments when you encounter any problems and check the imported data carefully.

6.2.2 Unknown Data File Formats

If you try to load an unknown data file you will be presented with the Unknown File Dialog. This dialog allows you to load arbitrary, column-based data files.



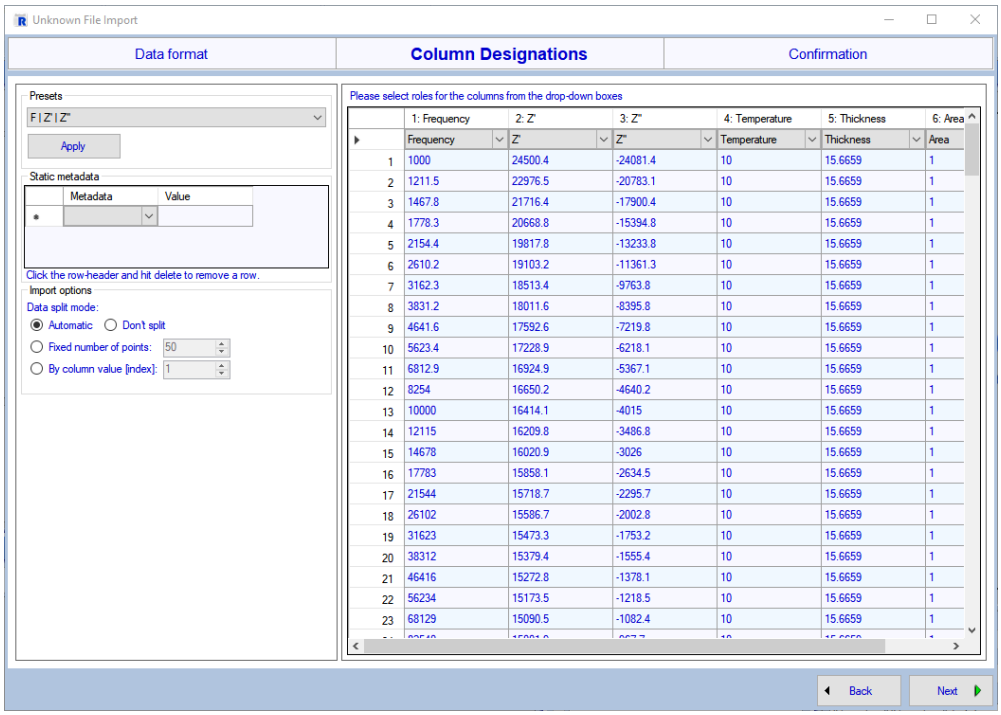
The dialog is built as a wizard, with 3 steps: Data format setup, column role selection and confirmation.

6.2.2.1 Data Format Setup

The first page shows the input data as a text file and highlights special characters (orange) as well as numbers (purple) in it. RelaxIS automatically tries to determine the data settings but you may need to supply the correct format options on the left:

- Select the text characters that separate columns. These can be for example tabs, commas or whitespace (“space” characters). Custom characters can also be supplied
- Designate the number of header lines, i.e. lines that are skipped before the data import starts. The header lines are shown in blue, and the last header line is shown in green.
- You can skip specific lines in the import by typing the line numbers in to the Skipped Lines input box. Add commas between numbers. You can also enter ranges, example: 2, 3-9, 12
- The “Columns Repeat after” field is used in cases, where a file contains multiple spectra in repeated sets of columns. For example, the file contains the columns: Freq 1, ZR1 ZI1, Freq2, ZR2, ZI2, … then the Columns repeat after field would be 3.
- Number format allows you to select which format the numbers have for the import, e.g. decimal separated with dot or comma.
- Selected formats can be saved in the confirmation step. If you have previously saved a format, you can select it from the list of existing formats and apply it directly. This restores both format settings as well as selected column roles (next step).

Once the format is selected, click Next to move to the Role Selection step:



Here you need to select which role the individual columns serve. Not every column needs to be designated, but enough data needs to exist to calculate the impedance.

RelaxIS tries to automatically assign roles based on the values in the last (green) header line. This header line will be split alongside the data and the column values are then checked against certain keywords.

⚠ Please note

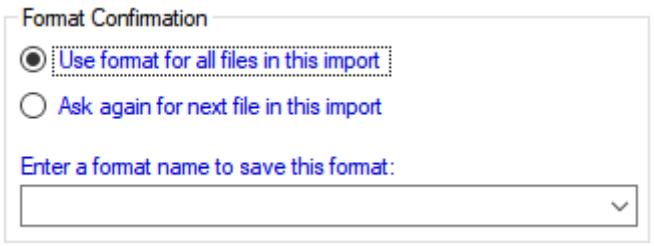
Always check the automatic selection. The algorithm uses simple word matching and may not identify the columns correctly.

Next to impedance data, you can also select metadata. The values from these columns will be split with the rest of the data and then averaged per spectrum.

The dialog also allows you to enter additional static metadata values, that will be applied to each imported spectrum.

Last, you can choose between different splitting options. Automatic splitting uses the frequencies to find boundaries between spectra and splits the spectra on these boundaries. Select Don't Split to keep the data together in one spectrum. Or supply the number of datapoints per spectrum if automatic splitting fails. Last, it is possible to define a column index that that is used for splitting the data. Whenever the value in the specified column changes, a new spectrum is started.

Once you have made all settings, click Next to move to the Confirmation step.



Here, you can select if this format should be used for all files in the current import. Otherwise, the dialog will be shown again for the next file, which is helpful if you import files with different formats in the same go.

You also have the option to enter a name for the file format settings. Simply enter a text into the box (or select one from the dropdown), and once you click Finish, the format is saved and can then be used in subsequent imports.

6.2.3 Modifying the Datasource Format

By default, the path of the file that contained the spectrum is displayed as the Datasource property of each spectrum. If a file contained more than one spectrum, a running index is added to the filename. You can change the format of the filename using the **Settings** dialog, available from using the **Settings** button on the **Main** tab.

In the Settings dialog select **Value formats** and edit the **Filename Datasource Format** section. You can enter a format string using various tags, that are always lead by a # character. The possible tags are (as an example the file *C:\Test1\Test2\test.txt*, containing multiple spectra is used):

Tag	Meaning
#F	The full folder, e.g. C:\Test1\Test2
#1	The last folder in the path, e.g. Test2
#2	The second to last folder in the path, e.g. Test1
#3	The third to last folder in the path, e.g. C:
#N	The filename without extension, e.g. test
#E	The file extension, e.g. .txt
#P	The running index of the extracted spectra, e.g. 1, 2, …

You can combine these tags with arbitrary text to produce the format of your liking. Some examples are:

Datasource format string	Result
#F\#N#E_#P	C:\Test1\Test2\test.txt_1
\#1\#N#E (#P)	\Test2\test.txt (1)
#N from folder #F of type #E (Spectrum no. #P)	test from folder C:\Test1\Test2 of type .txt (Spectrum no. 1)

6.2.4 Behavior of Data Files After Being Added to RelaxIS

Once data files from your disk were added to RelaxIS, the data in RelaxIS **holds no tie to the actual files** on your drive. The active project is held in memory, while inactive projects in the project folder are stored in their respective SQLite database. This means that you are free to move, delete or rename the files on your drive, without any data being altered in your RelaxIS project. The same is true for the opposite direction. No source file on your drive is altered by adding it to RelaxIS, even if the actual data in RelaxIS is modified. **The data files are opened as read-only and are never modified**.

6.2.5 Extracting Metadata from Filenames

RelaxIS offers a method to automatically extract metadata values from the source file names when importing new files. Values are selected in the filename by means of a user-defined Regular Expression (RegEx).

⚠ Please note

Explaining the full syntax of regular expressions is beyond the scope of this manual. However, given that they are a very common concept in computer languages, abundant resources can be found online. For example:
Quick reference:
https://docs.microsoft.com/en-us/dotnet/standard/base-types/regular-expression-language-quick-reference
Regex Tester:
https://regex101.com/

Regular expressions define a contents of a text in a more abstract way. For example the text “Test12345” could be seen as “Some upper- or lowercase letters followed by some numbers”. A regular expression is a way to express such abstractions as a universal expression, in this example the corresponding regex would be “[A-Za-z]+[0-9]+”. Once defined, software can check of an input string matches the regular expression. For example, the text “12345Test” would not match, because it is not letters followed by numbers.

Further, regular expressions can define so-called capture groups, which are usually introduced by brackets, e.g. "[A-Za-z]+**(**[0-9]+**)**". Here, the numbers after the letters would be captured in a group and therefore extracted by the software. The groups can be given a name by adding ?'Name' to the beginning of the group, e.g.: "[A-Za-z]+**(?'MyName'**[0-9]+**)**".

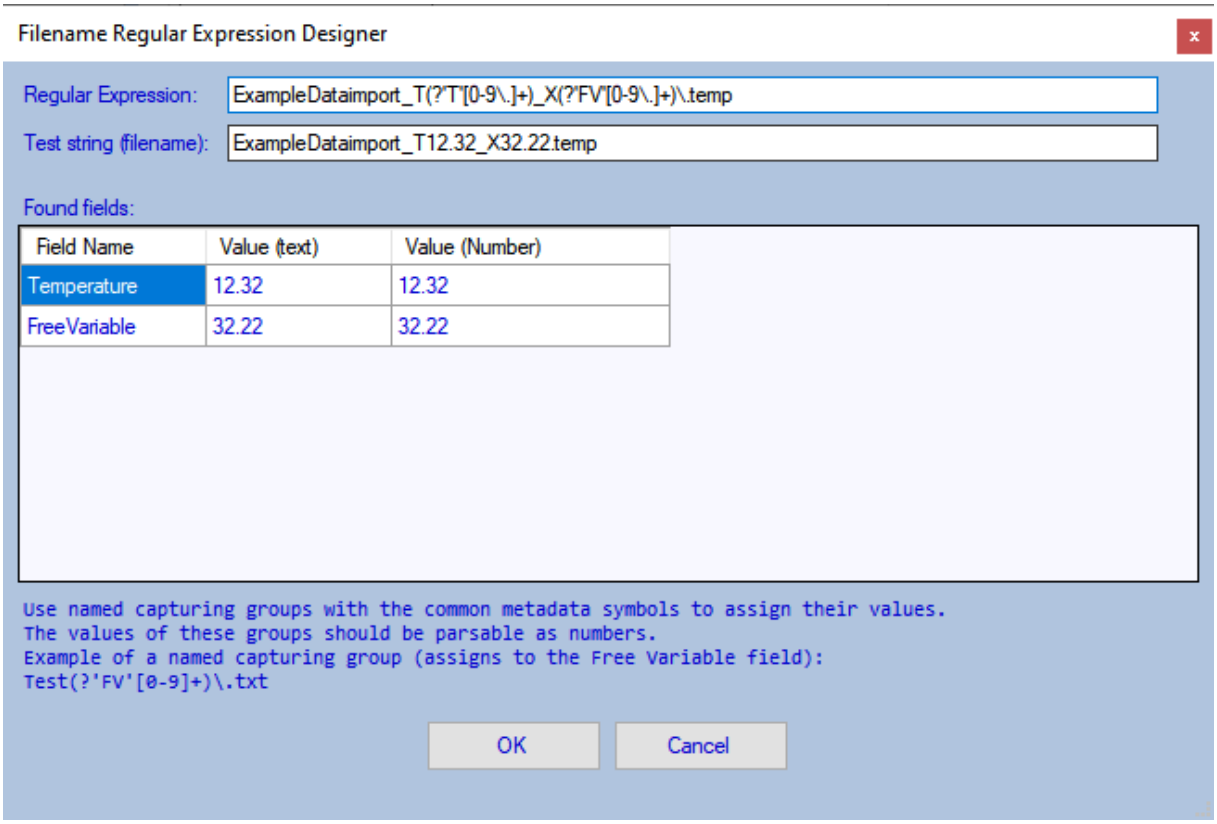
In RelaxIS, such named capture groups are used to define which values should be extracted for which metadata field. The group names should correspond to the common metadata abbreviations like T or FV. If the values of the captured groups are numerical then RelaxIS can parse them and assign the values to the respective field. In addition to the metadata abbreviations, a group named "DATASOURCE" can be used to assign a part of the input to the data source field.

To define the regular expressions used for parsing filenames, open the settings dialog from **Main -> Settings** and then Data & Import. Here find the "Metadata from Filename" panel. The regular expression is entered into the **Regular Expression** field. If the **Match full path box** is activated, the input to the regex contains the full path instead of just the filename. This is useful if relevant information is contained in the path. Please note though, that your regular expression must parse the full path in this case!

The **Datasource prefix** input allows you to add a fixed text in front of the potentially captured data source field.

To make designing the regular expression easier, you can click on the … button next to the input field to show a designer window.

The designer allows you to enter the regular expression as well as a test string. The test string is automatically populated with the path to the source file of the first spectrum in the current project, if there is one.



You can change the test string however you like. While you enter the test string or the regular expression, RelaxIS will automatically try if the regex matches. If it does, all captured groups will be evaluated, and the results placed into the fields table. If the regex doesn't match the test string, or if no groups are captured a warning is displayed next to the input field.

If the groups are captured, but the name wasn't recognized, a question mark will be placed next to the name.

You can also check the Value (Number) column to check if the value is correctly parsed to a number.

6.3 Auto Saves

If enabled in the Settings dialog under **Main→Settings→General** the currently loaded project folder can be automatically saved as a copy every *n* minutes. The data can either be saved into the user data folder (commonly in the My Documents folder), or alongside the already saved source file. **Auto saves do not alter the manually saved project folder!** If the data is saved in the user

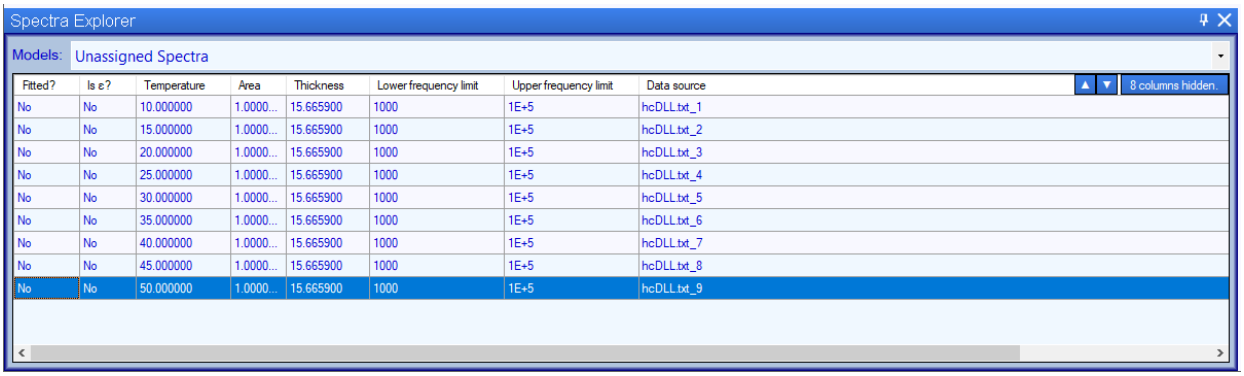
folder an individual file per running instance of RelaxIS is created. The names of these files are chosen as follows:

1. The saving instance of RelaxIS (*RxS*) gets a list of all running RelaxIS processes.
2. This list is sorted by the start time of the process.
3. *RxS* determines its position in this list.
4. The auto save file is named “Autosave Instance X.eis3”, where X is the position determined in step 3.

This method ensures that all currently actively used data files are auto saved and the different instances of RelaxIS don’t overwrite each other. At the same time, the number of created files stays at a minimum.

6.4 The Spectra Explorer

The loaded spectra are listed in the Spectra Explorer window together in their respective models.



The list shows all metadata associated with each spectrum. You can switch between models (once created) by clicking the model designation and selecting another model from the dropdown menu.

The “**x columns hidden**” button allows hiding metadata columns, for which no spectrum in the list has a value.

You can move spectra in the list by using the up/down buttons in the top-right corner.

The **Fitted?** column displays whether or not the spectrum has an up-to-date fit, white the **Lower** and **Upper frequency limit** columns display the active

frequency limit in which fits are performed. This will be further explained in section 10.5.

RelaxIS distinguishes between the **Active Spectrum** (or *Current Spectrum*), which is displayed at all times in the **Data Explorer** plot, **selected Spectra**, which you can select from the list of spectra using the CTRL, SHIFT (while selecting files with the mouse) or CTRL+A keys, and non-selected spectra.

6.4.1 Copy & Pasting Spectra

Spectra can be copied to the clipboard and pasted into the same or other Spectra Explorer windows. This can be in another open instance of RelaxIS, or you can e.g. switch the active project of the current project folder after copying spectra and paste them into the other project.

To copy spectra, select them in the Spectra Explorer window (select multiple by holder CTRL), then right-click and select “Copy spectra to clipboard” from the context menu.

To paste the spectra, navigate to the target Spectra Explorer, right-click in it and select “Paste spectra from clipboard”. An exact copy will be created in the target Spectra Explorer.

6.5 Selecting multiple spectra: The Spectra Selection Dialog

Many features of RelaxIS can be applied to multiple spectra at a time.

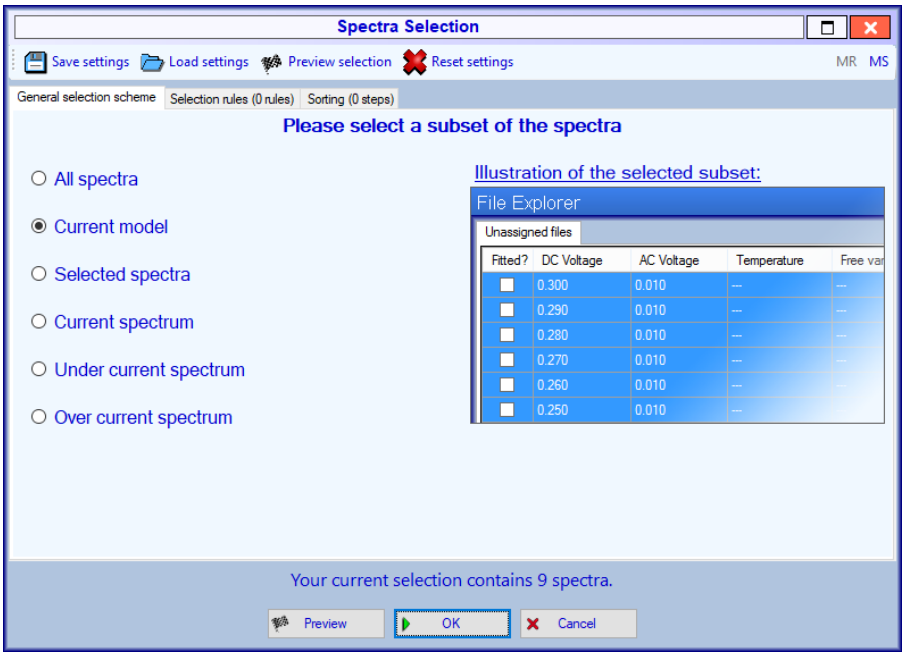
RelaxIS contains two modes of operation in this regard: a) Use of the currently selected spectra in the Spectra Explorer list, called “direct selection mode”, or b) the Spectra Selection dialog, called “dialog selection mode”.

To switch between the two modes, use the “**Always use selected spectra for data-related functions**” setting from the General section in the Main → Setup dialog.

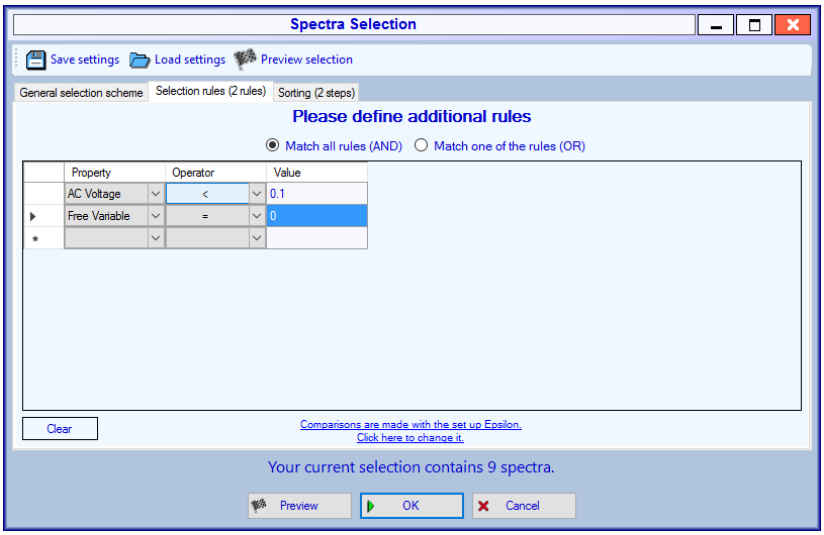
In mode a), first select the spectra you wish to apply a function on, and then execute the function by i.e. clicking the respective ribbon button. Note that some function will still use the spectra selection dialog shown below if

required, usually if the currently active spectrum is important. One example is the “Spread Spectrum Data” function.

In mode b) you will often encounter the **Spectra Selection dialog**. The dialog allows you to define a specific selection of spectra and is split into three pages, where pages 2 and 3 are optional. At any point, you can preview the current selection using the **Preview selection** button from the toolbar. You can save and load settings as well by using the corresponding buttons. For small, temporary changes you can quicksave and quickload a configuration by using the MS/MR buttons in the top-right corner of the window.



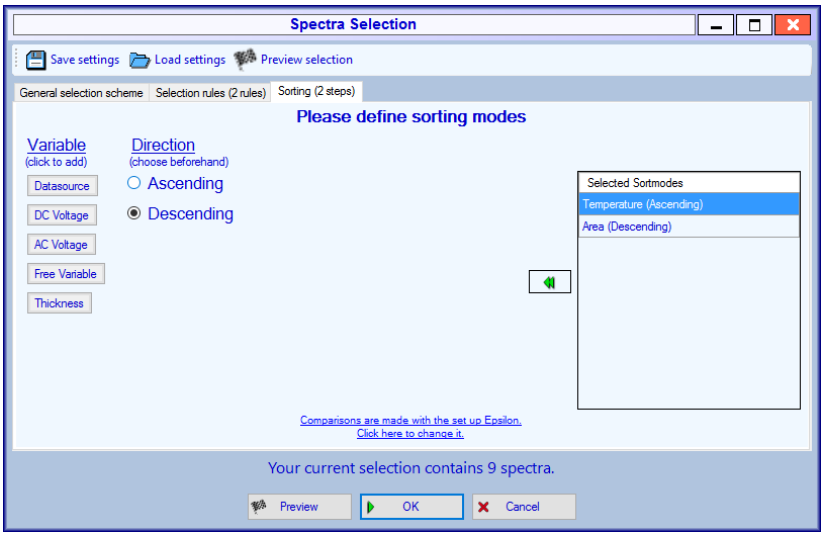
The first page (or tab) designates the overall selection scheme. Not all operations allow the selection of **All spectra**, since they can only work if the spectra are assigned to the same model. **Under** and **Over current spectrum** refer to the Active Spectrum and select all spectra in the current model into the chosen direction, **including** the Active Spectrum.



The second page allows a refinement of the selection by using the metadata available for the spectra. You can enter selection rules by three steps:

1. Select a metadata category like temperature or dc voltage.
2. Select a Boolean operator like “equals” or “greater than”.
3. Enter a value to compare the metadata with.

You can also choose if spectra are selected only when they match all rules (meaning an AND concatenation of the rules) or if they should be selected if they match any one of the rules (OR concatenation).



The third page allows sorting of the selected spectra. The spectra can be sorted by various properties and in either ascending or descending order for each selected property. The sorting steps are performed from top to bottom in the list. In the example image above all spectra are first sorted ascending by

temperature. Spectra with the same temperature are afterwards sorted descending by Area. You can remove steps from the list using the green button in the middle.

6.6 Removing Data from the Project

Spectra can be removed from the project permanently by selecting the spectra in the Spectra Explorer list and either clicking **Remove** from the **Data and Quality** tab or by pressing the Delete key.

⚠ Please note

Deleting spectra from your project CANNOT be undone! All fits or metadata is permanently lost and you need to add the original data file to RelaxIS again and redo the changes made to it yourself.

6.7 Removing Duplicate Spectra

You can search for and remove duplicate spectra in the project by clicking the **Search Duplicates** button on the **Data and Quality** tab of the main ribbon.

In the dialog, you can select the basis on which duplicates are identified. Two spectra must match perfectly in the selected attributes like data or metadata in order to be classified as duplicates. Click **Start** to begin the search.

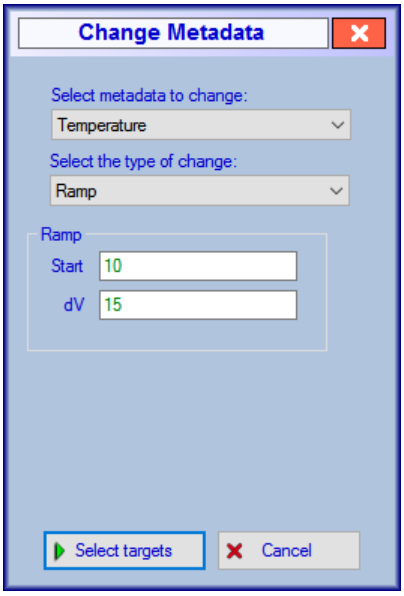
If duplicates are found they are listed under the heading of the first found spectrum of each set of duplicates. To remove duplicates, **uncheck** the box in front of the name. By default, only the first found spectrum of each set is kept. After you made your selection, please click OK to remove all unselected spectra from the project.

6.8 Modifying Metadata

You can modify metadata associated to spectra using the **Change metadata** and **Spread parameters** buttons in the **Change spectra** section of the **Data and quality** tab. These functions are also available from the context menu in the Spectra Explorer window (right-click a spectrum to open it).

Furthermore, you can enter the metadata values directly in the Spectra Explorer window by **double-clicking the respective value** or clicking the cell and just start typing. By default, RelaxIS hides metadata columns that contain no data. To enter values for these, first **unhide the columns** by clicking the blue button in the top right of the Spectra Explorer list. After entering the data, you can safely hide the remaining empty columns again.

The **Change metadata** dialog allows you to set or change metadata for one or more spectra using different methods.



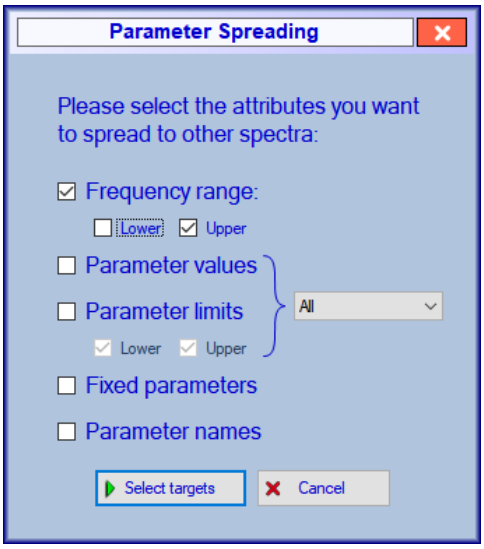
To change metadata, please perform the following steps:

1. Select the parameter you want to change with the combobox at the top.
2. Select a modification method using the second dropdown menu.
    a. **Setpoint** sets the variable to a specific value.
    b. **Additive** adds a specific value to the current value of the parameter. If the parameter is currently unavailable for a spectrum, it is set to the selected value instead.
    c. **Multiply** multiplies the current value with the selected value. If the parameter is currently unavailable for a spectrum, the spectrum is ignored.
    d. **Ramp** starts with the first entered value for the first selected spectrum and then continuously adds the *dV* value to create a ramp of values.

e. **Rounding** allows you to round the metadata value to a given number of (significant) decimal places.
f. **By Formula** lets you enter a mathematical formula to calculate the metadata value for a spectrum.
g. **From List** lets you enter, or more likely, paste a list of values that are assigned from top to bottom to the selected spectra.
h. You can **Remove a Metadata** value from the spectrum entirely.

Click **Select targets** button to be led to the Spectra Selection dialog (if dialog selection is enabled), or the change will be executed on the selected spectra. In case of the Ramp and From List methods, keep the sorting order of the selected spectra in mind.

The **Spread parameters** dialog in turn allows you to spread spectrum parameters like frequency limits or fixed fit parameters to other spectra in the same model.



To do this, please perform the following steps:

1. Select the source spectrum in the Spectra Explorer as the active spectrum.
2. Click the **Spread parameters** button.
3. Select one or more parameter types to spread.

4. For parameter values and limits you can choose, if spreading should be done for all parameters, or for fixed/non-fixed parameters only.
5. Click the **Select targets** button to be led to the Spectra Selection dialog and choose the spectra the parameters will be spread to. Direct selection mode is not supported.

The Frequency Range and Parameter Limits options further let you select if you want to spread the lower, upper or both limits. Simply mark the settings you want to spread with a checkmark.

6.9 Dielectric Data

Normal spectra in RelaxIS use non-normalized transfer functions, based on the Impedance. Without further knowledge of the data, the data can be recalculated into the other transfer functions (admittance, complex capacitance, elastance).

In order to use typical dielectric transfer function (permittivity ε, modulus), a geometric factor, e.g. based on the sample area, and thickness, needs to be known. While for many techniques, this factor is known, some dielectric techniques, especially in the high frequency domain, only provide e.g. the permittivity as the measurement result.

To accommodate such spectra, the spectrum can be marked as an ***ε*-only spectrum**. To enable this functionality, select **Main → Settings → General → Enable Dielectrics Functions** from the main menu. ε-only spectra are marked in a corresponding tab in the Spectra Explorer list

In the background, the data of ε-only spectra is treated the same as other data, since in the mathematical sense e.g. the permittivity behaves exactly like the complex capacitance. However, all display elements in RelaxIS, like axis titles on graphs, now display the correct names for the normalized transfer functions.

Transfer Function Non-normalized	**Mathematical equivalent transfer function, normalized**
Impedance	Area Impedance

Admittance	Complex Conductivity
Complex Capacitance	Permittivity
Elastance	Modulus

Not all transfer functions can be used without restriction! The permittivity can be consistently recalculated to the modulus, and the conductivity. However, since for the impedance not the specific impedance is chosen as the normalized function, but the area impedance, the *Impedance* transfer functions produces **invalid values** when used with ε-only spectra.

If area and thickness metadata for a spectrum is known, it can be transformed into an ε-only spectrum. To do this, click the **Dielectrics → Convert to ε-only spectrum** button from the main menu. The Dielectrics tab is only visible, if the dielectrics functions are enabled in the settings. In the dialog, you can choose to override the individual area and thickness metadata of the spectra, and you have to select the correct unit for the area and thickess. The function then recalculates the impedance values stored for the spectrum, such that the complex capacitance values are now permittivity values. It will also mark the new spectra as ε-only spectra.

The dielectrics menu also allows the conversion of ε-only spectra to normal spectra, if the cell parameters are known. The conversion works just as described above for the opposite direction.

You can use the **Data and Quality → Change Metadata** dialog, to mark spectra in the Spectra Explorer list as ε-only.

A typical workflow could be

1. Import regular dielectric data (with cell geometries)
2. Import e.g. a waveguide measurement. A textfile contains columns Freq|eps'|eps''
    a. Use the Unknown File Dialog, mark the Eps columns as C' and C'' respectively
    b. Select the imported spectrum in the Spectra Explorer list

   c. Select Data and Quality → Change Metadata → Metadata type: Spectrum Type → ε-only
   d. Note, that the Data Explorer graph now shows e.g. ε instead of C
3. Select the regular dielectric spectrum, convert it into an ε-only spectrum by using Dielectrics → Convert to ε-only spectrum
4. Select both ε-only spectra and merge the data by clicking Data and Quality → Merge Spectra (see 6.10.3).

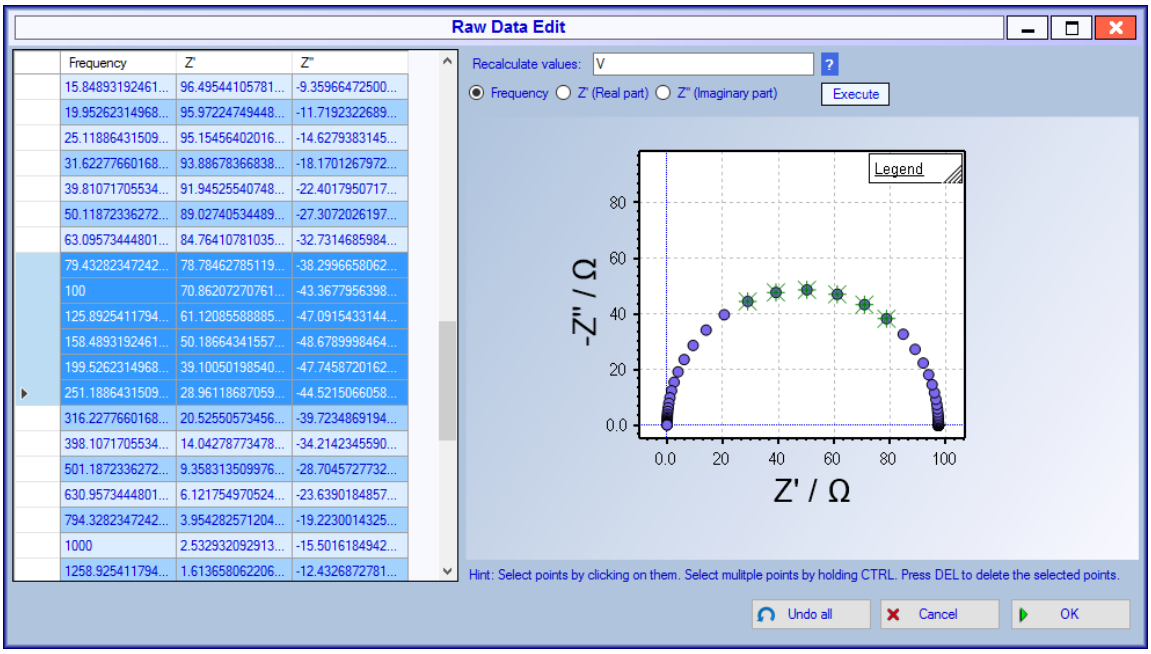
This will create a combined ε-only spectrum of your regular and waveguide data.

6.10 Modifying Raw Data

RelaxIS allows you to change the raw data of a spectrum in various ways, once it is loaded in a project. Please note, that the source files on your hard drive are entirely unaffected by these changes, and you can restore the original data by reimporting the data file into the project. The changes to the raw data of the loaded spectra is however **mostly irreversible, so please take care** and critically evaluate any changes in regard to the integrity of the spectra.

6.10.1 Raw Data Edit

The **Raw Data Edit** dialog can be accessed using the **Edit raw spectrum data** button in the Data and Quality tab. It allows you to directly manipulate or recalculate the data stored for the spectrum.



You can use the table to **change the value** of each data point by simply selecting the corresponding cell and entering a new value.

Jump or select data points by **clicking on them** in the graph. Hold *CTRL* while clicking to select multiple points at once.

You can **delete data points** by clicking on the respective row header (or on the data points) and pressing the *Delete* key on your keyboard. This, for example, allows the elimination of outliers, such as a 50 Hz artifact.

Furthermore, it is possible to **recalculate** whole columns using an arbitrary formula that you can enter in the textbox in the top-middle.

The formula can contain numbers, mathematical functions like sin(), cos() or exp() or various variables. A list of functions can be found in the appendices. Aside from some special occasions the variable **V** usually corresponds to the source value, in this case either to the frequency, Z' or Z'', depending on the selected radio button below the textbox.

Other variables include the active spectrums metadata and can be found by clicking the **?** button next to the textbox.

⚠ Please note

All variables are case sensitive and need to be entered exactly as noted in the help text.

Some examples are:

Formula	Result, Use Case
V*-1	Invert the selecting value, e.g. for negating the imaginary part
V/A	Divide the value by the spectrum's area, e.g. for reverting an area normalization in the source data

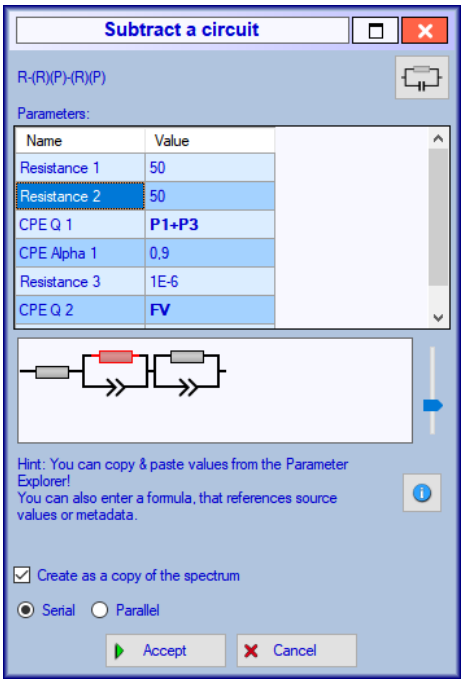
You can reset the changes done in the **CURRENT SESSION** of the data edit, by clicking the **Undo** button.

⚠ Please note

Once you accept the changes using the **OK** button, the changes **cannot be undone!** You need to reimport the data from the original source file to get the original state back.

6.10.2 Model Subtraction

RelaxIS allows you to subtract the calculated impedance values of a model from the data of your spectra. This sometimes allows the elimination of influences of unwanted processes from the spectrum and can probably allow the evaluation of underlying processes. You can access this feature using the **Subtract a Model** button in the **Data and Quality** tab.



Click the button at the top-right to select a model to subtract. Please refer to chapter 8 for details on how to design a model.

Afterwards enter the parameter values for the model or copy & paste values from the Parameter Explorer. In addition to entering raw parameter values you can also enter formulas for the parameters directly into the respective fields. Formulas allow you to refer to element values indirectly, which is especially useful when subtracting model values from multiple spectra in one step. Click the **information button** for a list of variable names that may be used in the formulas.

Finally, you need to select if you want to subtract the model in serial or parallel.

In case of subtracting in serial the impedance will be subtracted as

$$\hat{Z}_{new}(\omega) = \hat{Z}_{old}(\omega) - \hat{Z}_{model}(\omega).$$

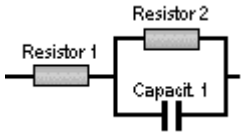
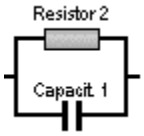
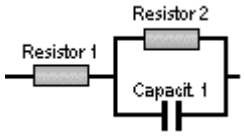
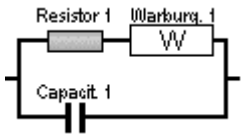
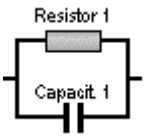
In case of subtracting in parallel the impedance will be subtracted as

$$\frac{1}{\hat{Z}_{new}(\omega)} = \frac{1}{\hat{Z}_{old}(\omega)} - \frac{1}{\hat{Z}_{model}(\omega)}.$$

This allows you to subtract elements depending on how you define their influence on the data.

Often you need to subtract parts of a model one after another in multiple steps in order to achieve your goal. You **can't just subtract any single element from any model!**

Some examples are:

Assumed data model	Desired data model	Required operations
		Subtract *Resistor 1* in series
		Subtract *Resistor 1* in series, **afterwards** subtract *Capacit. 1* in parallel
		**Impossible!** You could only subtract *Resistor 1* and *Warburg 1* together.

6.10.3 MERGING SPECTRA

RelaxIS allows you to merge multiple spectra into one. In order to do this, select **Merge spectra** from the **Data and Quality** tab of the main menu. The option dialog allows you to choose,

- If only active data should be included in the new spectrum.
- If equal frequencies in the spectra should be merged into one by either averaging their Z' and Z'' values or summing them.
- If the originating spectra should be removed from the project.

Afterwards, use the Spectra Selection dialog to select the spectra you want to merge if dialog selection is enabled, otherwise the currently selected spectra are merged. If you choose not to average the same frequencies, the merged spectrum will contain multiple data points with the same frequency.

7 Data Quality Assessment

7.1 The Linear Kramers-Kronig Test

7.1.1 Introduction

The Kramers-Kronig relations under certain conditions allow the calculation of the real part of the impedance from the frequency and the imaginary part, or of the imaginary part from the frequency and the real part.

For this to be possible, the data needs to fulfill certain rules:

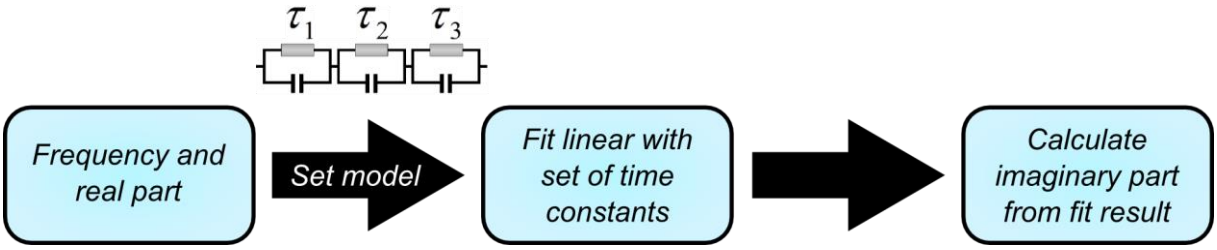
- Causality: The system response may only be caused be the sinusoidal excitation.
- Linearity: The excitation must be mild enough that the system response is linear only.
- Stability: The system response must not change with time while the excitation is applied.

The derivation of the common formulas for most models, and equivalent circuits in particular, are all based around the idea that these rules are valid. **If a system does not follow these rules an evaluation using such models is usually not suitable.**

Kramers-Kronig-tests are based around this idea. One tries to transform the real- into the imaginary part or *vice versa* and **compares the result with the actual spectrum**. If they match, then the measurement is trustworthy and can be evaluated. If not, the measurement parameters should be critically reviewed.

Problems arise from the formulation of the relations. For the calculation, integrals from zero to infinity over the frequency must be solved. This frequency range is obviously not accessible in the measurement. Therefore, the data needs to be extrapolated in some way. **This extrapolation step is the main reason why different implementations of the Kramers-Kronig-test usually lead to different results**, especially since details about the implementation are often not fully disclosed.

The KRAMERS-KRONIG-Test in RelaxIS is based on two methods described by BOUKAMP et al. (*J. Electrochem. Soc.* **1995**, *142*, 1885-1894). In this method, the data is first modelled by a **long series of (R)(C) elements**. You can use as many of these elements as there are data points. Since a chain of (R)(C) elements follows the rules above one may derive the fact that **if the data can be described by the chain it also follows the rules**. The method furthermore linearizes the problem by introducing a fixed set of relaxation times $\tau = R \cdot C$ for the elements. This simplifies the procedure because the problem can be broken down to a linear fit.



RelaxIS implements two methods: A **Complex Fit** that fits both real and imaginary parts simulatenously and can contain a series capacitor and inductor in addition to the (R)(C) chain, and a **Partial Fit**, that fits either the real or imaginary parts separately.

In the **Partial Fit**, RelaxIS first performs the linear fit on either the real or the imaginary part of the spectrum. The linear fit describes this part perfectly, if the number of time constants is equal to the number of datapoints, and yields a set of resistances for the (R)(C)-elements. This set is used to calculate the other part directly. The calculated part is then compared with the measured data.

The Complex Fit is more like a normal EIS fit, in that it fits a model to both the real and imaginary parts simultaneously. However, it does so by also using the pre-defined set of time-constants which simplifies to fit to a linear system. From the results of the linear fit, both real and imaginary parts can be calculated and compared with the data.

The times-constants are chosen logarithmically in the frequency range of the measurement. It is often **favorable to use less time constants to lessen the**

impact of random noise on the simulation, also called **overfitting**. The number of time constants and therefore of (R)(C)-elements can be chosen freely up to a maximum equal to the number of datapoints.

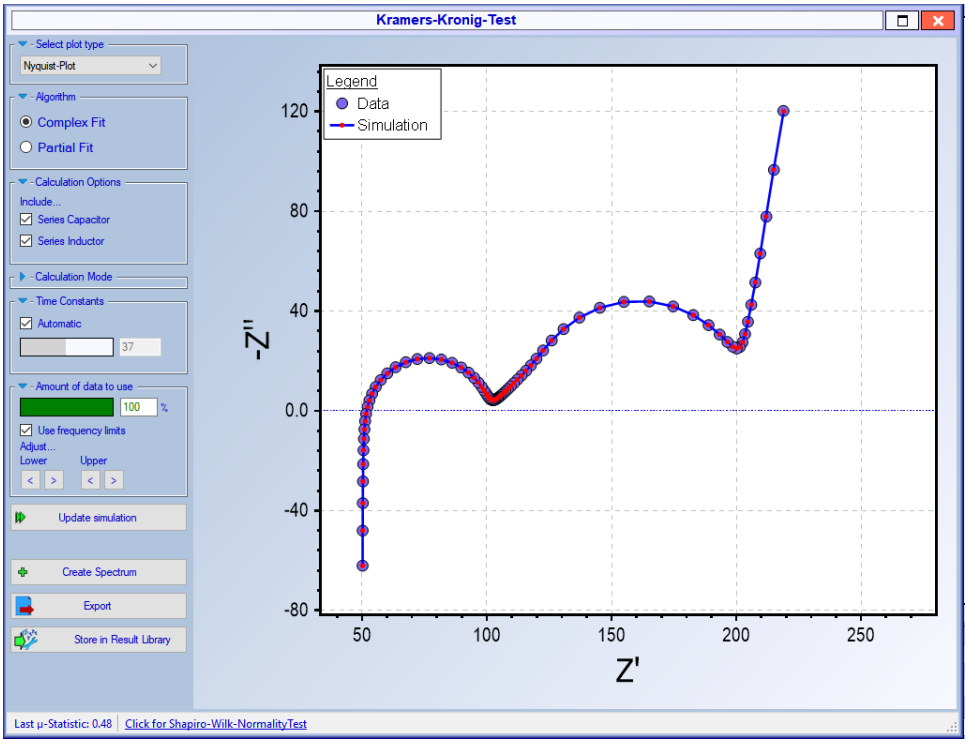
To minimize the effects of overfitting, RelaxIS implements an **automatic determination of the optimal number of time constants**, using a method by SCHÖNLEBER et al. (*Electrochim. Acta* **2014**, *131*, 20-27). Overfitting is often apparent in the appearance of negatice resistances in the (R)(C) elements and can be quantified by the μ-statistic. The nearer μ is to 1, the less overfitting occurs. With increasing number of time constants, μ drops sigmoidally to zero. The number of time constants where μ passes through 0.5 is chosen as the optimal number.

Please note

We suggest that you use the Complex Fit with included capacitor and inductor and automatic determination of the number of time constants.

7.1.2 USING THE LINEAR KRAMERS-KRONIG-TEST

After selecting a spectrum use the **Kramers-Kronig Test** button on the **Data and Quality** tab of the main ribbon bar.



After opening the dialog, a KRAMERS-KRONIG-Test is automatically performed once with default settings. If you alter any settings you need to manually click the **Update simulation** button for the settings to take effect.

On the left side of the dialog you can alter several settings:

- Select the type of plot to show in the graph.
- Select the **Algorithm** to use: Complex Fit or Partial Fit
- *For Complex Fit*: Under **Calculation options** choose to include a series capacitor and/or inductor in the fit.
- *For Partial Fit*: **Calculation mode** allows you to choose if you want to calculate Z' from Z'' or *vice versa*.
- **Number of time constants** allows you to decide how many (R)(C) elements should be used for the linear fit. Select Automatic to perform the automatic determination based on μ. You can calculate a μ vs. number-of-τ plot by clicking the μ number in the status bar.
- **Amount of data to use** allows you to use only a certain percentage of the data points for the fit and to limit the frequency range to the limits set for the spectrum.

When the Complex Fit is used, the option is given to perform the simulation in the **admittance** instead. In that case, the input data is converted into the admittance, which in effect causes the simulation to fit parallel connected series RC elements, e.g. (RC)(RC)…, where each RC element has a preselected time constant. This option is useful in cases where the impedance data reaches into e.g. the 2nd complex quadrant (negative real parts). To fit this, negative time-constants would be required in the impedance case, while the admittance case still fits with only positive time constants. Details are described in Boukamps paper cited above.

In the "Amount of data to use" box, you can furthermore change the current frequency limits of the spectrum by clicking on one of the four left/right buttons. The two buttons on the left change the lower frequency limit while the two rightmost buttons change the upper frequency limit. The left-arrow changes the respective limit to lower frequencies, while the right-arrow button changes it to higher frequencies.

Use the **residual**, **histogram** or **CDF** plots to evaluate how well the simulated data matches the measured data. The latter two plots are calculated for the absolute residuals.

You can calculate **Shapiro-Wilk-Normality** tests for all residuals by clicking the Shapiro-Wilk-field in the status bar at the bottom of the window.

You can work with the results in multiple ways:

- Export the result data via the typical export dialog
- Store the result in the Result Library of the current project folder
- Create a new spectrum from the simulation and add it to the current project. You can use this new spectrum like any other spectrum, e.g. fit it with a model.

⚠ Please note

The Kramers-Kronig-Test can only be performed on the **impedance**!
Don't immediately dismiss data if it shows deviations from the simulated data! The linear method has limitations just like other extrapolation modes.
If no series capacitance is included in the fit, **electrode polarization effects or Warburg behavior may skewer the results**, since they rise to infinity at very low frequencies. The same is true for inductivities.
Hence why we suggest that you use the **Complex Fit** because it can describe such effects as well.
Only some parts of spectra may be invalid. The KK-Test may find such problematic frequency ranges. Avoid using too many time constants to avoid overfitting artifacts in the data!

7.1.3 KRAMERS-KRONIG VIEW

A Kramers-Kronig test can be permanently shown in the RelaxIS user interface by means of the Kramers-Kronig View. To show it, select **Plotting → Create new spectrum view → Kramers-Kronig View** from the main menu.

The view by default uses the following settings:

- Algorithm: Complex Fit incl. series capacitor & inductor

- Automatic number of time constants

These settings can be adjusted using the **Settings** button in the left menu (extend with the arrow button).

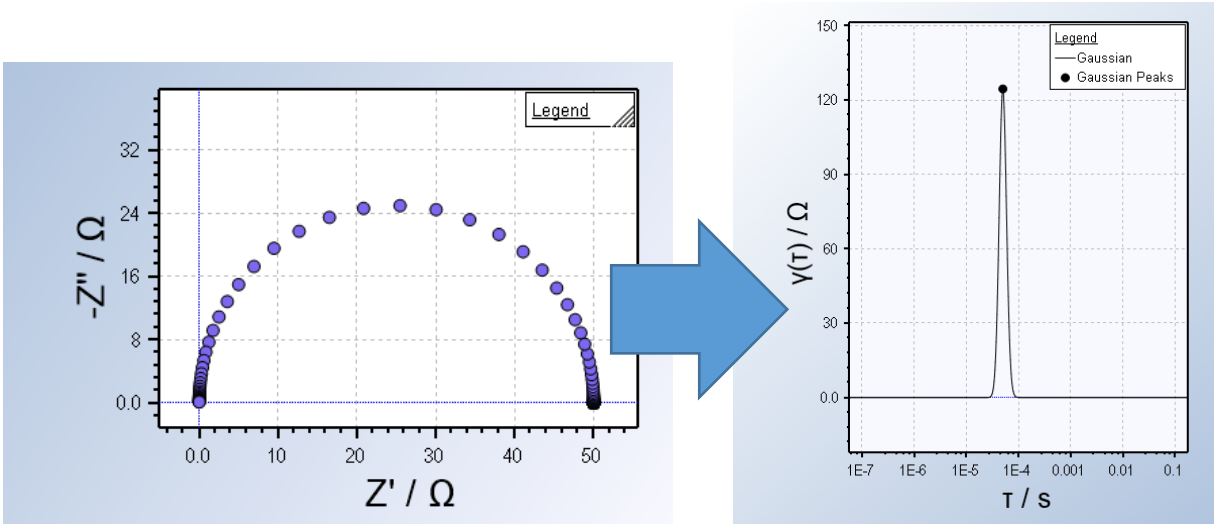
The simulation only uses the active spectrum data.

The result of the Kramers-Kronig simulation is shown as a red line (in case of default plot styles) on top of the impedance data. The plot uses the same plot settings as the Data Explorer and can be changed likewise.

Using the menu to the left (extend with the arrow button) you can show results of a Shapiro-Wilk normality test of the simulation's rediduals. This also displays the maximum relative residuals.

7.2 DRT: Distribution of Relaxation Times

The relaxation time of an (R)(C) circuit is given by $\tau = RC$. If an impedance spectrum is modelled by an infinite sum of (R)(C) elements and the time constants for each is analysed statistically, the distribution of relaxation times is found. That means, that for some time constants a lot of many (R)(C) elements are present, while some time constants are not found at all.



This is a layman's explanation of the DRT theory. For more thorough explanations the reader is referred to scientific literature, e.g. DOI: 10.1016/j.electacta.2015.09.097.

If the distribution function can be found for an arbitrary impedance spectrum, it will show peaks at time-constants that are physically present in the spectrum. This can allow a finer separation of processes and can give answers to the question, if certain semicircles should be described by one or more than one (R)(C) elements.

Optimal data for DRT has little noise and has a constant low-frequency limit. If the data shows, e.g. diffusion of polarization (a constant rise in Z'/Z''), the DRT can often include nonsensical additional peaks (often at high time-constants).

⚠ Caution

Due to the multitude of different calculation parameters, the DRT method can be prone to **misinterpretation of the results**. We strongly recommend, that you first use simulated spectra (e.g. created in the Circuit Simulator, see chapter 17) with a known result, like an (R)(C)-(R)(C) circuit with two time-constants to become intimately familiar with the method.

7.2.1 Calculating a DRT

Select the spectra you wish to use from The Spectra Explorer. Open the DRT dialog using **Data and Quality → DRT**.

On the **Settings** page, you can define the calculation jobs. Each job contains one set of settings, and the DRT dialog will calculate each job for every selected spectrum. You can add or remove jobs using the Add or Remove buttons. To change a job, select it in the list and adjust the settings below it. The settings are saved in the job automatically.

It is possible to save and load a list of jobs to and from an XML file. Right-click the list of jobs on the settings page and use the respective buttons in the context menu.

Advice

For every selected spectrum, the DRT for every job is calculated.
This can quickly amount to a very large number of DRT calculations, which can take a long time. An ongoing calculation can be canceled.

Data settings allow you to include/exclude real and imaginary parts of the impedance. You can also choose to **interpolate the data** to a given number of points. This can improve the resolution of the calculated DRT.

Please note

Interpolation creates data based on the assumption of continuity of the points. Especially if the data is noisy or discontinuous, this can lead to insensible results. Please use the interpolation option with care!

You can also enable the **subtraction of low-frequency polarization** data. This is done in multiple steps:

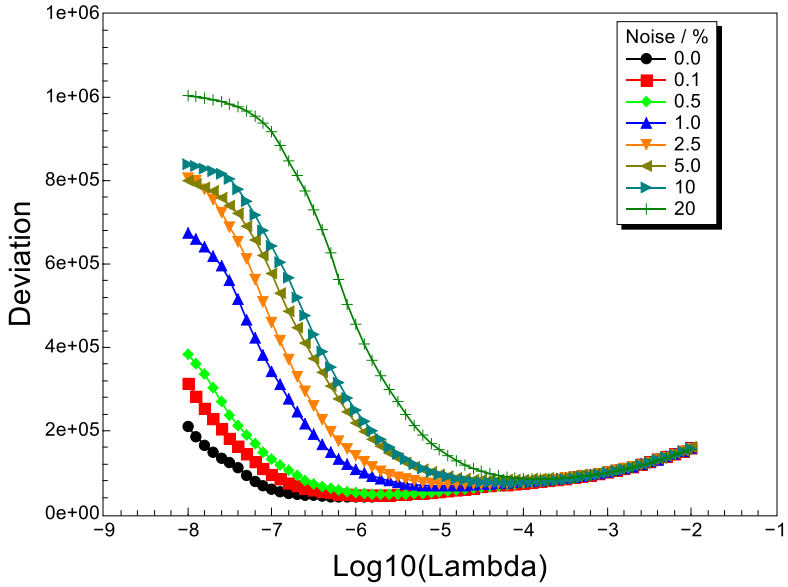
1. A continuous increase of -Z'' is detected and a suitable number of points for analysis is selected
2. An R-CPE model is fitted to the points
3. Values for a CPE with the fitted results are subtracted from each datapoint in the spectrum
4. (optional) a number of most affected datapoints may be removed from completely from DRT calculation

This process may reduce of remove pronounced peaks in the DRT at high time-constants caused by the polarization.

Calculation settings are the most important settings. The data is discretized by a radial basis function. **Gaussian** discretization is often a good choice.

The **Lambda** factor is the so-called discretization factor. Lower values lead to narrower peaks, thus allowing a better separation of peaks. However, it also increases oscillations and can lead to satellite peaks around a process' peak. The noisier the data, the higher Lambda should be chosen. For a known

distribution function, of e.g. an (R)(P) circuit the effect of Lambda can be visualized.



Plotted is the deviation of the calculated DRT from the true DRT as a function of Lambda and of normal-distributed noise added to the simulated spectrum. It can be seen, that Lambda has a minimum at intermediate values. The minimum shifts towards higher values the noisier the data is. A value of 10^{-5} often shows promising results.

The RBF Derivative and shape factor also determine the peak shape and resolution.

If the data has an inductive part at high frequencies, this part can be included in the calculations by checking the respective box.

Output settings determine, how many datapoints are calculated of the DRT function, and what range is used (Extrapolation factor).

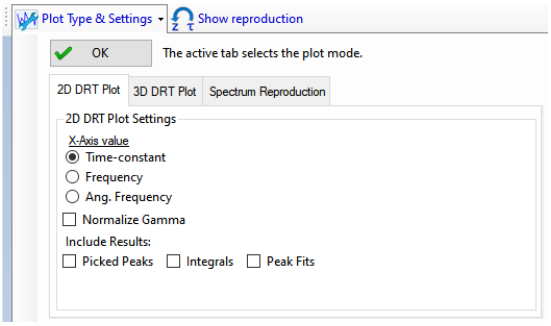
$$\tau_{min} = \frac{1}{f_{max}} \cdot \frac{1}{Extrapolation\ Factor}$$

$$\tau_{max} = \frac{1}{f_{min}} \cdot Extrapolation\ Factor$$

You can always click the **Preview** button. This will allow you to select a spectrum and calculate the DRT for it. The currently selected job is used for the preview.

7.2.2 DRT Plots

The DRT dialog contains plots of DRTs at various steps along the way. Each plot can be configured by clicking the Plot Setup button above it. This opens the settings window for the plot. Clicking Close or away from the window will accept the changes to the settings.



Usually you can plot the DRT in both a 2D and a 3D plot, or you can plot the spectrum reproduction (see section 7.2.3). To select the plot type, switch to the respective tab and click OK. Not every plot offers i.e. the 3D graph or reproduction. In these cases, the respective tabs are disabled.

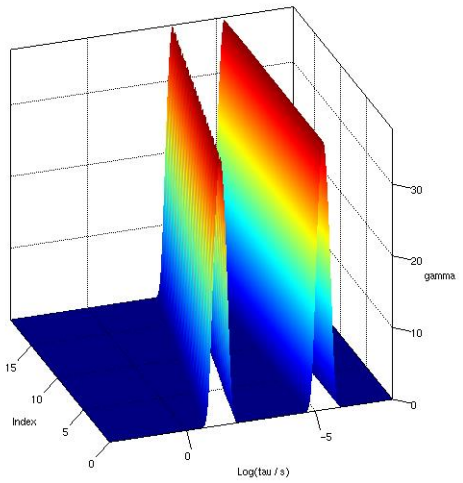
Both 2D and 3D plots allow a selection of the X-Axis value. You can choose between time constant, frequency or angular frequency.

Both plots also have the option to normalize the gamma (DRT) value. In this case each datapoint in a DRT is divided by the maximum gamma value of the DRT.

For 2D plots you can choose which types of analysis results are plotted alongside the data in case they are available for a particular DRT. DRT analysis options are described in section 7.2.5.

For 3D plots you can select the data used to provide the additional axis. This can either be an index, or a metadata value like temperature. If a metadata value is selected but not available for a DRT, this DRT is omitted from the plot.

You can also select if and how thick the DRT lines should be shown, and if a surface should be plotted. For the surface you can select a color map.



7.2.3 Spectrum Reproduction and Lambda Plot

From the DRT, and the fitted series resistance and inductance (found during calculation of the DRT) it is possible to calculate an impedance spectrum by what RelaxIS termed Zarc-integration. Integrating the DRT of e.g. the spectrum of an (R)(C) element over $\ln(\tau)$ the result is the resistance of the (R)(C) element:

$$R = \int \gamma\big(\ln(\tau)\big) d\ln(\tau)$$

RelaxIS calculates a discrete number of time constants of the DRT. To calculate back to the spectrum, the DRT is split into a series of Zarc elements with one element for each calculated DRT datapoint (minus 1).

The nth Zarc element has the parameters (for a sorted list of τ):

$$\tau_n = \frac{\tau_n + \tau_{n-1}}{2}$$

$$R_n = Abs\big(ln(\tau_n) - ln(\tau_{n-1})\big) \cdot \frac{\gamma_n + \gamma_{n-1}}{2}$$

$$\alpha = 1$$

The impedance at frequency f is then given by

$$Z(f) = R_{ser} + i\omega L_{ser} + \sum_n Zarc(f, R_n, \tau_n, \alpha = 1)$$

By calculating the impedance from the sum for each of the initial input frequencies of the spectrum, the spectrum reproduction is found.

As mentioned above, the influence of the Lambda parameter can be estimated by comparing the calculated DRT with the analytical DRT of e.g. an (R)(P) element. For a real spectrum however, the analytical DRT is unknown. An alternative is to reproduce the initial spectrum with the given method and compare the reproduction with the source spectrum. This can be done by calculating the sum of squared residuals, SSR, between the two spectra.

RelaxIS offers the **Lambda Plot** function, that calculates this SSR for a series of values for the lambda parameter. This lets you inspect the influence of the quality of the reproduction as a function of lambda.

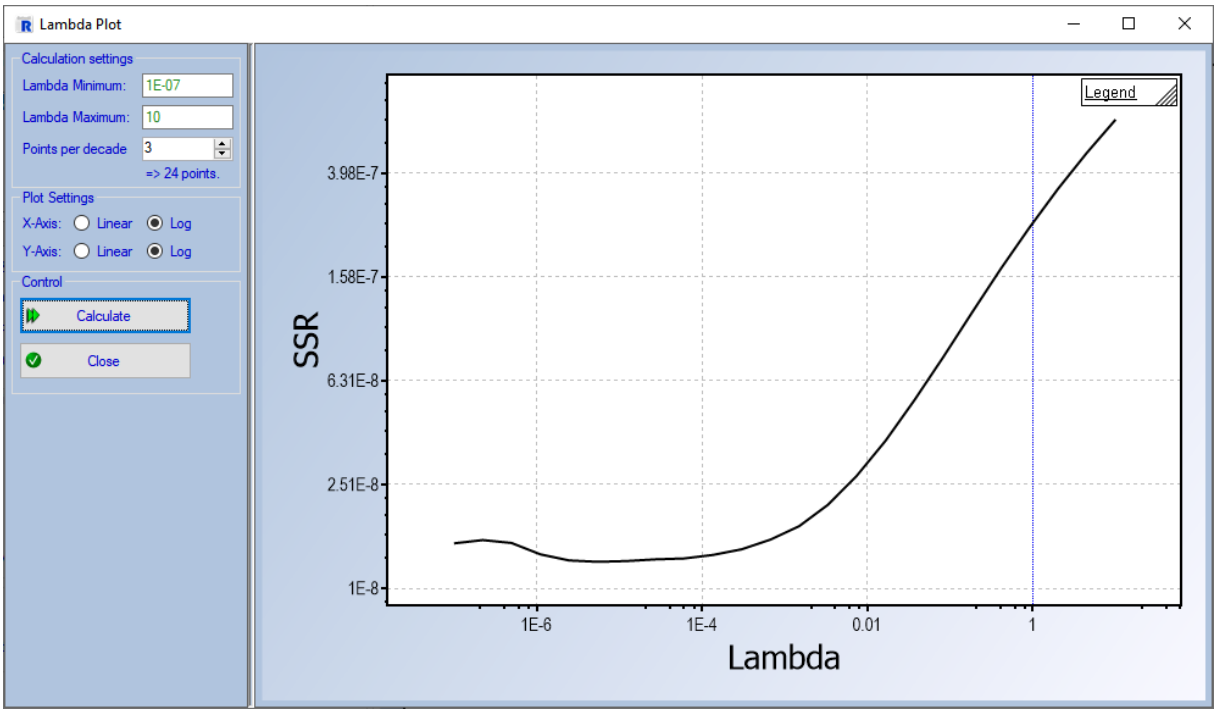
Usually you will find that the SSR first decreases with decreasing lambda until it reaches a point where the improvement is no longer significant. This is in contrast to the comparison of the calculated DRT with the analytical DRT above, where the quality started to decrease again at lower lambda values, due to increased oscillations and ghost peaks, which apparently do not actually lead to a decrease in quality of the reproduction.

⚠ Please note

While the lambda plot usually shows a sigmoidal or exponential decrease it should be noted that this method here is purely empirical. You may be able to find a more reproducible way of selecting lambda from the plot, but this selection is not immediately based on a physical understanding!

What that effectively means is that the same spectrum can be described by multiple DRTs, which is similar to the often-established problem of equivalent circuits, where multiple different models can fit the same spectrum.

To **create the Lambda Plot,** click the Plot button next to the Lambda input field on the settings page. This lets you select a spectrum to perform the calculation for and then shows the Lambda Plot dialog for the selected job.



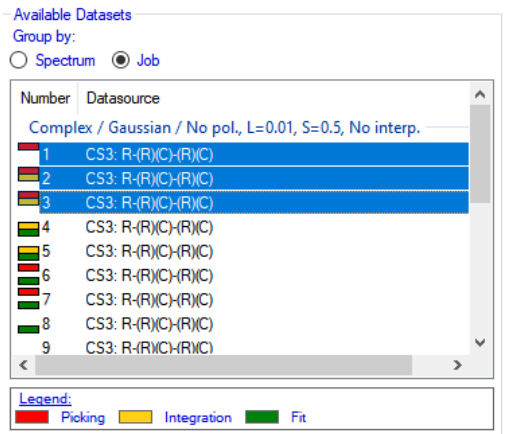
On the dialog you can define the range of lambda values to use. Select the minimum and maximum values and how many points per decade. The plot will use logarithmic spacing between the limits. Please note, that a DRT has to be calculated for each point, so you should keep the number of points at a reasonable amount.

After the selection, use the Calculate button to create the lambda plot.

The data may be exported by using the graph's raw data export function, accessible through the right-click menu on the graph.

7.2.4 DRT Result Lists

After calculating the DRTs, you will find a list of results on the Results page and various sub-dialogs.



The list is used to select datasets for both plotting, applying analysis functions and data export. For instance, the Results Page plot will automatically overlay the results of all selected datasets.

The datasets can be grouped by either source spectrum or job by selecting the respective radio button. A suitable grouping is selected automatically. If i.e. a single job is calculated for each spectrum, the data is grouped by job.

You can select all data sets in a group by clicking on the group header.

The dataset list also indicates which analysis functions were applied to each dataset. Analysis functions are further discussed in section 7.2.5. The indicators are colored bars next to the list entry.

- Red bar: Peak-picking
- Yellow bar: Peak integration
- Green bar: Peak Fitting

7.2.5 DRT Analysis

7.2.5.1 General DRT Analysis

For each calculated DRT data set you can perform further analysis functions. The available functions are:

- Peak Picking
- Peak Integration
- Peak Fitting

The analysis functions are designed to be applied to multiple data sets at the same time. To perform an analysis, first select the data sets you wish to analyze together and then click the respective button in the toolbar on the Results page, which opens a sub-dialog.

Each analysis function has some common behaviors:

- The dialog allows switching between Display and Edit mode using the **Edit Mode** button. In display mode no changes to existing analyses are done and you can inspect existing results or export them.

- In Edit Mode, use the Accept or Cancel buttons to switch back to Display mode.
- The **List / Export** button shows analysis values in tabular form for export. The table also offers a **quick plot** function to plot the analysis result values against i.e. metadata or an index.

7.2.5.2 Peak Picking

Peak picking selects all peak points above a certain threshold from a DRT. A peak point is defined as a point in the DRT where $\gamma(\tau_{n-1}) \leq \gamma(\tau_n) > \gamma(\tau_{n+1})$ and ${\gamma(\tau_n)}/{\gamma_{max}} > Threshold$.

That means that a threshold is applied to the normalized gamma values of the DRT. For example, a threshold of 0.5 means that a peaks gamma value has to be larger that half the maximum gamma value in the DRT.

Further, to reduce the number of peaks in i.e. oscillations, a window function is applied after the peaks have been picked. Here the minimum distance between peaks is defined in units on ln(tau). If two peaks are closer together than this distance, only the larger of the two peaks is kept. This is done repeatedly until no peaks are closer together then the defined limit.

The function also allows a peak refinement. Here, a second order polynomial is calculated for the peak point and adjacent point, and the peak analysis value is then calculated as the extreme value of this polynomial.

The peak analysis results contain the peak position time constant as well as the height (gamma).

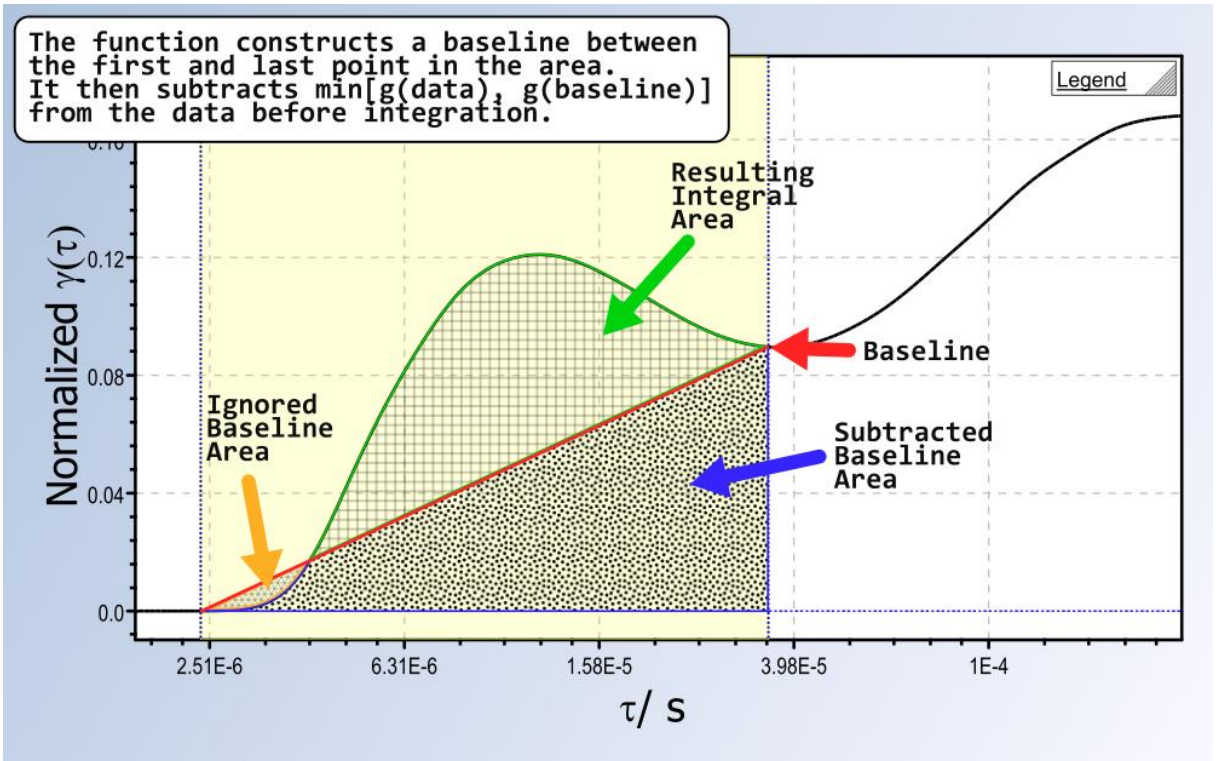
To perform peak picking, select the data sets to use from the Results list, click the **Peak Picking** button in the toolbar and activate the Edit mode. The plot in the dialog shows an overlay of all selected DRTs. You can adjust the height limit by dragging the horizontal bar in the plot. Use the input on the left of the plot to adjust the minimum peak distance and the peak refinement option.

Once satisfied with the options, click the Accept button to accept the picked peaks. Picked peaks are (per default plot style) shown as circles on the plot.

7.2.5.3 Peak Integration

Peak integration analysis integrates the DRT curve in one or more area. The integral is calculated over the $\gamma(\ln \tau_n)$ function. In this case, for example the integral of the single peak of an (R)(C) model gives corresponds to roughly the size of the resistance.

Peak integration also offers rudimentary baseline correction. The process is illustrated in the figure below. The intersection between the left and right window limit and the DRT curve is used as start and end point for the baseline. The integral then only counts data between the baseline and the DRT curve. If the DRT curve is below the baseline, then this area is ignored.



The integral analysis results contain the window position time constants as well as the integral area.

To perform peak integration, select the data sets to use from the Results list, click the **Peak Integration** button in the toolbar and activate the Edit mode. The plot in the dialog shows an overlay of all selected DRTs. You can add areas for integration by clicking the **Add Area** button, remove the last added area with the **Remove Area** button or remove all areas with the **Clear Areas** button.

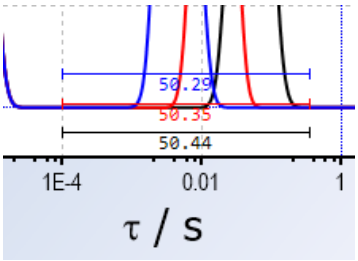
Move the areas on the plot by moving the mouse over the area and dragging the arrows shown.

Each area applies to all selected data sets. If there are conflicts, close the Peak Integration dialog, select fewer and more similar datasets and perform the integration in multiple steps for groups of data sets.

You can enable the baseline subtraction using the checkbox left of the plot.

Once satisfied with the areas, click the Accept button to perform the integration.

Integral values are shown as bars with numbers attached on the plots.



7.2.5.4 Peak Fitting

Peak fitting analysis uses a function consisting of one or more gaussian peaks to the DRT curve. The gaussian peak function is

$$\gamma\big(\ln(\tau)\big) = A \cdot \exp\left(-\frac{\big(\ln(\tau) - \ln(\tau_0)\big)^2}{w^2}\right)$$

For the total fit function, a sum of multiple of such peaks is calculated, with individual parameters A (height), τ_0 (peak position) and w (peak width).

The peak position can be restricted to a certain range for each peak.

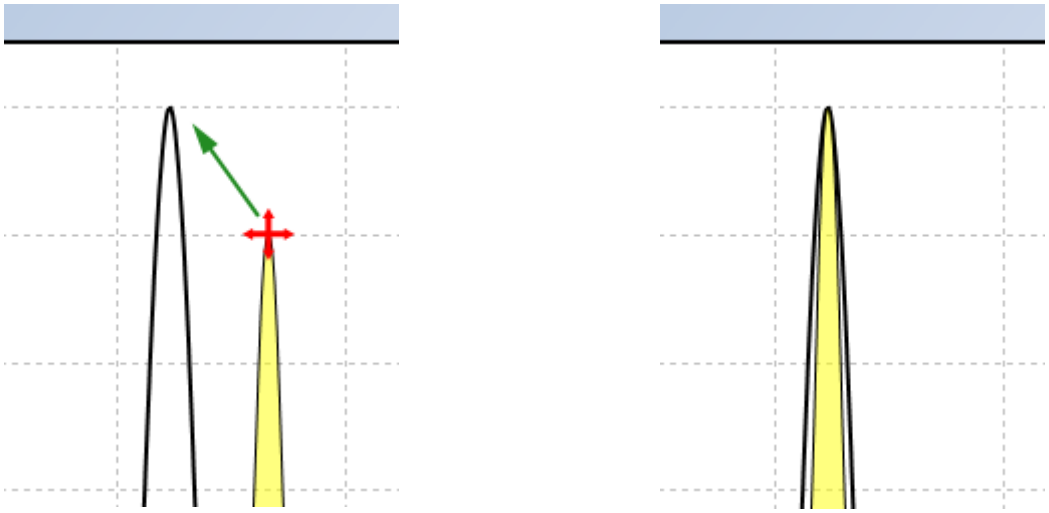
It is further possible to define the data to use via two settings: a **data threshold** (Relevant gamma limit) and **time constant limits**. Only data points with larger γ than the threshold and that have time constants between the limits are included in the fit. The threshold is defined as a percentage of γ_{max} of the particular DRT curve.

The peak fitting analysis results contain the peak positions and individual peak areas.

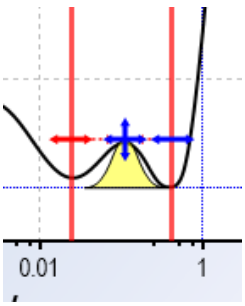
To perform peak fitting, select the data sets to use from the Results list, click the **Peak Fitting** button in the toolbar and activate the Edit mode. The plot in the dialog shows an overlay of all selected DRTs. You can add peaks for integration by clicking the **Add Peak** button, remove the last added peak with the **Remove Peak** button or remove all peaks with the **Clear Peaks** button.

To remove a specific peak, right-click the blue handle that appears when hovering over the peak, and then select “Delete object”.

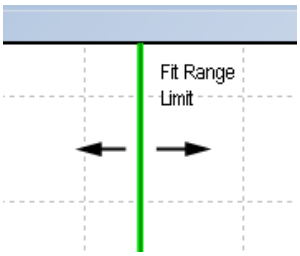
The **peaks define the initial parameters** for the peak fit. Move the initial peaks by moving the mouse over the peak figure in the plot and drag the handle shown. Only the initial peak height and position can be adjusted. The initial value for the peak width is chosen automatically.



If peak position constraints are activated, each peak in the plot will have two additional handles that can be freely adjusted. The spanned window defines minimum and maximum value for the peaks center time constant parameter.



You can change the Fit Range time constant limits either by changing the values directly in the inputs to the left of the plot or by dragging the green, vertical markers in the plot. It does not matter if limit 1 is smaller or larger than limit 2, since RelaxIS will sort the values automatically.



7.2.6 Analysis Result Tables

Each analysis result offers access to a tabular form of the data. To access these tables, select the results you wish to view on the DRT Results page, click the respective analysis function button in the toolbar and then then **List / Export** button on the dialog. The tables are displayed in two separate ways, depending on the number of displayed data sets. For a single data set, the table lists i.e. the result of each picked peak on separate rows, including an index column. If multiple results are selected, the table shows all results for a particular data set on a single row. The row then also includes available metadata of the source spectrum, to allow for plotting of i.e. peak positions as function of temperature.

The analysis table also includes access to a quick plot of the displayed data. To access the plot, click the **Quick Plot** button in the analysis table command. You can select the values to plot on the X and Y axis by changing the value in the dropdown boxes left of the plot and you can select if the axes should be plotted logarithmically.

7.2.7 DRT Data Export

The DRT dialog offers various methods to store and export the calculated data.

- You can store the current result data in the Result Library by clicking the **Save in Result Library** button on the Results page.
- Export DRT curves by selecting the sets to export in the Data Set list, then click **Export Data > DRT Curves** in the tool bar.

- Export DRT spectrum reproductions by selecting the sets to export in the Data Set list, then click **Export Data > Reproduced Spectra** in the tool bar.
- Export analysis results by selecting the sets to export in the Data Set list, entering the respective analysis dialog with the button in the tool bar and then using the Table Display by clicking the **List / Export** button. The table display has buttons to save the data in a file or in the clipboard.
- Export all graphs directly as image or raw data, by right-clicking on the graph and selecting the respective export option from the context menu.

7.2.8 THE DRT VIEW

A DRT test can be permanently shown in the RelaxIS user interface by means of the DRT View. To show it, select **Plotting → Create new spectrum view → DRT View** from the main menu.

The DRT is calculated for the currently selected spectrum and plotted in the view.

Using the **Settings** button in the menu on the left (extend using the arrow button) you can show a dialog that allows you to select the calculation settings of the DRT. Please refer to the descriptions above to learn more about the meaning of the available settings.

7.3 ZHIT

The ZHIT algorithm is similar to the Kramers-Kronig transformation in that it allows you to calculate the modulus of the impedance from its phase-angle. It has the great advantage over KKT in that the calculation doesn't need to integrate over the full frequency range from $0 \rightarrow \infty$, so an extrapolation is not required.

In practice, the algorithm is performed in four steps:

1. The phase-angle data is smoothed over the (natural) log(f)
2. The smoothed data is spline-interpolated

3. |Z| is calculated at each original frequency point by a combination of integration and differentiation to and at the original frequency
4. A |Z| offset is determined by a linear fit

For further details regarding the mathematical background, you can refer to original literature:

- C. A. Schiller, F. Richter, E. Gülzow, N. Wagner, *Phys. Chem. Chem. Phys.* **2001**, 3, p. 374–378.
- W. Ehm, R. Kaus, C. A. Schiller, W. Strunz *in* F. Mansfeld, F. Huet, O. R. Mattos: *"New Trends in Electrochemical Impedance Spectroscopy and Electrochemical Noise Analysis"*, Electrochemical Society Inc., Pennington, NJ, **2001**, vol. 2000-24, p. 1–10.

Step 4 is performed, because the result will have an arbitrary offset in |Z|. This is corrected by a linear fit so the offset between simulation and data is minimal. This linear fit may be weighted, if the respective option is enabled. In most cases, not much difference should be noticeable.

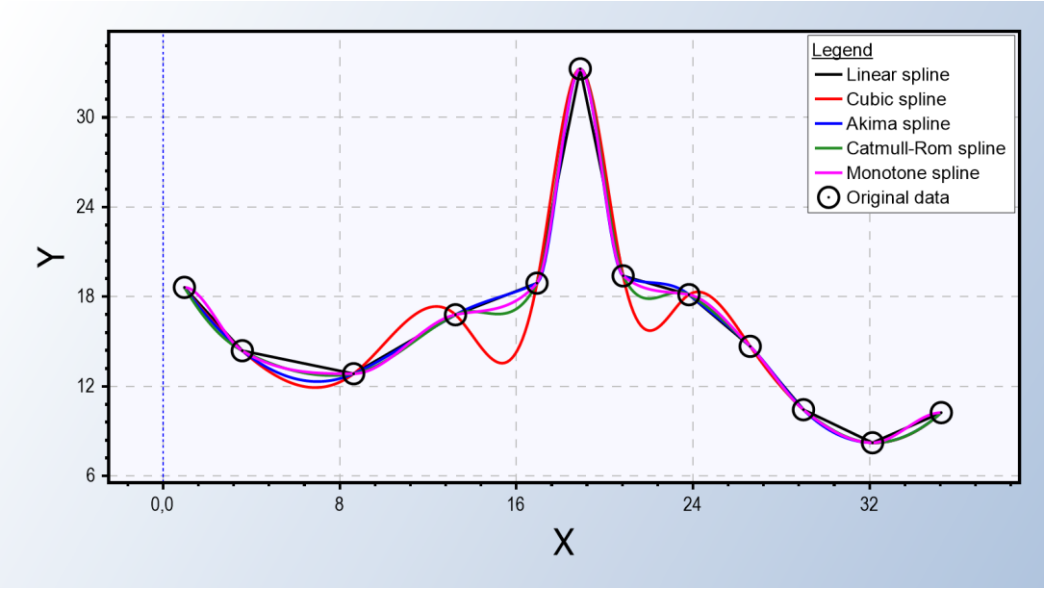
7.3.1 SMOOTHING

RelaxIS offers three different algorithms for smoothing of the input data: LOWESS, LOESS and Savitzky-Golay. Each of the algorithms has a "Smoothing factor", g, as its input, that determines the amount the data is smoothed. For a dataset of n points, the smoothing factor defines how many points, z, are selected for smoothing around a given datapoint, with $z = n \cdot g$. The algortihms typically calculate a linear or polynomial fit through this data and interpolate to the point-to-smooth. The Savitzky-Golay algorithm expects evenly spaced points to function correctly. If your data is not evenly spaced in log-frequency space, deviations may occur.

We recommend the **LOESS** algorithm

7.3.2 INTERPOLATION

The smoothed data is interpolated using a spline. Various types of splines are available. As can be seen in the image below, you can note that different splines react differently at points of sudden changes.



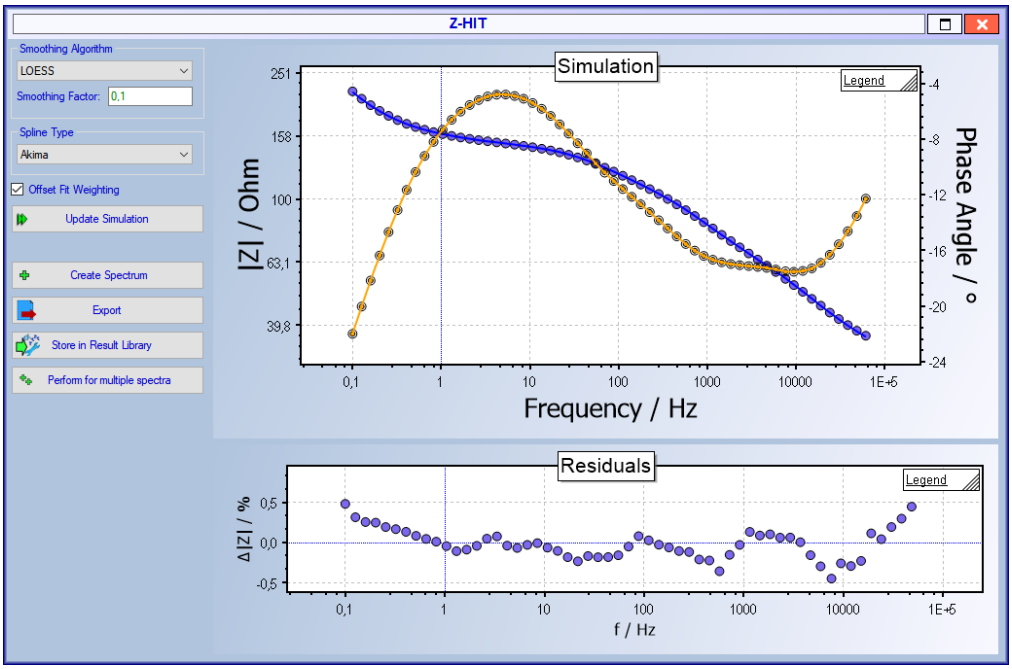
We recommend using **Akima splines**, as they typically follow the "intended" curve quite nicely in the case of impedance data.

7.3.3 CALCULATING THE RESULTS

After selecting the desired options, click the "Update simulation" button to recalculate the result. Both the simulation in a Bode plot as well as the residuals in |Z| are displayed. The Bode plot contains the original data, the smoothed and interpolated Phase Angle plots, and the simulation result.

You can work with the results in multiple ways:

- Create a new spectrum from the results and add it to the current project. This spectrum can be used like any other, e.g. fitted.
- Export the results using the normal export dialog
- Store the results in the Result Library
- Use the currently selected options to calculate the ZHIT result for multiple spectra. This creates a spectrum from each simulation and adds it to the current project.



7.3.4 ZHIT VIEW

A ZHIT simulation can be permanently shown in the RelaxIS user interface by means of the ZHIT View. To show it, select **Plotting → Create new spectrum view → ZHIT View** from the main menu.

The view by default uses the following settings:

- Smoothing: LOESS (smoothing factor 0.1)
- Interpolation: Akima
- Enable offset weighting

These settings can be adjusted using the **Settings** button in the left menu (extend with the arrow button).

The result of the ZHIT simulation is shown as a red line (in case of default plot styles) on top of the impedance data. The plot uses the same plot settings as the Data Explorer and can be changed likewise.

Using the menu to the left you can show results of a Shapiro-Wilk normality test of the simulation's rediduals.

This also displays the maximum relative residual in the data.

8 PLOTTING DATA

The Data Explorer window always shows the currently selected spectrum. By default, the Nyquist Plot of the Impedance is shown here. The plot contains the data points of the spectrum, as well as an always up-to-date plot of the spectrum's current fit (meaning a plot of the spectrum's model, using the spectrum's current parameter values). Whenever you change a parameter value, the plot is updated to reflect the changes.

You can open additional plot and information windows from the Plotting menu, as will be described further down.

8.1 GENERAL GRAPH FUNCTIONS

These points apply to all graphs you encounter in RelaxIS or its other components.

8.1.1 THE CONTEXT MENU

Right-clicking in the graph opens the context menu where you can select the actions performed by the left mouse-button and various other functions.

1. There different modes for the left mouse-button:
    a. **Zoom** allows you to left-click and drag a box on the graph and zoom in onto this area. At all times, you can also use the **mouse wheel** to zoom in and out.
    b. **Drag** allows you to left-click and drag the currently shown part of the graph to a different area.
    c. **Draw circle/line** allows you to draw lines and circles onto the graph. This feature is only used for the Data Explorer graph for initializing fits and will be explained in chapter 10.
    d. **Draw annotation** allows drawing an arrow with a textbox into the graph. If the arrowhead is near data, information about these points can be automatically added to the textbox.
    e. **Drawing objects** allows adding shapes like lines and textboxes to the graph for illustrations. Right-click on the blue mouse handles to access styling options for each object.

   f. In **every** mode, you can always use the **middle-mouse** button to **drag** the graph.
2. **Graph Layout Options** allows customizing the graph's appearance and will be further explained below.
3. **Set Axis Limits** allows settings specific minima and maxima for the axes.
4. **Zoom out once** takes back the last box zooming step. It does not affect the mouse-wheel zooming directly but removes any additional zoom between the current state and the last box zoom step.
5. **Reset zoom** returns the view to the autoscaled values.
6. **Remove all objects** removes all drawn lines and circles.
7. **Export graph image** lets you export the current view of the graph into an image in the Windows clipboard or to a file. This will be explained in more detail in the next section.
8. **Export graph raw data** allows exporting the raw X/Y data of all data curves currently displayed on the graph in the TSV format.

Per default the graph's legend is minimized. Move the mouse cursor over it to expand it. After a graph was selected by clicking on it, the hotkey **Ctrl+L** can be used to permanently show and hide the legend.

8.1.2 Graph Layout Options

To customize the graph's appearance, right click any graph and select **Graph Layout Options**. The options are organized on multiple tab pages.

General Layout gives the following options:

Scaling factor is the overall scaling of the graph. If set to e.g. 2, all elements are rendered twice as large.

Show graph message allows hiding of the graph message.

Scale X/Y1 axes proportional enables or disabled the proportional scaling of these two axes. Proportional scaling means, that the minima and maxima of the axes are scales, such that the value/pixel ratio of them is the same.

Show inactive axes causes, if disabled, that axes without data are not drawn in black.

The **Chart Area Layout** tab gives the following options:

Chart title allows you to set a title that is displayed at the top of the graph.

Inner Chart Area Border allows increasing or descreasing the width of the borders around the inner chart area.

The **Legend** tab gives the following options:

Show legend allows hiding the legend altogether.

If *Keep legend open* is enabled, the legend will not be minimized if the mouse leaves its area.

Set legend title – if enabled – allows you to change the title text of the legend. It supports advanced formatting, as described below.

Legend position allows you to change the position on the chart, where the legend is displayed. Click on one of the green squares to set the position.

The **Axis Layouts** tab is itself divided into three identical pages for each of the three axes of the graph. On each page, you have the following options:

Title allows overriding the title of the axis. The title supports advanced formatting as described below.

Font size allows settings the font size of the title and of the tick labels.

Ticks allows you to set the number of major (long, labeled) and minor (short, not labeled) ticks displayed on the axis. The number for minor ticks refers to the number of minor ticks between each two major ticks.

Show gridlines allows enabling or disabling drawing of the gridlines for the axis. *Show origin line* does the same, but for the line at the zero-value (or one, if logarithmic) of the axis.

Please note

Since several characteristics of graphs are set by templates in RelaxIS, e.g. by the different plot preset plugins, the settings on the Graph Layout dialog may be volatile and be overridden at certain events. The settings are intended to e.g. customize the graph for exporting as an image.

8.1.3 Advanced Text Formatting

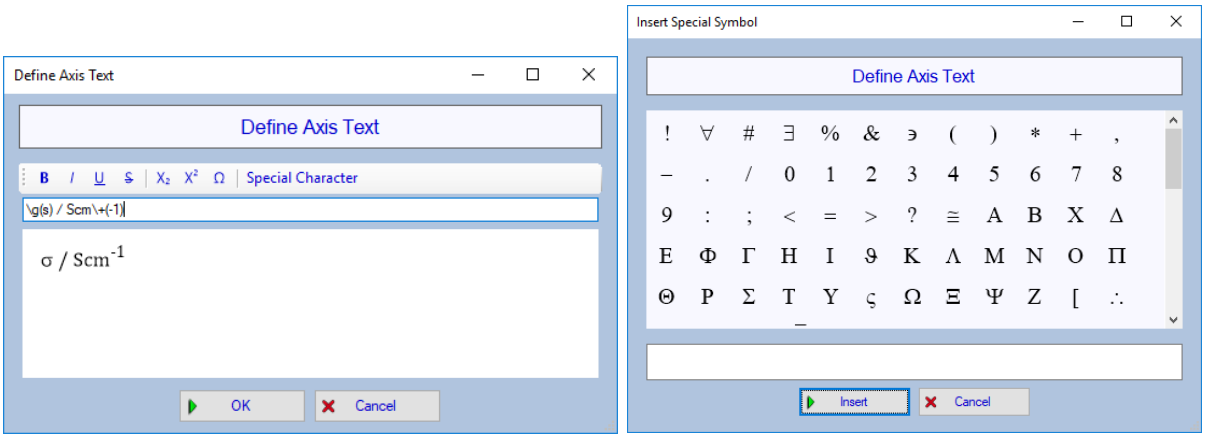
The axis titles and the text in the legend support advanced formatting. This means text can be printed bold, italic or underlined, as well as using the Symbol font, e.g. for greek letters. Text can also be defined as sub- or superscript text. Advanced formatting can be applied from the Graph Layout Settings dialog, or during the export of the graph as an image.

The formatting is applied by using several format tags. Each tag starts with a backslash \ character, followed by a single-letter identifier and a set of brackets (). The text to apply the format to is put into the brackets. Tags can also be nested to apply multiple formattings.

The available tags are:

Tag	Meaning	Example	Example Result
\b()	Bold	\b(Test)	**Test**
\i()	Italic	\i(Test)	*Test*
\u()	Underline	\u(Test)	Test
\x()	Strike-Through	\x(Test)	~~Test~~
\+()	Superscript	Just a \+(Test)	Just a ^{Test}
\-()	Subscript	Just a \-(Test)	Just a $_{Test}$
\g()	Symbol	It's sigma: \g(s)	It's sigma: σ

In addition to using the tags directly, an interface is provided:



E.g. in the Graph Layout Settings dialog click the "…" buttons to show the text input dialog. Enter the text in the textbox in the center. At the bottom, you will see a preview of what you entered. You can use the various buttons to insert a tag fo the respective style. If you select text and the click a button, the tag will be inserted surrounding the selected text. To enter symbols, you can use the "Special Character" button to show a list of special characters. Double click a symbol to place it in the list of symbols to insert. Click "Insert" to place the selected symbols at the current cursor position in the text input dialog.

8.1.4 Exporting the Graph as an Image

When you select to export the graph as an image from the context menu you will be presented with the Graph Export dialog.

To customize the export, you have the following options:

1. Select a size for the image.
    a. You can use pre-defined sizes or enter your desired size by selecting the corresponding radiobutton and entering the values for width and height.
    b. If you select the checkbox to apply the size to the inner chart area the size defines the size of the inner rectangle of the graph and the overall image will be larger.
    Please note: The box size may vary by a few pixels due to scaling details.
2. If larger sizes than the current graph size is chosen, the graph's scaling factor is changed to keep the graph elements in proportion. This can be disabled with the "Scale graph elements" option. By default, the

elements are also only scaled up. Alternatively, you can set a fixed scaling factor to keep the layout of the image independent of the source graph size.

3. Enabling **White background** sets the graph background to white, making it more compatible and easy to print.
4. You can override the titles displayed on the axes by enabling and entering text into the respective textboxes.
5. You can force the graphs legend to be open on the exported image.
6. You can adjust the titles of each series that is displayed in the legend.
7. You can define if you want to export the image to the Windows clipboard, to a PNG file or to an SVG vector image file.

Once you set the desired options, click Export to export the graph into the format of your choice. Afterwards click the Close button to close the export dialog.

It is possible to export the image as an SVG vector graphic by selecting the respective format box. How vector graphics look is up to the viewing software, because a vector image is just a text-based description of the graphic's contents (as compared to bitmap images, that tell the exact color of each point). While we strive to make the SVG image as identical to the source as possible, due to some incompatibilities in the creation of the SVG as well as in the reproduction of the image by your SVG viewing software some differences may occur.

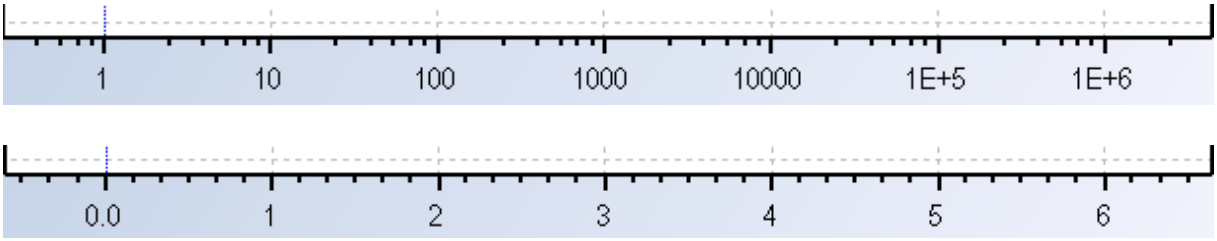
8.1.5 Graph Raw Data Export

Every graph supports the export of the raw data that is currently displayed on it. You can select this function with the **Raw Data Export** button on the graph's context menu.

You can select the export target (clipboard or a textfile) and the contents of the export.

An important setting is what happens with logarithmically plotted values, as for example in Bode-plots. In the Bode-plot, the frequency is plotted logarithmically by default. This means, that the plot's raw data contains the

actual logarithms. For the main graph in the Data Explorer window RelaxIS offers the option (*Main→Settings→General Options→Graph axis number format*) to show the original number instead which changes the linear looking axis to the commonly known logarithmic style. This is illustrated in the following images:



Whenever the latter is used, it may make sense in the Raw Data Export to also enable the export "As original number". In this case the export will contain 10^x instead of *x* for each value in the respective column. If the former number style is used from the Settings dialog, this export option will have no effect.

8.2 Special Options for the Data Explorer Graph

General plot display options can be selected in the **Miscellaneous** section of the **Plotting** tab of the main ribbon:

- **Show gridlines** toggles the display of helper lines in the plot.
- **Equal axes scaling** causes the X and **primary** Y axes to be scaled symmetrically. This means that the shown data ranges are adjusted such that the d_{Value}/d_{Pixel}-quotient is equal. In Layman's terms, data representing a circle will be shown as a circle and so on.

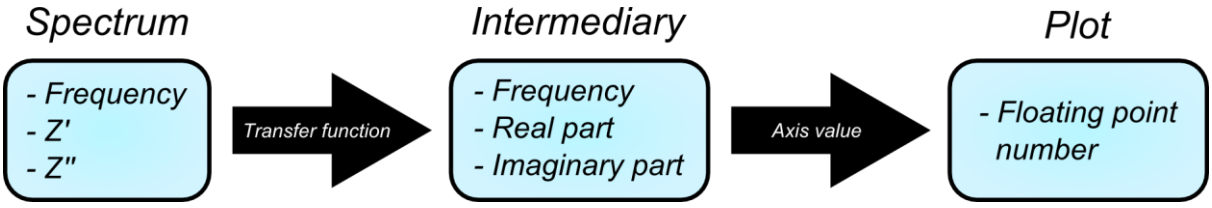
> **⚠ Please note**
>
> Whenever you encounter weird looking plots, especially with logarithmically scaled axes, please check if this option is still enabled.

- **Only zoom to data** causes the autoscaling function of the plot to only take the spectrum's data points into account while ignoring the fit curve drawn alongside it. This is enabled by default, since – especially before

a fit is performed – the fitted curve often lies way off the interesting data and makes the graph confusing.

8.3 Axis Values

The Data Explorer plot can be fully customized to show the information you prefer. What is shown on each axis is defined by selecting an axis value (that is calculated from each complex value of a data point). You can create different axis values using the **RelaxIS SDK**. The calculation process for data on the plot is visualized in the following diagram.



The axis values provided by RelaxIS are:

Value	Explanation
Real part	The real part of the intermediary number
Imaginary part	The imaginary part of the intermediary number
Negative imaginary part	The imaginary part multiplied with minus one
Magnitude	The magnitude of the intermediary number
Frequency	The frequency of the data point
Phase angle	The phase angle (or argument) of the impedance
Angular frequency	The angular frequency $\omega = 2\pi f$ of the data point
Empty	Shows no value on this axis

8.4 Changing Axis Values

You can change the values shown on each axis in the Data Explorer window by

1. Clicking one of the 3 **Axes display options** buttons in the **Plotting** tab.
2. Double-clicking one of the axes directly in the plot.

You will be presented with a dialog listing all available axis values. Select a value and click **OK**.

Furthermore, you can choose to plot the respective axis **logarithmically** by selecting the corresponding checkbox in the dialog.

8.5 Plot Templates

Plot templates combine a set of axis values and additional graph options to produce commonly used plots like the Nyquist or Bode plot. Plot templates can be created using the **RelaxIS SDK**. They also take the currently selected transfer function into account. For example, the Nyquist plot uses the negative imaginary part for the impedance, but the non-negative imaginary part for the admittance.

The three plot templates available in RelaxIS by default are:

Plot name	**Description**
Nyquist	• X-Axis: Real part • Y1-Axis: (Negative) imaginary part • Y2-Axis: Empty • Same axis scaling
Bode	• X-Axis: Frequency (logarithmic) • Y1-Axis: Real part (logarithmic) • Y2-Axis: Imaginary part (logarithmic)
Bode Phase Angle	• X-Axis: Frequency (logarithmic) • Y1-Axis: Magnitude (logarithmic) • Y2-Axis: Phase Angle

You can change the Data Explorer graph to a template with the **Change preset** button in the **Plotting** tab.

8.6 Creating an Overlay of Multiple Spectra

You can display multiple spectra at a time using the **Combined Data Plot** button on the **Plotting** tab. By default, the Combined Data Plot plots an overall of the currently selected spectra in the group.

The selected spectra, presented in the **same graph style as currently selected for the Data Explorer** graph. That includes axis values and styling.

The buttons on the left side allow you to switch between plotting the currently selected spectra and plotting spectra selected through the Spectra Selection dialog. If you disable plotting the currently selected spectra, use the now enabled button underneath to select the spectra you wish to plot.

You may also pause automatic updating of the graph using the Pause button.

The plot can be controlled using two configuration dialogs – one for general graph options (wrench symbol) and one for data normalization and recalculation (calculator symbol).

In the general graph option dialog, you can select which type of graphs (data and or fits) should be included. Fits are always plotted as lines but you can choose between different plot types for the data. You can furthermore adjust symbol sizes and line width for the plots.

Furthermore, you can define a format for the automatic legend entries. You can create a text containing various tags. All tags start with the # sign and are followed by one or more characters indicating the value to be inserted at this position in the string.

The usable tags are:

Tag	Description
#N	The Datasource of the spectrum
#AX	The series' axis given as "Y1" or "Y2"

#AL	The series' axis given as "Left" or "Right"
#AT	The current title of the series' Y axis
#XT	The current title of the X axis
#G	The spectrum's current model
#Y	The series' type, being either "Data" or "Fit"
#I	The spectrum's index
#HASH	The literal # (hash) character
#P	A list of available metadata, separated by a comma
#T	The temperature metadata
#DC	The DC Voltage metadata
#AC	The AC Voltage metadata
#FV	The Free Variable metadata
#FV2	The Free Variable 2 metadata
#A	The Area metadata
#d	The Thickness metadata
#H	The Harmonic metadata
#TM	The Time metadata
#C	The Concentration metadata
#J	The Current metadata

Combining these with an arbitrary string can produce the legend text you like. Some examples are:

Legend text	**Result**
#N (#P)	C:\Data\Data.txt (T=20, A=1, d=13.2)
#N (T=#T˚C)	C:\Data\Data.txt (T=20˚C)
#T, #DC	20, ---
#Y #HASH#I, #AT: (#P) #N	*Default legend format* → Data #2, Z' / Ohm: (T=20) C:\Data\Data.txt

Even though RelaxIS uses only geometry-dependent transfer functions, the Combined Data Plot allows you to plot the normalized transfer functions if you provide Area and Thickness values.

To normalize the data, check the **Normalize values** checkbox in the recalculation settings dialog. If the spectra don't contain Area and Thickness values in their metadata, you can check the override box and enter values manually. Please also select the correct units for the values. **Metadata values are considered to be given in m and m²!**

The dialog furthermore gives you the option to recalculate the X and Y values for all datapoints. You can give separate formulas for Y1 and Y2 values.

8.7 Showing Additional Plots

You can open additional plot windows that can show different plot presets alongside the main Data Explorer window. To open a new window select **Create New Spectrum View→Plot View** from the **Plotting** tab. The window can be docked in the main window and will always show the plot of the currently active spectrum. The menu on the left allows you to select either a plot preset, or individual axis values, just like the Data Explorer. You can also select, if gridlines should be shown, as well as scaling options.

Clicking the Settings button in the menu on the left allows you to adjust advanced settings. You can set the window title, as well as the Transfer Function that is used for the plot. If you select *Globally Selected,* always the currently active transfer function is used to plot the data.

Furthermore, you can enable normalization of the data with the geometric parameters **Area** and **Thickness**. All default transfer functions support normalization, but custom plugins may not. This enables you to display plots of e.g. **conductivity** or **permittivity**. This only works, if the Area and Thickness metadata is defined for a spectrum. If it is not, you can choose to use globally defined geometric parameters instead. Last, you need to define in which **unit** the **Area** and **Thickness** is given, to allow correct calculations.

8.8 Fit Extrapolation

The Data Explorer and Plot View contain additional series that show the current model functions, as will be explained in the following sections.

Selecting **Fit Extrapolation** from the **Plotting** menu, will open the Setup dialog on the Display tab, where you can use the **Extrapolate** checkbox to enable fit extrapolation. Instead of calculating the model curve only in the frequency range of the data RelaxIS will use the frequency limits set in the text boxes in the Setup dialog as the lower and upper limits for the model curves.

This allows you to check, how the model behaves outside of the data's frequency range, and read off, for example, where a low frequency semicircle drops back down to the real axis.

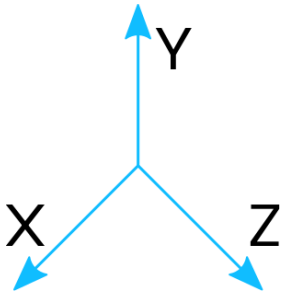
8.9 3D Graphs

RelaxIS allows you to view 3D graphs of your data. You can select axis values for an X, Y and Z axis and RelaxIS will create series for each selected spectrum.

8.9.1 General Setup

To show the 3D graph, select **Plotting → 3D Graph** from the main menu. The graph with use the currently selected transfer function, so please select it beforehand. Use the spectra selection dialog to select which spectra you wish to include in the plot if enabled, or the currently selected spectra are used.

The plot's axes are arranged as depicted on the right. The figure shows the axes in their increasing direction.



By default, the axis values are selected as follows:

- X-Axis: Logarithmic frequency
- Y-Axis: Negative imaginary part
- Z-Axis: Real part

This means, that you will see a mix of a Bode and Nyquist Plot, where the former is seen in the XY- and XZ-planes, while the latter is visible in the YX-plane.

To set another axis arrangement, click the Settings button on the left.

The settings dialog is split into 3 tabs: Axis settings for selecting the data to plot, Data Series settings to change data series display style options and Surface plot settings to change styling of the surface plot.

On the axis settings tab you can select which value is shown on which axis. Please note, that you can select the typical plot values, but in addition you can also select metadata. This allows you to e.g. set the temperature to the X-axis and get a staggered Nyquist plot with the spectra separated via the temperature.

Use the checkboxes next to the axis values to select if a value is calculated logarithmically. Currently, the graph only supports displaying the actual logarithmic values instead of the source values on a logarithmic scale.

You can also override the axis titles by enabling the respective checkbox and entering a title.

On the Data Series settings tab, you can influence the display and styling of the graph by setting point and line sizes/width. Setting either to 0 will disable the trace. You can also override the colors of the series to a fixed color. Otherwise the color list defined the respective plot style is used (see chapter 8.10).

The Surface plot settings tab allows you to change the display of the surface plot. You can change the color map for the graph, and decide if a wireframe surface should be shown. For more details about the surface plot see chapter 8.9.3).

8.9.2 EXPORTING

You can export the graph as an image by clicking the “Export Screenshot” button. The screenshot can be set to the Windows clipboard or saved in a file.

You can also export the raw data that is currently plotted by clicking the “Export” button. By default, three columns per spectrum are created. You can also enable the export of all series combined in one XYZ-column set. This is helpful if you want to use a different software to create e.g. a surface plot.

8.9.3 SURFACE PLOTS

The 3D graph in RelaxIS offers two ways of displaying a surface plot. You can add the surface plot in the built-in plot by enabling it in the graph settings as discussed above. The second method is to show the surface plot in an **External Browser**, using the Plotly.js javascript library to create the surface plot. The Plotly library offers additional customizability for the plot and may be your preferred option.

The surface uses a color map. This map is a list of colors that are interpolated alongside the vertical (Y) axis. The default is a rainbow map.

For the Plotly surface, first setup the graph with the axis values you want to see. Please note, that for the surface plot datapoints from all series are combined into a single dataset, and the surface will be drawn over over it. You can think of the datapoints as points measured in a land survey. Scattered at various locations in the XZ-plane the height of the ground is measured (Y-values). From this data a surface elevation map is reconstructed. This is then displayed as the 3D surface.

To display the surface plot in a browser, click the “Surface Plot” button on the left.

You can customize the plot using the Plotly Chart Studio, accessible via a button in the top right of the plot.

⚠ Please note

Using the Chart Studio redirects you to an external site, that may or may not process your spectra data. Please use this site at your own discretion and review their data privacy policy at:
https://plot.ly/privacy/

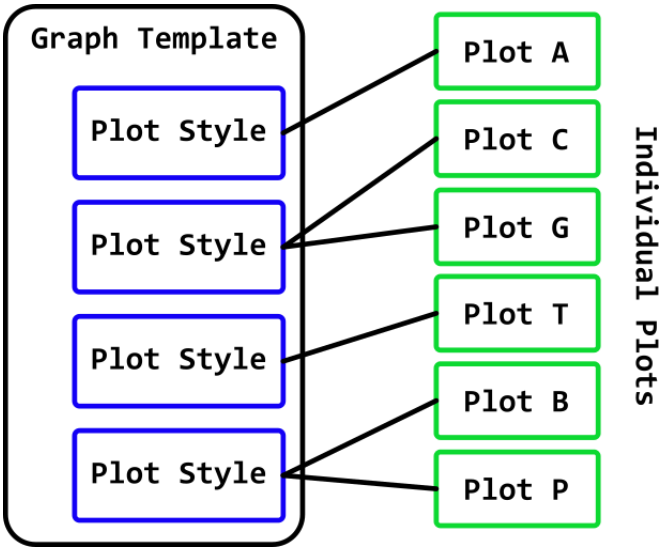
8.10 Customizing the Graph Layout with Styles

8.10.1 General Introduction

RelaxIS contains a large number of different plots, that have individual number of series and meanings of the series. This basically requires different styling of the series for each plot. However, many graphs are at least similar, and hence can share their styling.

RelaxIS offers the possibility to freely adjust the style of the graph, by using graph templates. A template contains all information about every graph in RelaxIS or the Circuit Simulator. You can switch from one template to the next easily. This for example offers the opportunity to use one template optimized for being used on a computer monitor, but switch to another template optimized for printing the graphs when preparing figures for papers.

A **graph template** contains multiple **plot styles**. A single plot style defines the visuals of the overall graph (background colors, axis thickness, etc.) as well as two lists of **series styles**, one list for the Y1 axis and one for the Y2 axis of a plot. A single **series style** defines i.e. series type (line, scatter..), line color or symbol size.

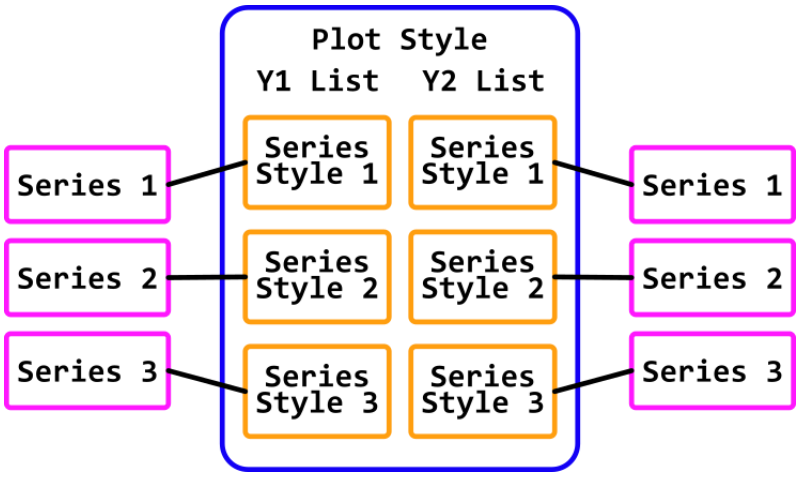


The template further contains an **association table** between particular plots in RelaxIS / CS3 (i.e. Data Explorer plot, or DRT result plot) and a **plot style**.

Often graphs are similar enough to share a plot style, and that way the required number of plot styles is reduced. It is always possible to change the

association. If you want one specific graph to look different, you can create a separate plot style and assign it to only this specific graph.

When a graph is plotted, it creates its data series for Y1 and Y2 and then the plot style is applied by selecting series styles from the respective lists for Y1 and Y2 one after the other.



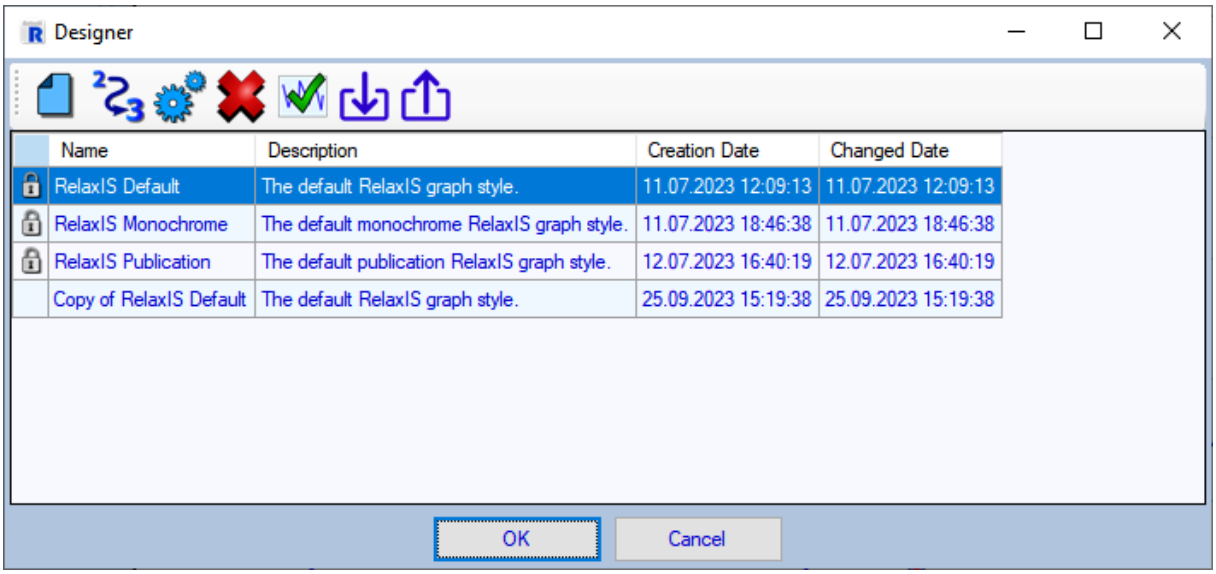
As an example, the Data Explorer plot has 4 possible series on Y1 and Y2: Data Points, Inactive Data Points, Fit Model Curve, Test Fit Curve. Hence, a graph template for this plot should contain 4 series styles in the Y1 list, and 4 series styles in the Y2 list.

Other plots may have varying number of series. For example, the Result Preview plot depends on how the data is split. In these cases, the series styles are still applied one after another to the created series. If the list of series styles is exhausted it wraps around and starts from the first series style in the list again. Hence, a suitable plot style template for the Result Preview should contain a relatively long list of styles to facilitate distinguishing between a good number of data series.

The required amount of work to create a graph template from scratch is quite large, given that over 50 different plots need to be taken into account. It is therefore recommended to clone a built-in template and then only change the styles you need.

8.10.2 Managing Graph Style Templates

Style templates are managed by the Style Library, accessible via the main menu **Plotting → Edit Graph Style**.



The currently active template is marked with a green background.

RelaxIS differentiates between built-in default templates of which there are three and user-defined templates. The built-in templates are marked with a lock symbol because they cannot be edited.

You can create new templates either from scratch by clicking the **Add** button, or you can duplicate an existing template by using the **Duplicate** button.

User-defined templates can be deleted using the **Delete** button and edited using the **Edit** button.

The **Import and Export** buttons allow easy sharing of style templates. The export button saves the style in an .XML file at a specified location, which can be shared with other users. They in turn can import the .XML file using the import button.

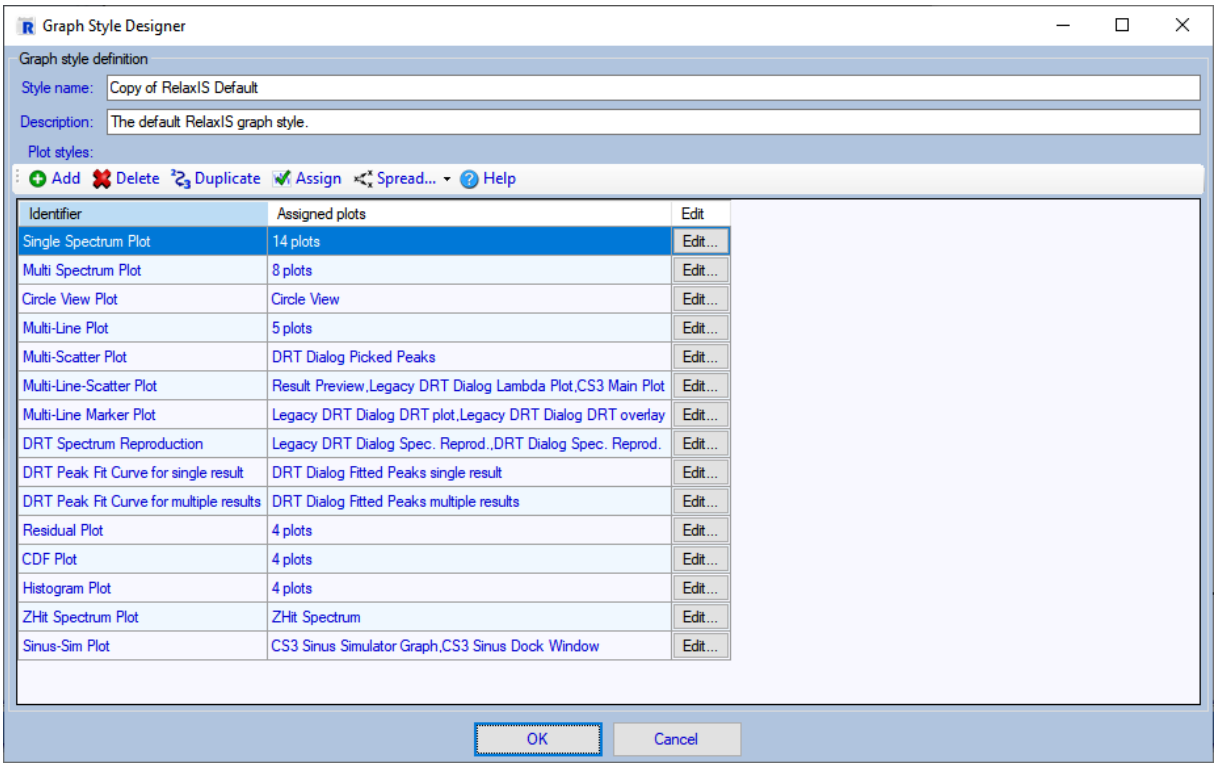
You can apply a template to all graphs in RelaxIS by selecting the template from the list and clicking the **Apply** button.

The Circuit Simulator 3 also uses the template selected in RelaxIS, but you can't access the style library from CS3. Instead, change or select the style

template inside of RelaxIS, and the, in CS3, click the **Main → Style settings → Refresh Active Style** button.

8.10.3 Editing Style Templates

To change a user-defined templat, select it from the list in the Style Library and click the **Edit** button to show the Graph Style Designer.



The Graph Style Designer shows options to change the template name and description at the top, and the list of plot styles, together with a toolbar of relevant actions. The list also shows how many different plots are currently assigned to each plot style.

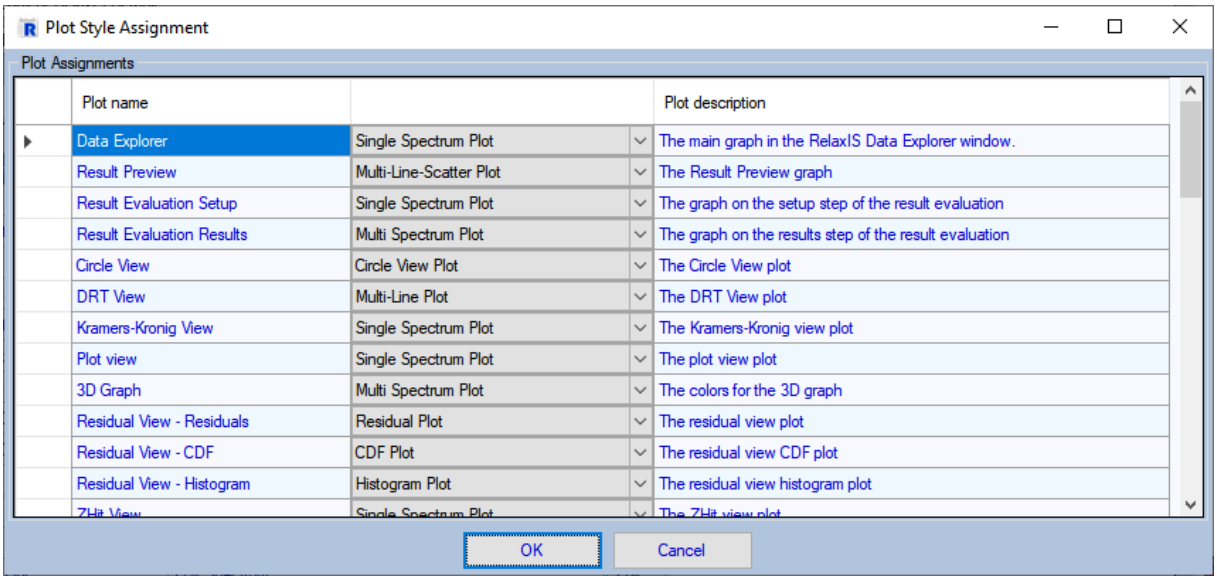
Use the Add, Delete and Duplicate buttons to manage the list.

Click the **Assign** button to change the assignment between specific plots and plot styles, as described below.

The **Spread** menu allows you to assign parts of the currently selected style to all other styles in the template. For example, if you change a graph background color and want all other templates to use the same, select the source style and click Spread > Outer Graph style. You can also share the axes or legend styles separately.

8.10.4 Assigning Plot Styles to Specific plots

Clicking the Assign button shows the plot assignment dialog.



In the list you will find an entry for every specific plot in RelaxIS and the Circuit Simulator. Next to each entry you will find a dropdown menu that contains all currently defined plot styles in the template. Change the dropdown for a specific graph to a plot style you wish to use for that graph.

Note that many plots share the same styles per default. Feel free to define individual style templates and assign them to one or more plots in this window.

8.10.5 Defining a Plot Style

Plot styles are defined in the Plot Style Editor and its sub-dialogs. The sub-dialogs are accessed by clicking **Edit**… buttons on the dialogs. The dialog structure with settings is as follows (*italic* marks sub-dialogs):

- Plot Style Designer
  - Identifier
  - Scaling factor
  - *Graph style*
    - Graph title
    - Outer graph border (between title and outer edge)
    - Inner back color

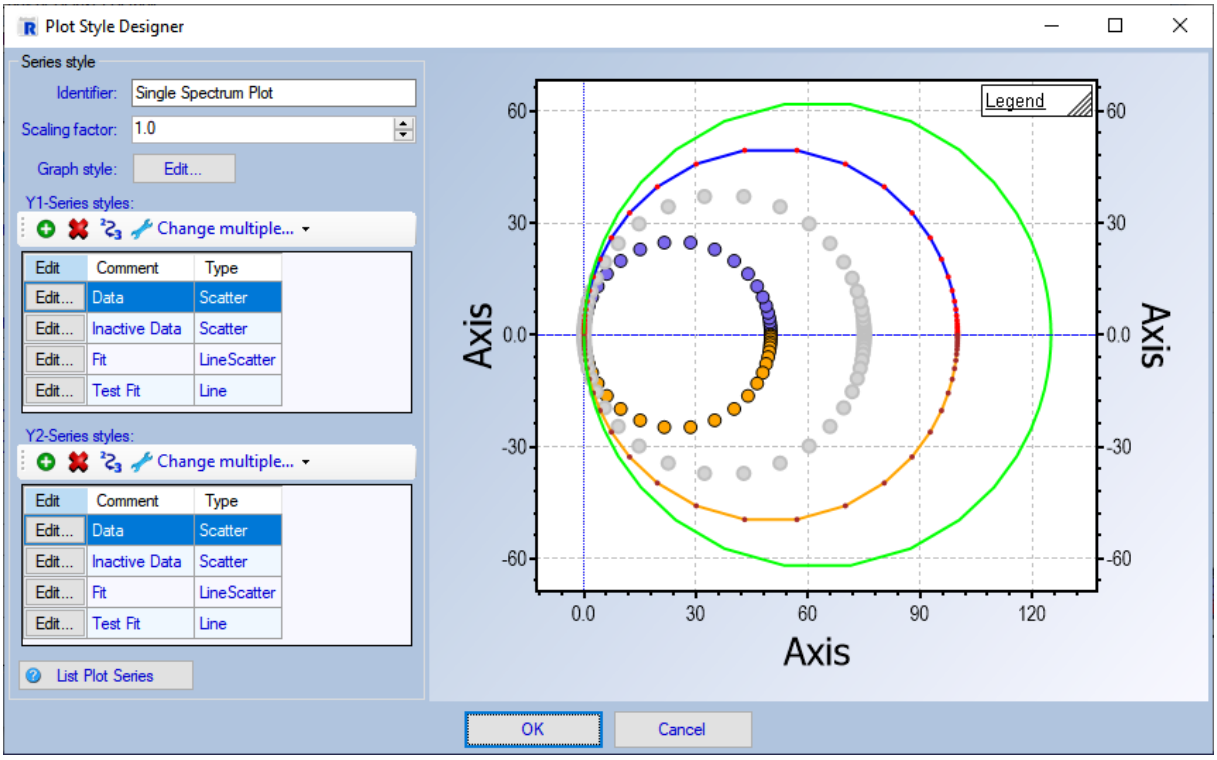
- Top-left color
- Bottom-right color
- *X/Y1/Y2 axes style*
  - *Title font*
  - Title color
  - Grid lines enabled
  - *Grid line style*
    - Line color
    - Line thickness
    - Line style
  - Origin line enabled
  - *Origin line style*
    - Line color
    - Line thickness
    - Line style
  - Axis line color
  - *Tick Style*
    - *Tick label font*
    - Tick label color
    - Tick label number format
    - Tick direction
    - Tick width
    - Number of minor ticks
- Axis thickness
- Legend Style
  - Legend enabled
  - *Legend font*
  - Title visible
  - Legend title
  - Legend position
  - Legend always open

- Y1/Y2 Series styles (can add, remove, duplicate…)
  - Comment

- Series type
- Line width
- Line color
- Line pattern
- Marker type
- Marker size
- Marker color
- Marker border width
- Marker border color

The editor dialogs show a preview of the style they are editing. In many editors when multiple series are previewed, the data series with positive Y values show the Y1 series styles, while the series with negative Y values show the Y2 series styles.

For a plot style you can define the **Identifier** (used for Plot assignment), as well as the overall scaling factor on this dialog. You can also change the series style lists.



Most editor value inputs should be intuitive. Special editors are used for defining colors and the legend position.

The color input contains to elements: A colored button, that, when clicked, shows a color selection dialog. Next to it is a slider that defines the transparency of the color. Move it to the left for fully transparent, or to the right for fully opaque.

Right-click on the color editor and select Copy from the context menu to copy the hex ARGB value into the clipboard. Click Paste in the context menu to paste this entry into other color inputs.

The legend position input contains 8 green squares that when clicked defines the position of the legend in the graph.

8.10.6 Defining Series

The Plot Style editor contains two lists, one for Y1-axis series styles, another for Y2-axis series styles.

Above each list are buttons to add, remove or duplicate a style. For the latter 2, first select the style you wish to delete or duplicate.

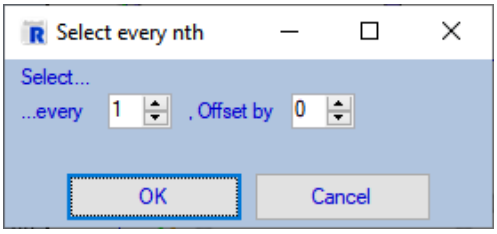
As mentioned in the introduction, it is important to know what series a particular graph creates, so that the correct list of series styles can be defined. On the Plot Style Designer click the **List Plot Series** button to show a list of all plots in RelaxIS and the Circuit Simulator. Selecting a plot in the list will display information about the plot on the right, i.e. the series it will create. Use this list to define the required series for the graph.

Click the **Edit**... button next to a series to edit its styles on the series style editor sub-dialog.

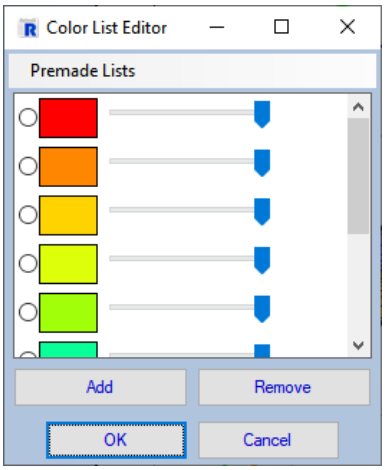
When changing a template, it is often useful to change properties of multiple styles from a list. To facilitate this, open the **Change multiple**... dropdown. Here you can apply various properties from a defined list to all currently selected styles:

- Marker colors
- Line colors
- Marker styles
- Line styles

First, select the series styles you wish to change. You can use the **Select every nth** button in the dropdown to select i.e. every 3rd series in the list, starting from the 2nd.



Next, click the button for the property you wish to change, i.e. line colors. This shows a dialog with a list of colors.



You can add entries with the **Add** button, or remove entries by selecting the radiobutton next to it and clicking **Remove**. Change entries by using the respective input.

After clicking **OK**, the list will be applied to the selected series from top to bottom, including wrapping around.

9 Equivalent Circuits and Models

9.1 Defining Models

Models are implemented as circuit elements in RelaxIS. Each circuit element has a specific impedance expression. The elements can be combined to more complex models by connection them in series or parallel.

Series connection: $\hat{Z}_{total} = \hat{Z}_1 + \hat{Z}_2$

Parallel connection: $\frac{1}{\hat{Z}_{total}} = \frac{1}{\hat{Z}_1} + \frac{1}{\hat{Z}_2}$

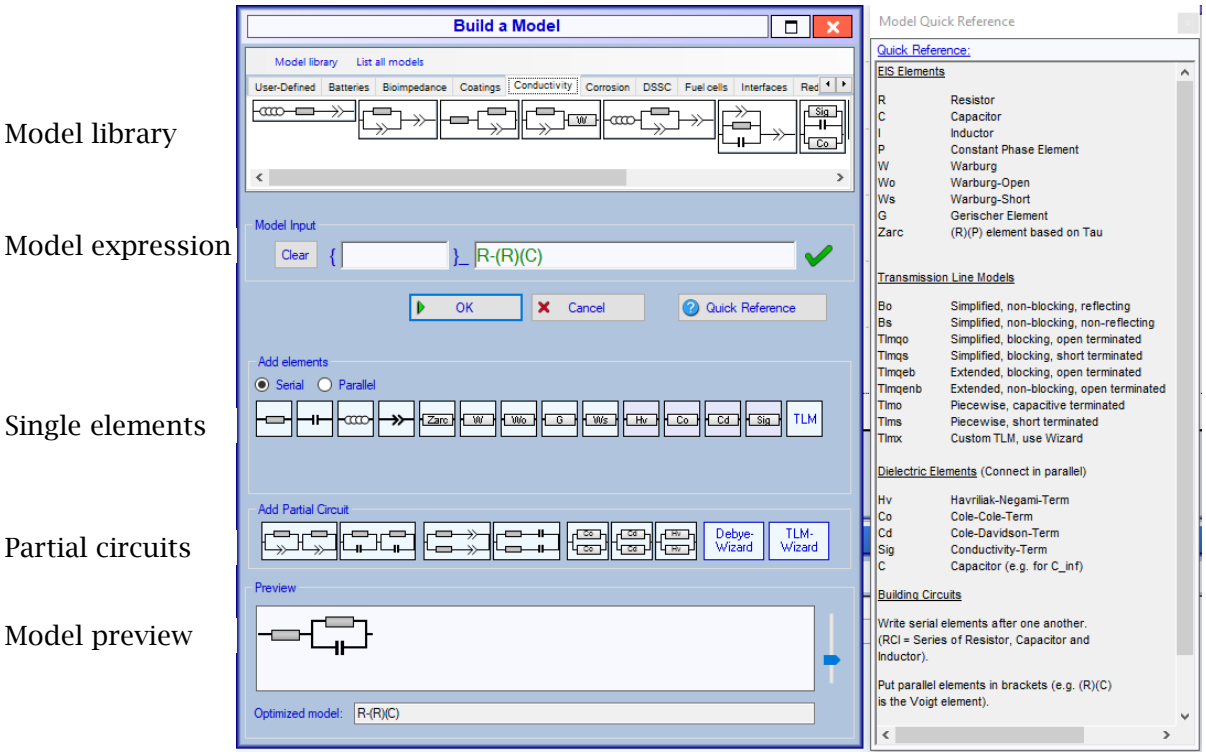
This means, that apart from equivalent circuits also models such as **Havriliak-Negami** models with multiple terms and e.g. C_{inf} and conductivity terms can be created, by placing the respective elements in parallel, hence adding their complex capacitances.

Please note

The terms “model” and “circuit” may be used interchangeably in this document, with both meaning a combination of one or more circuit elements.

RelaxIS uses a text representation for equivalent circuits and other models. When moving or copying spectra to different models, or for various other functions in RelaxIS you will need to define a model by creating the text representation.

This is in most cases done using the Model Builder dialog.

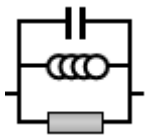
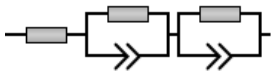
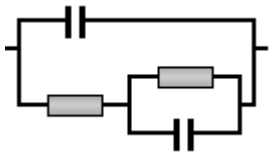


Enter the model expression in the textbox and click the **OK** button to accept the model. At any point, the **Preview** box will show a graphical representation of the currently entered expression, if it is valid. If the expression is invalid, the previous image will be crossed out. You can also check the validity using the expressions color, where green stands for a valid model and red for an invalid model. To the right of the textbox you will also see a green checkmark or a red cross. Hover your mouse over the red cross to see a description of the errors in your model expression.

You will only rarely have to type anything into the textbox by hand though, due to the various helper functions provided by the dialog. Nevertheless, with some experience you will most likely find it quite easy to adjust the expression to your liking by hand quickly and efficiently.

The syntax of the expressions can be summarized by the following rules:

Rule	**Example**	**Result**
Model elements are represented by letter combinations, always starting with a single capital letter, (sometimes) followed by lowercase letters.	R	

Model elements are connected in series by writing them one after another.	RC	
Model elements are connected in parallel by enclosing them in parentheses.	(I)(R)(C)	
Separate serially connected parts from parallel connected parts by a hyphen.	R-(R)(P)-(R)(P)	
You can nest subchains at will into other parts.	(C)(R-(R)(C))	

The helper functions provided by the dialog are:

1. The Model Library provides a large selection of premade models. You can enter the corresponding expression for any model in the library into the expression textbox by **left-clicking** it. The models are sorted into various groups. The model library is described in more detail below.
2. Click the **Add elements** buttons to add the respective circuit element at the current cursor location to the string. RelaxIS will try to insert the element with the correct concatenations based on the *Serial* and *Parallel* radio buttons.
3. You can add certain partial circuits using the **Add Partial Chain** buttons. These are parts of commonly used chains, like parallel RC elements. It is automatically selected if they are added in parallel or in series.
4. For Debye-Models, (e.g. **Havriliak-Negami Models**) you can use the Debye-Model-Wizard. Here you can select the number of terms, as well as additional terms and the model expression will be automatically created.
5. **Transmission-Line-Models** can be found in the TLM-Wizard. Please see below for a detailed explaination.
6. You can move the text cursor to certain elements in the expression textbox and **right-click**, to replace that element with another from the drop-down menu.

7. You can refer to the **Quick Reference** box to the right of the dialog for quick reminders about the used expressions.

RelaxIS provides many pre-defined model elements. You can find a list, together with the implemented impedance expressions for each element and an explanation of their functions in the appendices. You can create user-defined circuit elements by using the **RelaxIS SDK**.

Additionally, you can assign a title to the model. This does not change the impedance function of the model in any way. It however allows you to add the same model multiple times to the same project, to further subgroup your data. The title is prepended to the model expression and enclosed in the brackets of a `{}_` block. In the RelaxIS model builder you find an extra text field for the title and you do not need to enter `{}_` manually. If you are using advanced features like RelaxIS Remote you may find it neccessary to specify the title in this manner though. A full model expression with title is for example:

```
{Model Title}_R-(R)(P)
```

9.1.1 The Model Library

At the top of the Model Builder dialog you can find the model library. It contains a selection of commonly used models, as well as further information about them.

Click on any model in the library to set the model expression into the builder dialog input box.

To add a model to the library, click the “Model Library” menu button and select **Add model to library**. The dialog is pre-filled with the current model and the currently selected group. You can freely change the model expression and group name. If the group does not already exist it will be created. You can enter a comment and additional resource (link or DOI) which will be associated with the model and be shown in e.g. the model screening dialog.

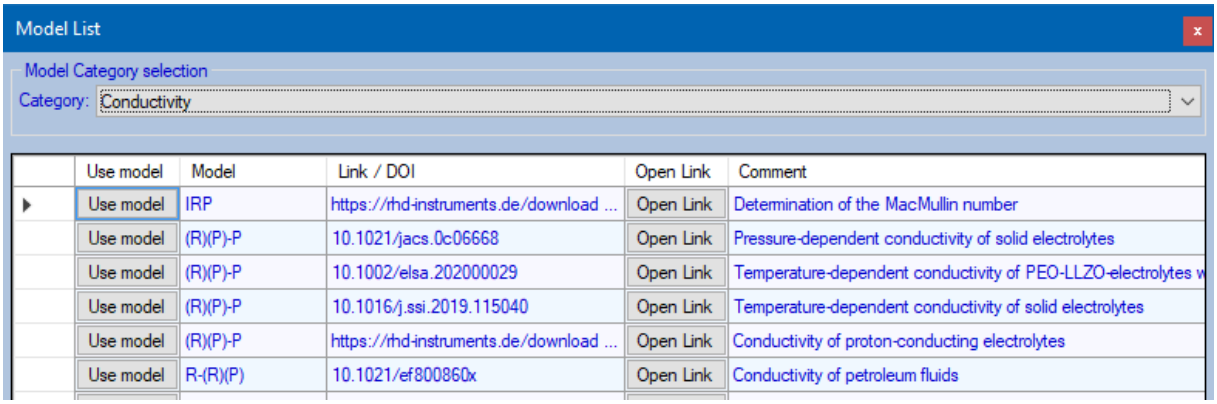
You can edit existing user-created models by right-clicking the model in the list and clicking the **Edit model** button in the context menu.

You can remove existing user-created models either by right-clicking them and selecting **Remove** from the context menu, or by clicking the **Remove models** button in the Model Library menu. The latter will show a dialog with all existing user-created models. Click the checkmark next to the ones you want to remove and click **OK**.

Please note

Only user-created models can be removed or edited. User-created models have a green border in the model library, while built-in models have a light-blue border.

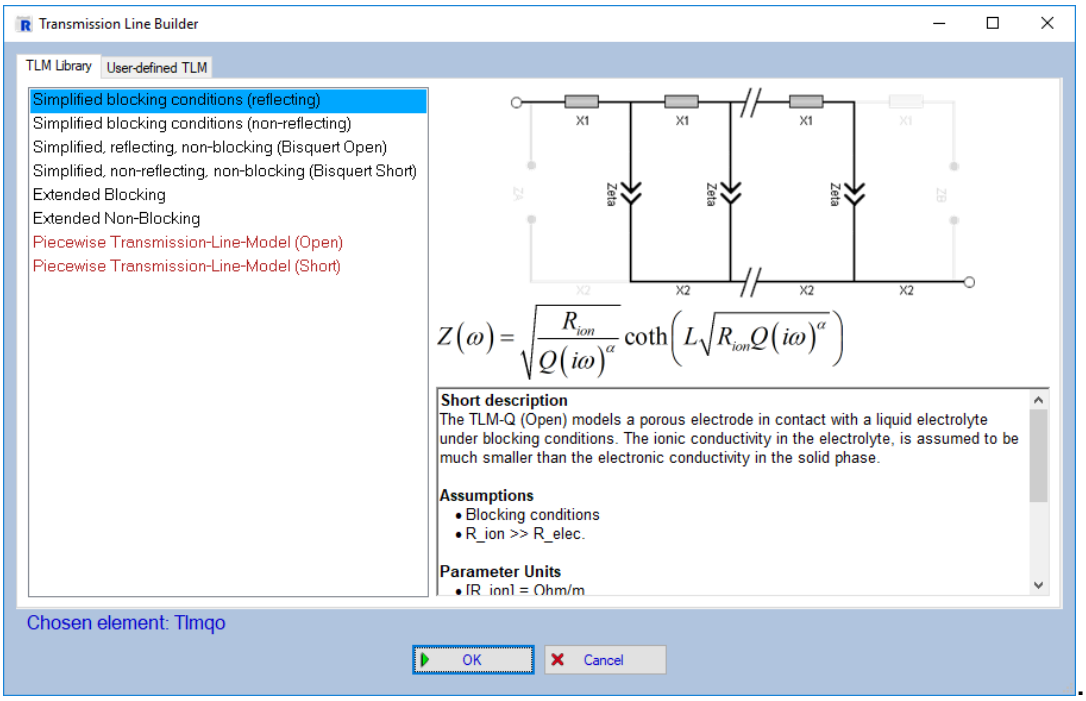
You can list all existing models by clicking the **List all models** button in the menu bar of the library.



In the dialog, you can switch through the exiting categories using the Category dropdown menu. When you click the **Use model** button, the model's expression is set to the model builders model input box. When you click the **Open Link** button, the model's resource is opened in your default browsers. In case of a DOI resource, the DOI lookup is started, while for Link resources, the link will be opened directly.

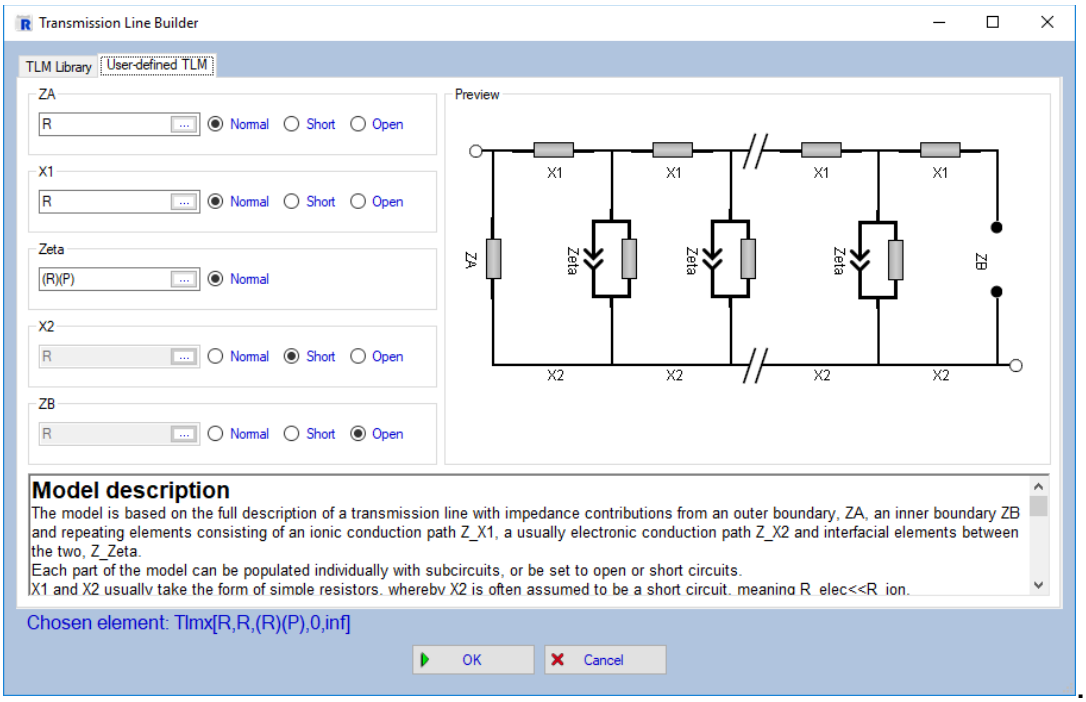
9.1.2 The Transmission-Line-Model-Wizard

The Transmission-Line-Wizard is divided into two parts. The first part is a library of predefined TLMs, together with a visualization and a short description, similar to what you will find at the back of this manual:



To select a TLM to insert into your model, select it from the list and click the **OK** button. The element will be inserted at the current location.

The second part of the wizard is a designer for a **user-defined TLM**:



User-defined TLMs use the mathematical description for a fully populated TLM by Bisquert (Phys. Chem. Chem. Phys., 2000, 2, 4185-4192) consisting of the outer and inner boundary impedances, ZA and ZB, the electrolyte and electronic conducter side, X1 and X2, and the interfacial impedance Zeta.

You can then define the subcircuit that is used for each of these sub-impedances. These can either be a normal sub-equivalent-model, or with the exception of Zeta can be set to open- or short-circuits.

To set the subcircuits either enter their expression directly into the respective text box or click the "…" buttons to open another Model Editor dialog to design the sub-circuit.

The User-Defined TLM has a **special syntax**, different from other circuit elements. The sub-circuits are listed in squared-brackets after the name, Tlmx, in a specific order:

`Tlmx[ZA,X1,Zeta,X2,ZB]`

For the parameters ZA, X1, Zeta, X2, ZB the individual sub-circuits are inserted.

For short circuits, a zero, **0**, is inserted, for an open circuit the abbreviation **inf** is inserted.

If, for instance, the non-blocking extended TLM, Tlmenb, should be replicated, the User-Defined TLM would read:

`Tlmx[inf,R,(R)(P),R,inf]`

From the element description, RelaxIS infers the required list of parameters, so you can use it normally for fitting or simulation.

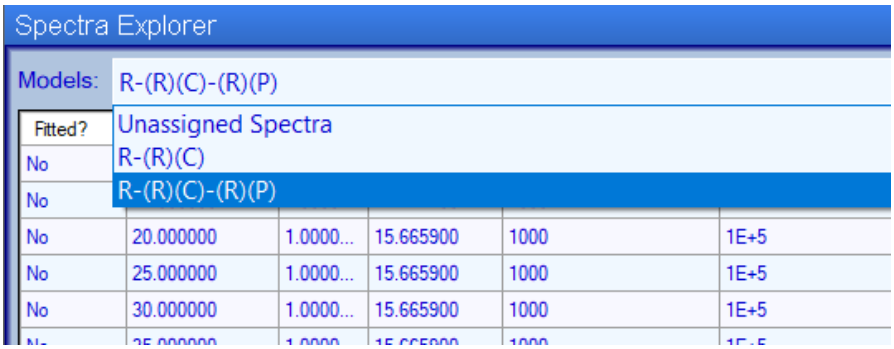
⚠ Please note

Due to the scaling with the length of the pore, L, the units of each parameter need to be inferred individually for each parameter. Their scaling with L depends on where and how the parameters are placed in the model. Please refer to the list of pre-made TLMs in the back of this manual for examples.

9.2 Assigning Spectra to Models

You assign the spectra you have loaded in RelaxIS to specific models.

The Spectra Explorer shows all spectra in the currently selected model. To **change the current model**, click the combobox at the top of the Spectra Explorer window and select the model you like.



To assign spectra to another model, select them and click the **Move to Model**, or **Copy to Model** buttons in the **Data and Quality** tab. Copying spectra duplicates the selected spectra and assigns the copies to the new model, while leaving the original spectra assigned to their current model.

To summarize, to assign spectra to a model, perform the following steps:

1. *Optional*: Select the spectra in the Spectra Explorer, if you want to treat specific spectra
2. Click either the upper or lower half of the Move or Copy button
    a. The upper half of the button always asks for a model
    b. The lower half allows quickly assigning spectra to existing models by showing a dropdown menu containing all existing models
3. If you clicked the upper half, the Model Builder is shown. Create and select the model you want to use.
4. The Spectra Selection dialog is shown (if dialog selection is enabled). Select the spectra you want to move or copy to the defined model and click OK.

9.3 Finding a Suitable Model

9.3.1 General Guidelines

Given the vast number of different systems that are investigated by Impedance Spectroscopy in modern research it is nearly impossible to give a universally

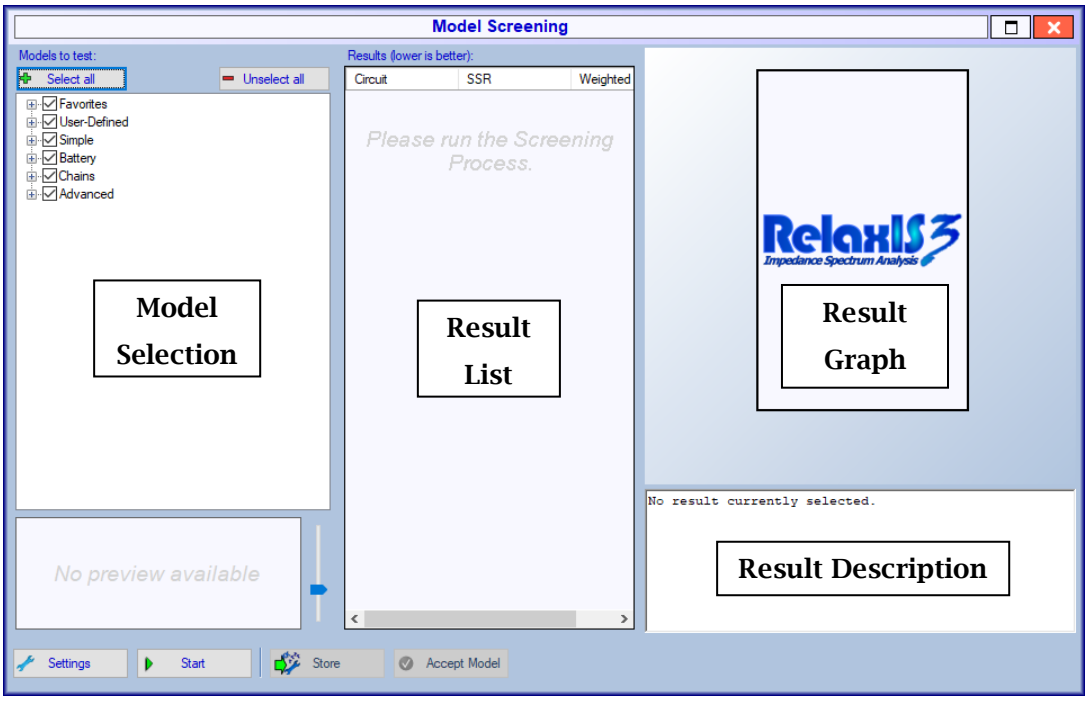
valid way of finding a suitable model to evaluate the measured data. Some guidelines are:

- Think about **the physical processes and their interactions** in the system. You might have double-layers that are being charged, electrochemical reactions taking place that need diffusion to provide the electroactive species and so on. Most of these processes have "default" elements in an equivalent circuit that describe them. A double layer is basically a capacitor, while a reaction requires energy and leads to resistive behavior. Diffusion is usually described by Warburg elements. Since the reaction and diffusion are coupled processes you connect them in series. But the reaction/diffusion is usually independent of double layer charging, so you connect the double layer capacitor in parallel to both (leading to the RANDLES-Circuit). **Try to infer model elements from the processes you measure**.
- Find shapes in the spectra and think about model elements that can describe them. A semicircle in the Nyquist-representation (impedance) may be described with an (R)(C) element. A 45° line indicates Warburg behavior. Bring these together to form ideas for suitable models and then assign physical meaning to the elements.

9.3.2 THE MODEL SCREENING TOOL

As shown above, RelaxIS comes with a large library of premade models. It is possible to evaluate these mdoels for their suitability in describing a given impedance spectrum. This is done by employing a genetic algorithm (GA). A GA is a so-called metaheuristic algorithm to check a large search space for suitable solutions to a problem. In the RelaxIS case, the genetic algorithm tries to search a large range of parameter values to find suitable initial values for the fit for arbitrary models. This is done in a semi-random fashion.

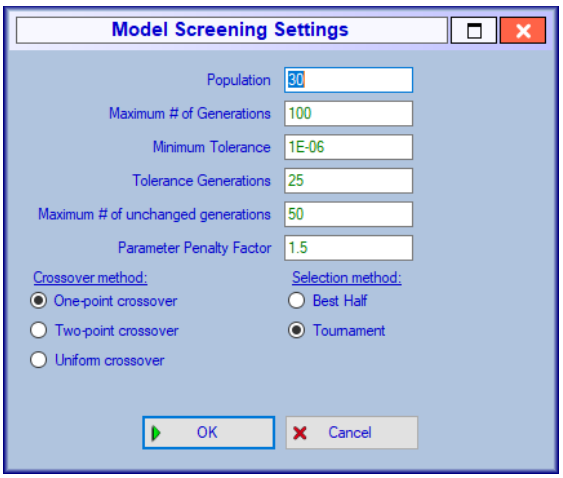
To perform a Model Screening, first load the spectrum in question and activate it using the Spectra Explorer window. Afterwards use the **Model Screening** button in the **Data and Quality** tab to open the Model Screening dialog.



The list at the top-left lets you select the models to include in the screening. You can use your own models by adding them to the model library in the Model Builder dialog as described in section 9.1. To speed up the process it is advisable to preselect models with a physical meaning for your data.

Use the checkboxes to include or exclude models. You can in- or exclude all models using the buttons below the list.

Clicking the **Settings** button allows you to change various options for the screening process and the operation of the GA.



The Population, Crossover method and Selection method relate to the Genetic algorithm and affect how the GA searches for optimal parameters. The other

options are tolerance criteria, that describe when RelaxIS will accept values for a model as the best for that model.

- # **Number of Generations**: RelaxIS will only accept an individual if at least this many generations have passed.
- **Minimum Tolerance:** While evolving the population RelaxIS continuously calculates a tolerance value from the current change rate of the best fitness. The lower this value, the more stable the best fitness needs to be from generation to generation. When the current tolerance value drops below the minimum tolerance, RelaxIS will accept the best individual.
- **Tolerance Generations**: This selects how many previous generations RelaxIS will take into account for calculating the tolerance value.
- **Maximum # of unchanged generations**: RelaxIS will accept the best individual once the best fitness has not changed for this many generations. This is usually overridden by the Tolerance criterium.

The **Parameter Penalty Factor** is used to calculate the Weighted SSR, using the formula

$$Weighted\ SSR = SSR \cdot nParams^{Penalty}$$

That means, that the more parameters and the higher the penalty factor, the larger the Weighted SSR. The higher the penalty factor, the more the impact of additional parameters in the model.

Sensible values depend especially on the chosen Selection method. **Best half** usually requires less maximum generations and less tolerance generations than **Tournament**, but is slower.

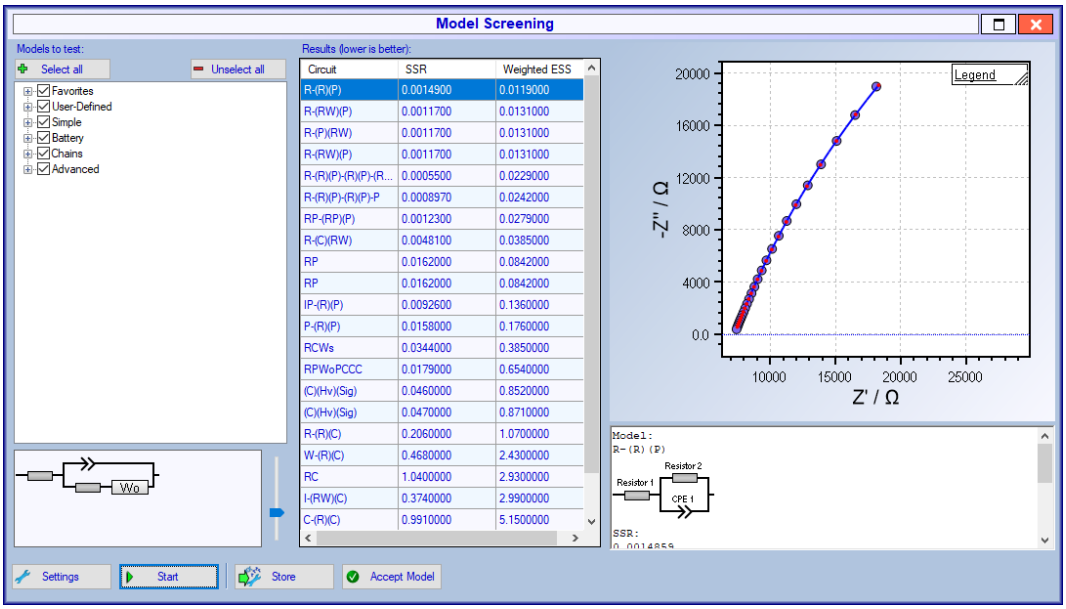
The selected settings dramatically alter both the speed and the reliability of the screening process.

Once you have chosen the correct settings and the models you want to include in the screening, use the **Start** button to start the screening process.

The process can take quite a lot of time!

While running, the already tested models are added to the Result list. Click the entries to see both a plot of the fit results and further information about the parameters found. Click the **Column headers** to sort the columns.

The SSR column designates the minimum ESS found for the model. The Weighted SSR column weights the SSR by the number of parameters of the model. The more parameters the higher the Weighted SSR becomes. This favors simpler models over more complex ones.



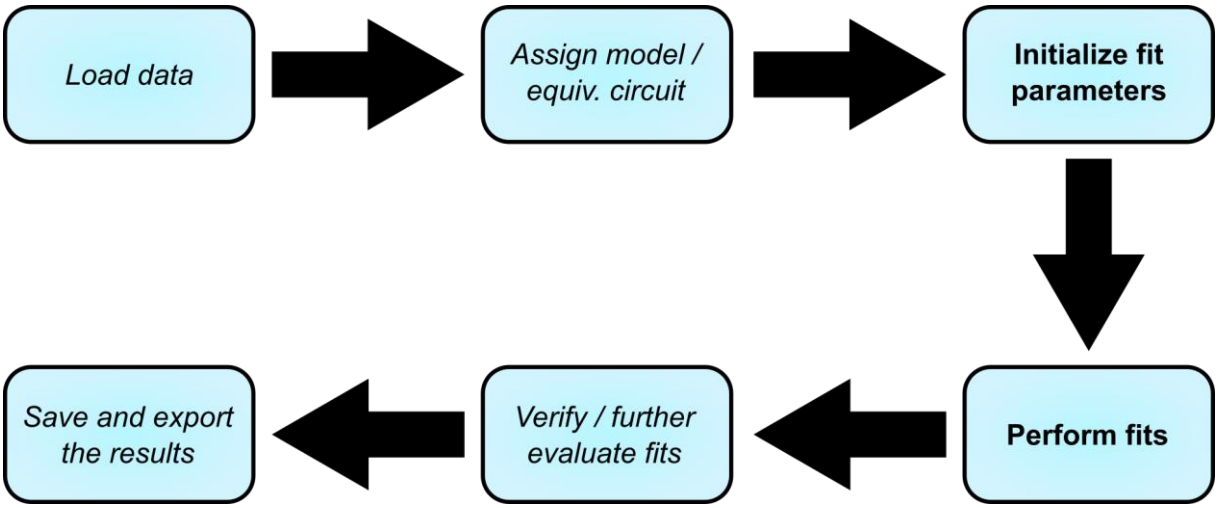
From the list, you can deduce suitable models, find similarities and thus find model elements you can use to find a physically sensible model to describe the data.

⚠ Please note

The GA relies on random variables to search the very large parameter ranges. While it usually searches quite efficiently and reproducibly, the process is nevertheless **not deterministic!** This means it is not guaranteed to always find the same results, because by chance the best parameter set could not be found for a certain run. Please keep that in mind while evaluating the results of the screening!

10 FITTING

A typical workflow for the evaluation of impedance spectra in RelaxIS is depicted in the following flowchart.

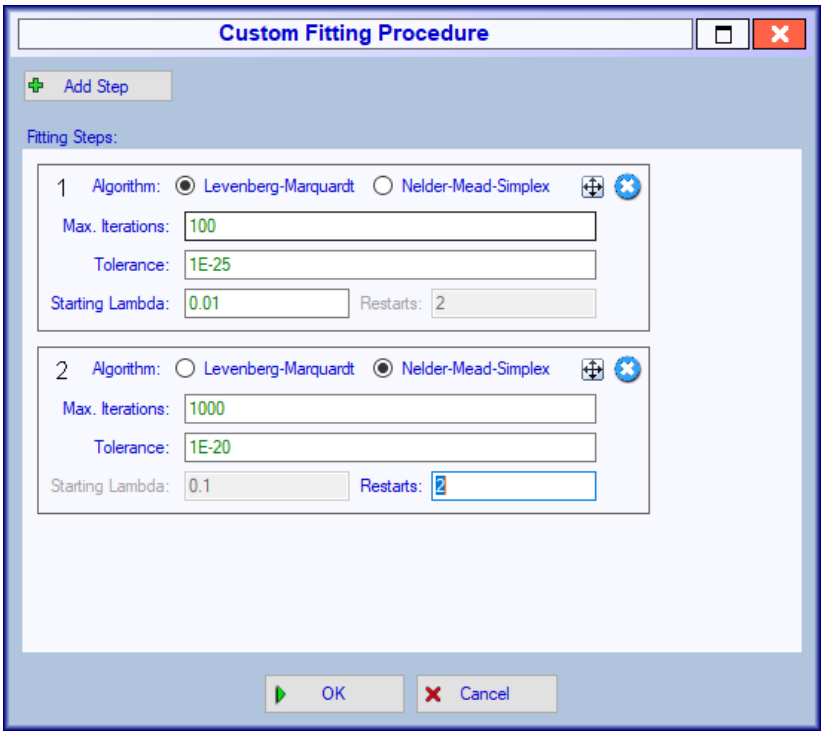


This chapter focuses on initializing fit parameters and performing the actual fits. For loading data, please refer to chapter 6, and for assigning data to a model, please refer to chapter 8.

10.1 ALGORITHM SETTINGS

The RelaxIS Settings dialog allows you to modify the settings being used for the fit algorithms. By default, RelaxIS uses algorithm settings that combine a fast fitting speed with reasonably good convergence characteristics (see also appendices 23.2). This mode is called **Automatic (Quick)**. You can select another mode, which is slower, but has tighter tolerances and allows for more iterations of the used algorithms which improves convergence. You can select this mode, called **Automatic (Thorough)**, be opening the Settings dialog from the main menu, **Main→Settings→Fitting**. Select the radiobuttons called Automatic → Thorough, to switch to the other automatic mode.

In the same settings dialog, you can also define your very own fitting procedure. Select the **Custom** radiobutton, and click the **Edit**… button to open the algorithm editor dialog.



You can chain multiple fitting steps. When you fit a spectrum, the first algorithm in the list is executed with the selected settings. The result of this fit is then used as initial parameters for the second step in the list, which can be the same or a different algorithm. This way you can combine the good properties of both available algorithms by creating a series of fits.

You can add fitting steps by clicking the **Add Step** button. Delete fitting steps by clicking the X icon in the top-left corner of the step. You can **rearrange** steps by clicking and holding down the mouse on the *move* icon, and then dragging the step to another position in the list.

Click **Ok** to accept the current list of algorithms.

In the Settings dialog, you can select to **Refine** the fit *n*-times. This means that after a fit is complete is it restarted automatically for as many times you select. This may help in ambiguous situations with many local minima to “jump” out of a local minimum into a better one.

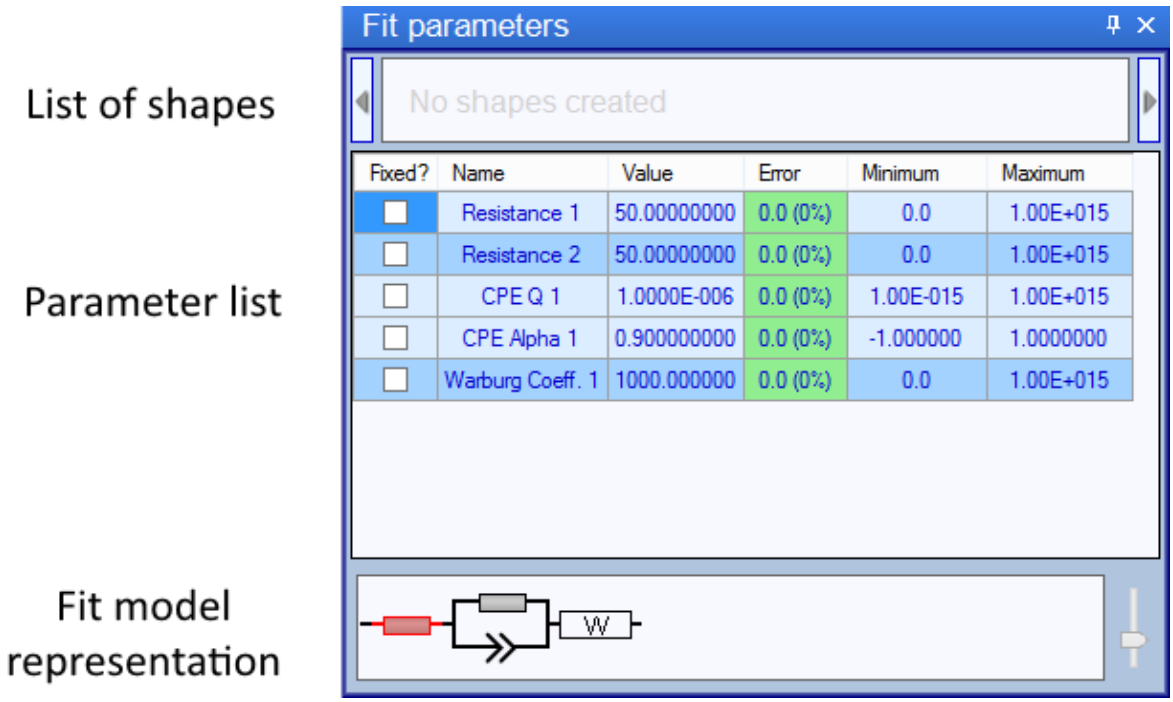
Some steps of algorithms can run in **parallel**. The Multithreading options allow you to limit the number of threads that the algorithms will use.

10.2 Initializing Fit Parameters

10.2.1 General Information

As outlined in the appendices chapter 23.2, a non-linear curve fit needs suitable starting parameters to succeed. Due to the complexity of impedance data and the models, initializing the fit is not a trivial undertaking. RelaxIS offers tools to help you in the initialization process, or automates this process completely for some types of spectra with the help of the Fit Wizard, that is described further down in this chapter.

Once you have assigned a spectrum to a model and activated it in the Spectra Explorer, you will see the fit parameters associated with that model appear in the Parameter Explorer window.



When you select different parameters, their source element in the model will be highlighted in red. That way you can easily find the role of each parameter.

Each parameter has the following properties associated with them

1. **Name**: The default name describes the role of the parameter and are numbered in ascending order.
2. **Value**: This is the active value, for example the resistance of a resistor in the circuit. This will be set to the fit result, after you perform a fit.

3. **Error**: These are not set or set to zero by default (depending on the corresponding **Setup** setting), until you have performed a fit. After that, the fields will contain the error calculated for the parameter on the last fit. Please note that the relative error is calculated on the fly, and can therefore change when you manually change the parameter value after a fit.
4. **Minimum** and **Maximum**: These are the bounds of a parameter. The parameter's value cannot lie outside of these bounds. You can set them manually and the fit will also respect these bounds. These values are also especially important for the Genetic Algorithm, as they describe the bounds of the search space.
5. **Fixed** state: Represented by the checkbox in the first column, this property defines if the parameter will be changed by a fit, or taken as constant. This allows you to set certain properties of a model to pre-defined values, you may have taken from complementary sources. When fixed, the error of the parameter is always set to zero by a fit.

You can change the error display through the Settings dialog. Under "**Value formats**" you can find the "Parameter Error Format" section. Here you can enter a formatting string containing tags. All tags start with the # sign and are followed by one or more characters indicating the value to be inserted at this position in the string. The usable tags are:

Tag	**Description**
#E	The absolute error value
#P	The relative error value

Combining these with an arbitrary string can produce the text you like. Some examples are:

Error format	**Result**
#E (#P%)	234 (19%)
#P	19

Tip

You can export the image of the circuit from the preview using the preview's context menu (right-click).

10.2.2 Quick Parameter Information

If you select parameters belonging to either to a) a single resistor or to b) a combination of a resistor and either a capacitor or constant phase element RelaxIS will display a status bar underneath the parameter list. In case a) the status bar will show the calculated conductivity for the resistance. If the active spectrum contains the Area and Thickness metadata fields the specific conductivity (σ) will be calculated. If not, the simple conductivity (G) will be given.

For the combination or R and C/P both the time-constant and the effective capacitance (from Brug's formula) will be calculated.

You can copy either of the values into the windows clipboard by right-clicking the status bar and selecting the value from the context menu.

10.2.3 Manually Changing Initial Values

You can manually enter initial values into the respective cells in the Parameter Explorer. Whenever you change a value, you can immediately see the changes to the fitted curve in the Data Explorer window. In many cases, this allows you to quickly find suitable parameters by deducing values from the spectrum or by trial-and-error.

You can use a list of values that will be assigned to a specific fit parameter value of a selected list of spectra. Click the **Set Parameter Values from List** button in the **Fitting** tab in the section **Parameter Helpers**. Here, first select the spectra you wish to assign parameter values to. Now select the parameter you want to change and type or paste in values into the text area.

The values will be assigned from top to bottom to the selected spectra in the order chosen from the Select Spectra dialog.

If you have less values in the text area than selected spectra, you can activate the **Continue**… checkbox at the bottom. After the text area values are all used up, this will take the last value in the text area and apply it to all further spectra.

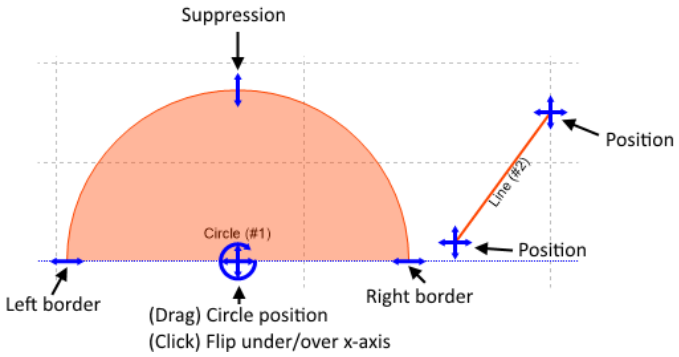
You can furthermore choose to fix all changes parameters.

10.2.4 Using Shapes to Find Initial Values

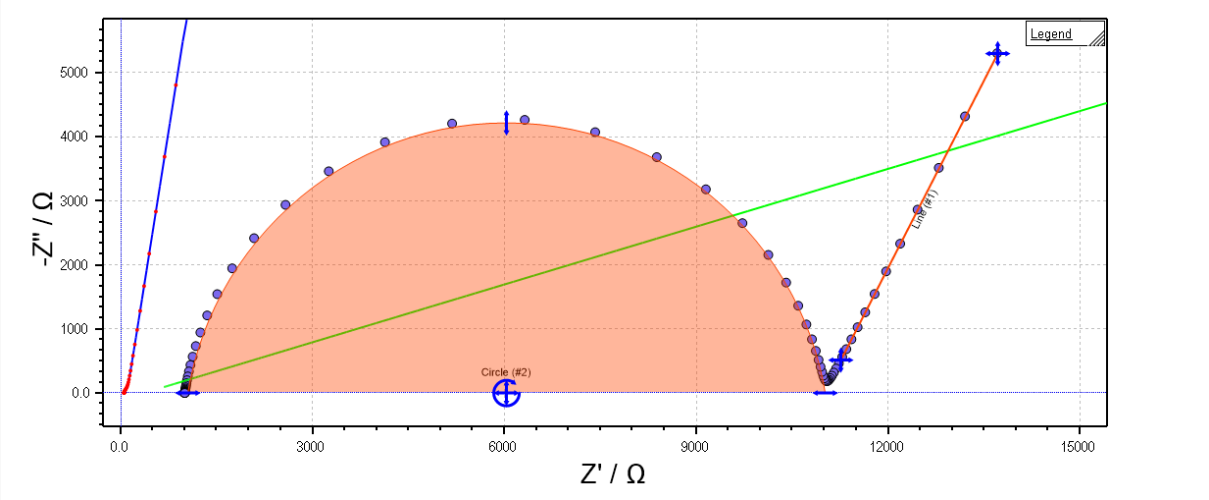
10.2.4.1 Step by Step instructions

RelaxIS offers the **Circle Tool** and the **Line Tool** to calculate initial values directly from a spectrum. The tools can be accessed through the **Fitting** tab in the section **Parameter Helpers**. To use the tools, perform the following steps:

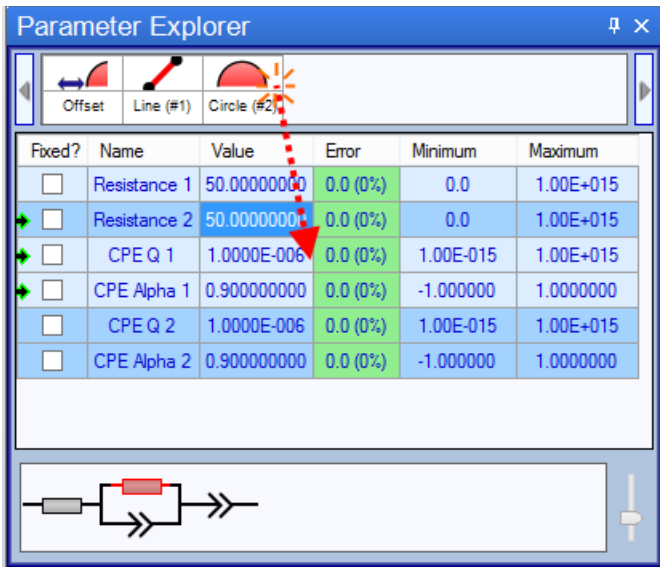
1. Assign the spectrum to a model that can represent all shapes in it. For example, it could contain an (R)(C) element for each semicircle in an Impedance Nyquist Plot. The Circle-/Line-Tools do not choose the correct model for you!
2. Select either the Circle or Line Tool from the menu.
3. With your mouse click and drag the mouse in the plot to add the respective shape. The exact position does not matter at first.



4. Use the handles on the created shape to move and reshape it to represent the shape of the data in the spectrum. If the handles are invisible, move your mouse in the vincinity of the shapes to show them.



5. You can find a representation in the Parameter Explorer window for each drawn shape. You now have to assign the shape features to suitable parameter combinations of the model. **Click on a shape and drag your mouse** into the parameter list below.
6. Depending on the currently selected transfer function and plot type, RelaxIS will choose suitable combinations of parameters that may represent the selected shape in the model. These are for example Resistor-Capacitor combinations for shapes in the Impedance Nyquist Plot. When you drag your mouse through the list, RelaxIS indicates the nearest parameter combo with green arrows.



7. Release the mouse on the desired parameter combination. RelaxIS will then calculate suitable parameter values and assign these to the selected parameters. If the calculated parameters lie out of bounds for a

parameter, RelaxIS will ask if you want to change the bounds to accommodate for the calculated parameter value.

8. The **Offset** shape describes the leftmost border of all drawn shapes. You can for example draw multiple circles and the offset can then describe the left border of the leftmost circle. This is useful to initialize a bulk resistance for example.

⚠ Please note

In some cases, RelaxIS will calculate unsuitable parameter values. This can have multiple reasons:

- The parameter combination does not really describe the selected shape. RelaxIS will select for example Resistance-Capacitance combinations, even if they are not really connected directly in an (R)(C) element that leads to a semicircle in the spectrum. Please check the selected combination carefully.
- In Nyquist Plots the frequency information cannot be calculated exactly for each point in the graph! Calculating the capacitance of an (R)(C) element requires the knowledge of the frequency at the maximum of the drawn semicircle. RelaxIS will try its best to **interpolate that frequency**. In case of noise this interpolation may lead to wrong results. When you draw a circle to the left or right of the data RelaxIS even has to **extrapolate the frequency** which can lead to very strange results, given noise and data point density at the extreme frequencies. When you move your mouse over the Data Explorer you can **see the calculated frequency** for the mouse position in the status bar. **Please check, if that frequency makes sense at the positions of your shapes, when you experience weird behavior.**

The shape/parameter combinations for different transfer functions are as follows:

Impedance

Circle	Resistor+Capacitor, Resistor+Constant Phase Element, Zarc Element
Line	Constant Phase Element, Warburg Element, Inductivity
Offset	Resistor

Admittance

Circle	Resistor+Capacitor, Resistor+Constant Phase Element
Line	---
Offset	Resistor

Complex Capacitance

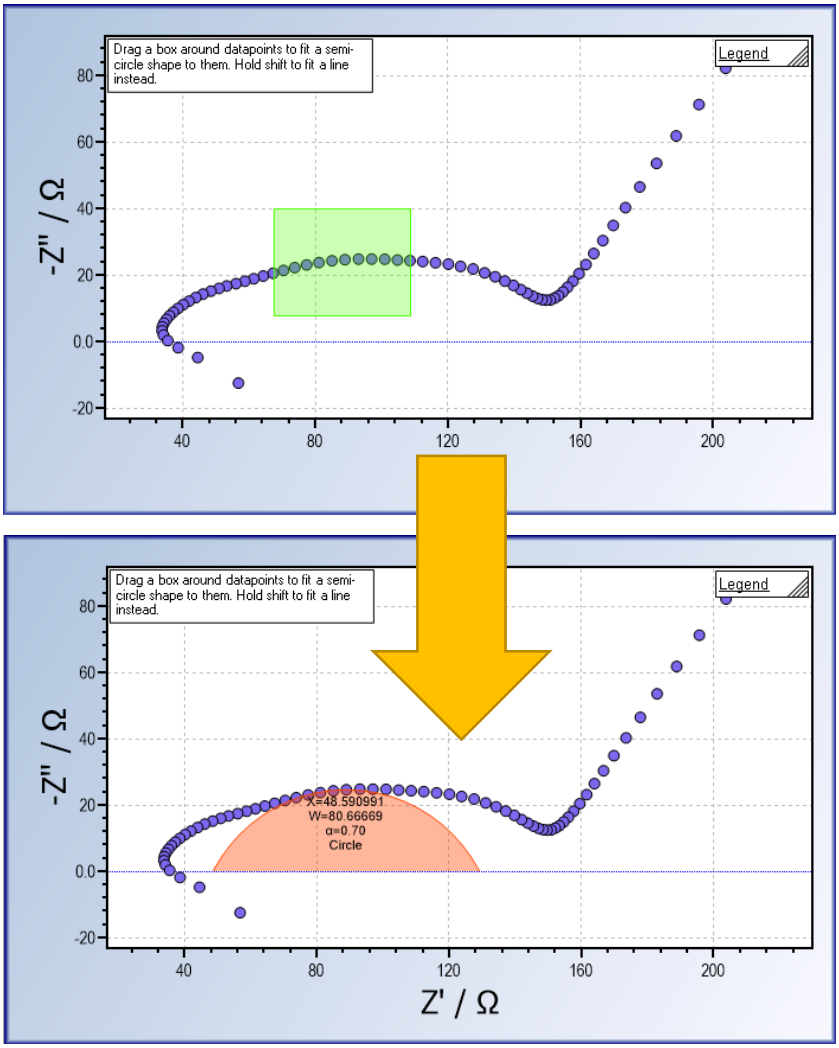
Circle	Resistor+Capacitor, Resistor+Constant Phase Element, Havriliak-Negami, Cole-Cole, Cole-Davidson
Line	Sigma Element
Offset	Capacitor, Constant Phase Element

10.2.4.2 CREATING SHAPES FROM SELECTED DATAPOINTS

Instead of drawing the semi-circles and lines manually into the data, it is possible to select some points of the spectra and let RelaxIS fit a shape to it automatically. To do so first select a supported transfer function and plot type (Nyquist), add the spectrum to the model you wish to use and then select the **Fitting -> Add Shape by Selection** option from the main menu.

Note, that the Data Explorer plot shows an instruction message while the tool is active.

Next, use the mouse to drag a selection box around the datapoints you wish to fit the shape to. Per default, a semi-circle is created.



To create a line instead, hold down the **Shift** key while dragging the selection box. The shift key must be held down until after mouse-button is released.

The created shapes can be used just as the manually created shapes.

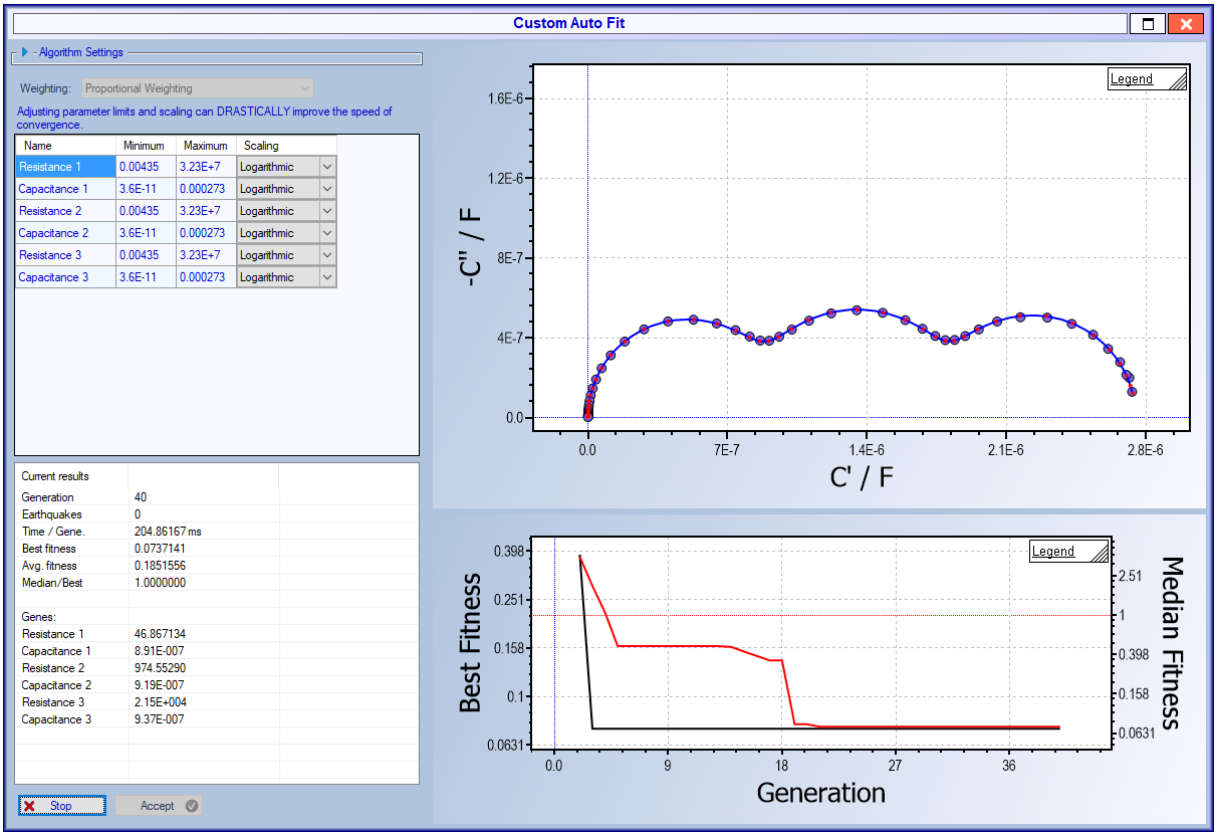
10.2.5 Using a Genetic Algorithm to Find Initial Values

As already explained in section 9.3.2 the genetic algorithm is a so-called metaheuristic algorithm to check a large search space for suitable solutions to a problem. In the RelaxIS case, the genetic algorithm tries to search a large

range of parameter values to find suitable initial values for the fit for arbitrary models. You can use this approach to search for suitable initial parameters for a spectrum with an already assigned model.

The genetic algorithm is implemented either as an advanced search mode, or as the **Auto Fit** feature, that will be described in section 10.8.

To use the advanced search mode, please open the Custom Autofit dialog from the **Fitting** tab by pressing the lower part of the **Auto Fit** button and selecting **Custom Auto Fit**. You do not have to initialize any model parameters after assigning the model.



In the top-left you can extend the algorithm settings panel to change settings related to the function of the genetic algorithm.

You can also perform the evaluations using different weighting modes. Please refer to section 10.3 for further description of weighting modes.

An important setting is the range for each parameter. You can thereby limit the search space of each parameter. The search space is automatically determined for most parameters based on the spectrum.

You can change the limits in the table on the left. By limiting the search space, you can **dramatically improve the speed** of finding suitable parameters. If the range covers multiple orders of magnitude you should enable **logarithmic scaling** of the search space by using the dropdown menu in the last column. That way, small values are equally likely to be chosen than very large values.

Once you have set the options, click the **Start** button to start the algorithm. You can see the development of the results in the graphs to the right. The chart shows the data and the resulting fit curve in red. Below you find a graph that displays the development of both the best and the median fitness over the various generations.

⚠ Please note

The best fitness may not change for a great number of generations and then suddenly drop again. This is due to the nondeterministic nature of the genetic algorithm and its reliance on random numbers, as mentioned in section 9.3.2.

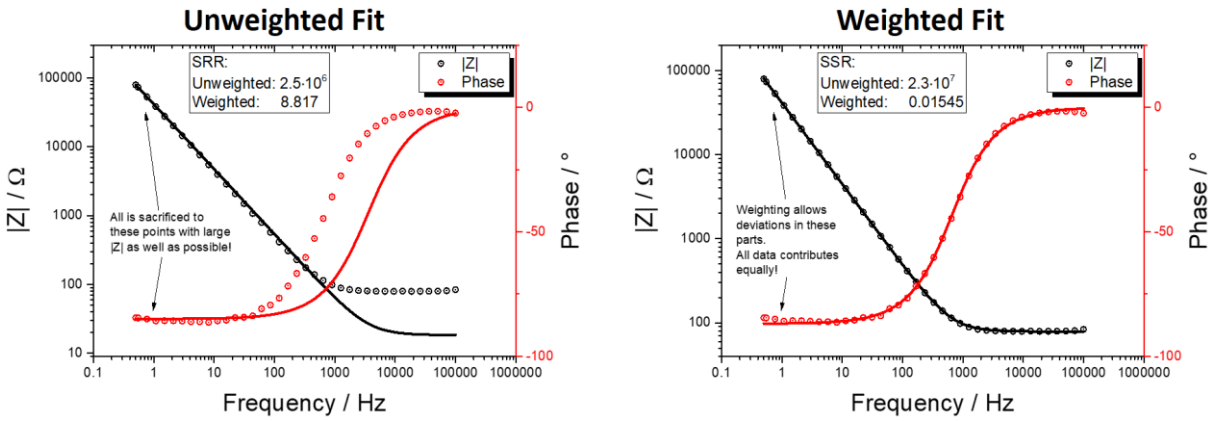
Once you are satisfied with the found results, you can stop the algorithm using the **Stop** button. Afterwards you can accept the values (and the chosen weighting mode) by clicking the **Accept** button. That way the current best parameters are set as initial values for the selected spectrum and the weighting mode is changed to the selected mode. Also, a single fit is automatically performed.

The main Settings dialog in the Fitting tab allows you to select, how the parameter limits are treated after the genetic algorithm completes. You can disallow the GA to change the limits, but this may prevent the best fit to be applied to the actual spectrum. By default, the limits are only widened but never shrunk, which is a useful way of handling the limits.

10.3 Weighting Modes

The fitting procedure minimizes the weighted sum of squared residuals. That means that a weighting factor is assigned to each real- and imaginary part of

a data point. This gives certain data points more or less influence on the fit result. Weighting the data can improve fits of spectra that span multiple orders of magnitude in their values. If unweighted, improvements in the fit of few large points are much more important than improving the fit for many small data points. An example is given in the following figure.



RelaxIS supports multiple different weighting modes, that influence the fit in different ways.

Weighting Mode	**Description**
No weighting	All weights are set to unity. Each data point adds its absolute deviation from the fit.
Proportional weighting (*recommended*)	Each data point is weighted by the inverse square of its value. That practically transforms the fit to sum up the relative instead of the absolute errors.
$Log10^2$(Frequency)	This weighs the data points by the squared base-10 logarithm of the frequency. This favors low and high frequencies.
Favor low frequencies	This also uses the base-10 logarithm, but only favors low frequencies.
Favor high frequencies	This also uses the base-10 logarithm, but only favors high frequencies.

Low freq. modulus	This uses the proportional weighting, but additionally favors low frequencies.
High freq. modulus	This uses the proportional weighting, but additionally favors high frequencies.

For most fitting procedures, the **proportional weighting mode** provides the best results. On some occasions, you may want to try other modes in order to fit certain features better than others.

You can develop your own weighting modes with the **RelaxIS SDK**.

10.4 Transfer Functions

RelaxIS allows you to use multiple different transfer functions to fit the data. You can by default convert the data from the impedance into the admittance, the complex capacitance and the elastance. RelaxIS only uses **geometry dependent** transfer functions instead of the often-common geometry independent transfer functions specific impedance, complex conductivity, permittivity and complex modulus.

Certain function like the *Plot View* or the *Combined Data Plot* **allow normalization**, if geometric metadata is available. The actual analysis, however, is still performed only with non-normalized transfer functions. You can also recalculate analysis result values during the export, if required.

You can change the current transfer function using the **Change Transfer Function** button in the **Fitting** tab of the main ribbon interface. The data displayed in the Data Explorer and other features are changed accordingly.

You can implement your own transfer functions with the **RelaxIS SDK**.

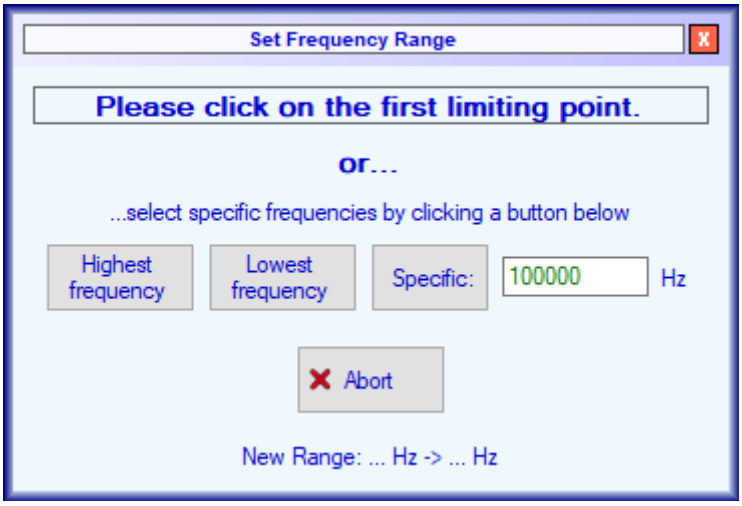
10.5 Changing the Active Frequency Range

RelaxIS allows you to only fit a certain frequency range of a spectrum. You can change this range using two different methods. Inactive data points are shown in gray in the spectrum and are ignored in every fit and in other functions of

RelaxIS. You can spread the selected frequency range to other spectra using the **Parameter Spreading** functionality as explained in section 6.8.

10.5.1 Select Frequency Range

The Set Frequency Range feature allows you to directly select the upper and lower frequency limit by either clicking data points or by entering the respective frequency. Click the **Select Frequency Range** button in the **Fitting** tab to show the respective dialog.



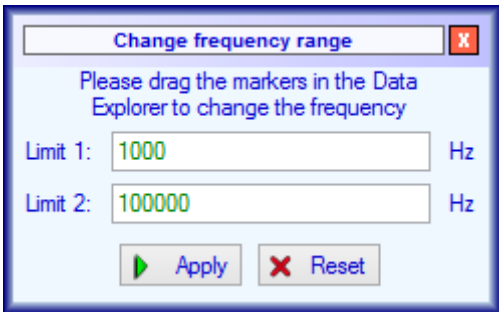
Now do one of the following:

- Click on a data point in the spectrum to set it as the first limiting point.
- Click the **Highest- or Lowest Frequency** buttons to select either the highest or lowest frequency of the current spectrum.
- Enter a desired frequency in the box and click the **Set** button.

Afterwards you need to do one these steps again to select the second limiting point. You can abort the procedure by clicking the **Abort** button.

10.5.2 Change Frequency Range

The Change Frequency Range feature allows you to select a frequency range by moving various sliders over the spectrum in question. From the points in the inner rectangle formed by the sliders the highest and lowest frequency are selected and set as the active frequency range.



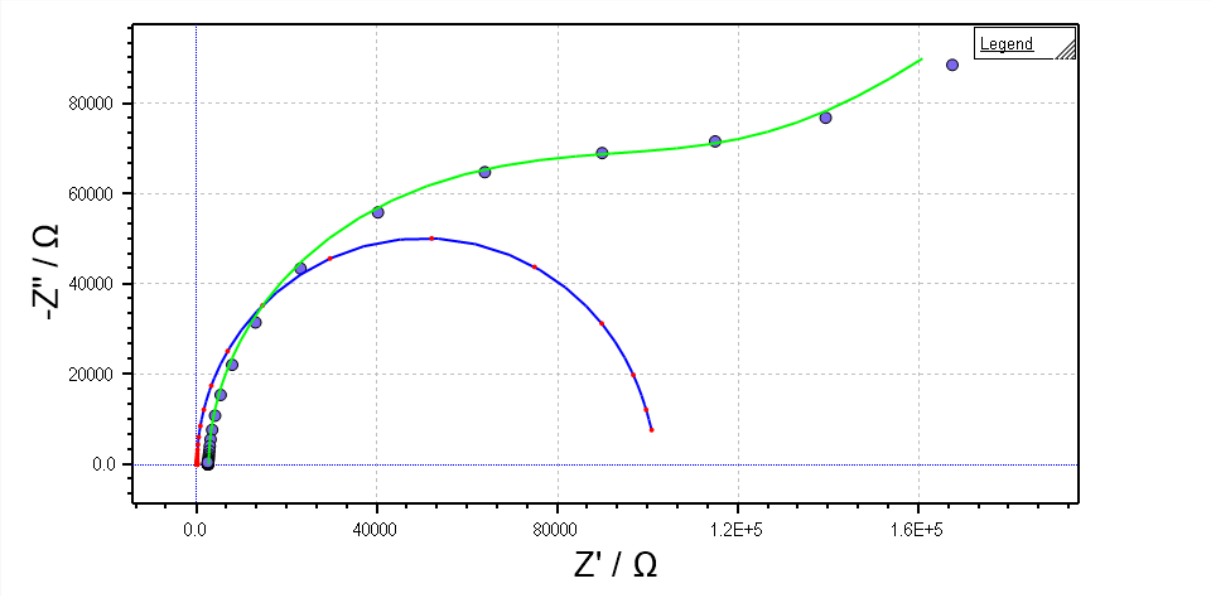
After moving the sliders to the desired positions, click the **Apply** button to accept the selected range.

If the plotted data in the Data Explorer has the frequency, or angular frequency, on the X-Axis, only two sliders are displayed, because the frequency range can be selected unambiguously in this case.

10.6 Testing the Fit

RelaxIS can show the results of a fit with the current settings, without actually changing any of the initial parameters you entered. The test fit is shown as a light green curve in the Data Explorer window. The testing is performed in two different ways in RelaxIS.

- Clicking the **Test Fit** button in the **Fitting** tab.
- Enabling the **Live Test** feature in the **Fitting** tab (it is also enabled by default). This automatically performs a test fit in the background whenever a significant variable like an initial parameter, the transfer function or the weighting mode is changed. That way you always have the current fit result in view.



You can remove the test curve by clicking the **Remove** button next to the Test Fit button on the **Fitting** tab.

10.7 Performing a Fit

After initializing the parameters, you can perform the actual fit by pressing the **Single Fit** button on the **Fitting** tab.

If direct selection mode is enabled, the button is called “Fit selected” and will perform a single fit on all currently selected spectra.

That will perform the fit and enter the resulting parameters and errors into the Parameter Explorer table.

10.8 Auto Fit

The Auto Fit feature uses the Genetic Algorithm to automatically determine suitable initial parameters and perform the fit.

In many situations, the Auto Fit is enough to successfully fit a spectrum, without the need to manually adjust any initial parameters.

The Auto Fit can be performed in two different modes: Quick and Thorough. **Quick** uses a setup with a smaller population and maximum number of generations, to find initial parameters more quickly. Using the Thorough search, allows for a more extensive search for initial parameters, using more

generations and a larger population. This gives a larger probability to find good initial values at the cost of reduced speed.

You can perform a **Quick Auto Fit** by clicking the upper part of the **Auto Fit** button in the Fitting tab of the main Ribbon. Clicking the lower part opens a dropdown menu that allows you to access the **Thorough Auto Fit** and the GA Search Mode, described in section 10.2.5.

You can also perform an Auto Fit on more than one file at a time, by a) selection spectra before clicking the Auto Fit button in direct selection mode, or b) selecting the (Multi) Auto Fit modes in the dropdown menu in dialog selection mode. The Multi Auto Fit uses the Settings→Fitting→Multi Threading: Lists option to process multiple spectra simultaneously.

Please note the settings for parameter limits in the main Settings dialog in the Fitting tab, as already explained in section 10.2.5.

The Auto Fit procedure can be more finely controlled using the Custom Auto Fit dialog, that can be accessed by clicking the **Custom Auto Fit** button in the Auto Fit dropdown. The dialog is introduced in section 10.2.5.

By default, after an Auto Fit is performed, a reordering of the time constants of the parameters is performed automatically. See the next paragraph for details on this procedure. This improves comparisons of multiple spectra fitted with the Auto Fit, as parameters have a better chance of correlating with each other. This functionality can be disabled from the Main→Setup dialog, in the Fitting tab.

10.8.1 Reordering Time Constants

Consider the model (R)(C)-(R)(C)-(R)(C). The three (R)(C)-elements each have a time constant. From the mathematical standpoint, it is irrelevant in which order these appear in the parameter list, so you can interchange e.g. *Resistance 1/Capacitance 1* with *Resistance 3/Capacitance 3* and you calculate the exact same impedance values from the model. Now consider you have measured a series of spectra and use the **Multi Auto Fit** to fit all of them. Due to the random nature of the algorithm, the order in which the time constants appear in the results is random. If you export the results to plot and analyze them,

this will get very confusing, because corresponding parameter values appear in different columns for each spectrum.

To alleviate this problem, RelaxIS contains the **Reorder Elements by Tau** plugin, in the **Plugins** tab. The plugin will analyze the model and find series (R)(C) and (R)(P) parts, or Co/Cd/Hv parts. For these it calculates the time constants and reshuffles the parameter values, such that the lowest time constants appear before the larger ones in the list.

Please note: This will only work for simple serial chains of (R)(C)/(R)(P), or parallel chains of Co/Cd/Hv elements! If the elements are nested in subchains, the definition of time-constants are not easily deduced from the model and the parameters cannot be reshuffled unambiguously.

After clicking the plugin button, use the selection dialog to select which spectra to change. After clicking OK, the plugin will analyze the model of the selected spectra and order the parameter values if possible.

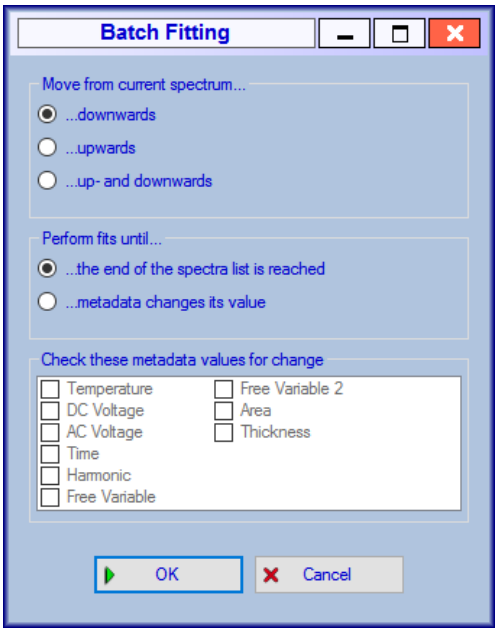
10.9 Batch Fitting

Often you measure a whole series of spectra, that gradually change, for example with time or with temperature. In this case, you can drastically speed up the fitting process by using the **Batch Fit** function from the **Fitting** tab.

A batch fit starts with the current spectrum, fits it, and moves to the next spectrum in the list of spectra. It then uses the results from the last fit as the initial parameters for the fit of this next spectrum. When parameters gradually change, this procedure will allow you to quickly fit all spectra at once.

To perform a Batch Fit, please perform the following steps:

1. Initialize the fit for the starting spectrum manually. It is advisable to use a spectrum that represents sort of a middle ground for all spectra to fit.
2. Click the **Batch Fit** button on the **Fitting** tab to open the Batch Fitting Dialog.



3. Select the direction you wish to process the spectra list. You can move both upwards from the current spectrum, as well as downwards (or do both).
4. Choose where you wish the algorithm to stop.
    a. The spectra list can be processed to the end (the first or last spectrum in the Spectra Explorer, depending on the direction).
    b. The algorithm can be instructed to stop, when the value of one or multiple metadata variables change. This is handy, if you have groups of spectra, e.g. with the same temperature.
5. Click **OK** to start the Batch Fit.

While the Batch Fit is running, you will see a status window, that will close, once the process is complete, and also allows you to stop the process after the next fit.

To speed up the process you can also quickly run the batch fit by clicking on the bottom part of the **Batch Fitting** button. This opens a dropdown menu. From this you can quickly run a batch fit upwards or downwards (or both) to the end of the list.

⚠ Please note

The “instant batch fit” function changes behavior depending on the used selection mode.

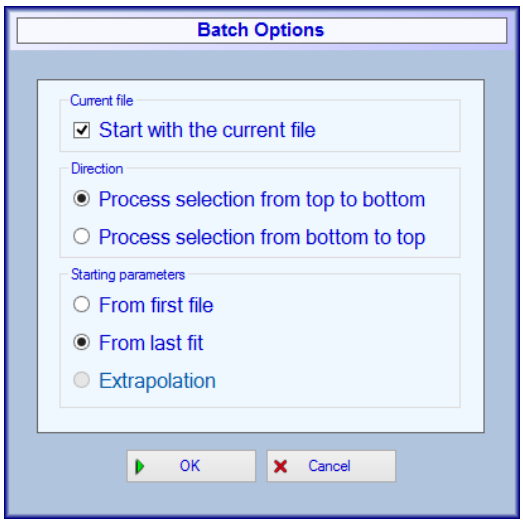
For direct selection mode, select the spectra to batch fit first. “Instant downward” then starts at the first selected spectrum and moves downwards through the selected spectra. “Instant upwards” starts at the last selected spectrum and moves upwards through the selected spectra. “Instant up and down” ignores the current selection, and instead starts at the active spectrum and moves through the full list.

In dialog selection mode, all functions start at the active spectrum and move through the full list of spectra.

The dropdown menu also provides access to a legacy interface for the Batch Fit (prior to version 3.0.1.13), that allows for a finer selection of the spectra to fit.

To perform a Batch Fit with the legacy interface, please perform the following steps:

1. Initialize the fit for the first spectrum in your desired list manually.
2. Click the lower part of the **Batch Fit** button on the **Fitting** tab and select **Legacy Batch Fit**. This opens the Spectra Selection dialog.
3. Select the list of spectra to perform the Batch Fit on.
4. The Batch Options dialog is shown



a. The option **Start with Current Spectrum** means that in every case the currently active spectrum is moved to the top of the batch list.
b. The **Direction** settings specify if you want to move through the batch list from first to last or from last to first.
c. Lastly you can select the Batch Fitting mode. Either you can initialize the next spectrum from the previous, or you can initialize all fits from the very first one. The Extrapolation option is currently not implemented.

10.10 Refinement Fitting

The **Refinement** function available through the **Fitting** tab, allows you to perform the fit again for every spectrum selected through the Spectra Selection dialog, shown after accessing the function.

This is often helpful when you have changed parameters like the frequency range or fixed parameters through the Parameter Spreading function to reapply a valid fit to all files at once.

⚠ Please note

The refinement fitting function is only available in dialog selection mode. In direct selection mode is equivalent to the “Fit selected” function.

10.11 Automatic local Minimum Improvement

In the Main→Settings dialog, in the Fitting tab, you can enable Automatic local minimum improvement. This function is run each time a fit has finished and tries to jump out of a local minimum. For this, a number of additional fits with slightly changed initial parameters (taken from the result of the just finished fit) is run. E.g. some parameters are increased in value while others are decreased. The resulting fits are compared, and the best is used as the eventual fit result.

10.12 The Fit Wizard

The Fit Wizard is a method to automatically evaluate certain common spectra and problems. The evaluation includes the selection of a suitable model, finding initial values and performing the fit. It may also include the calculation of further information from the fit result and assignment of these to metadata of the spectrum. Currently two different Wizards are included in RelaxIS – a wizard to evaluate conductivity measurements and a wizard to evaluate typical spectra of batteries.

To perform a Wizard Fit, please perform the following steps:

1. Open the Wizard dialog using the **Wizard** button on the **Fitting** tab.
2. Select the Wizard suitable for the spectrum you have selected. You can find a typical image of the spectrum as well as a description on the Wizard page.
3. Click the **Next** button.
4. Depending on the selected Wizard, you now need to set some basic options for the wizard. A detailed description for options of the included wizards can be found below.
5. After setting the options, click the **Next** button.
6. You see a summary of the settings selected by the wizard such as the selected model and the initial values.
7. Click the **Next** button and select the spectra you want to perform the wizard fit on from the Spectra Selection dialog (in dialog selection mode). Some selected options, such as selected positions in the spectrum are extrapolated to the ranges of each selected spectrum.

It may happen, that after the fits are completed you will be presented with a message box asking for permission to enter one or more further results into the metadata fields of the spectra. If such additional results were calculated you will also be presented with an export dialog that lets you export these results into the clipboard or a file. The export procedure is further described in section 14.

10.12.1 THE CONDUCTIVITY WIZARD

The Conductivity Wizard lets you automatically extract the electrolyte conductivity from typical conductivity spectra. This can include spectra showing a high frequency bulk semicircle, a high frequency inductivity, and electrode polarization. The wizard will automatically check for the occurrence of either of these and select a model accordingly.

The settings for this wizard are

Setting	**Description**
Cell Constant	The cell constant of your measuring cell. This can be set either directly, or from cell parameters, or from the Area and Thickness set in each spectrum. **REQUIRED** to automatically calculate the conductivity from the fit.
Transfer Function	The transfer function that is used for the fit. By default, the admittance is used.
High freq. inductivity	If inductive data points are found, you can choose to include these in the model, or ignore them in the fit.
Search for bulk semicircle	This lets you skip the search for a bulk semicircle, in case you run into problems with noise in the spectra.

Once the fitting is complete, the wizard will use the cell-constant and the correct resistance from the fit to calculate the conductivity. The conductivity can be assigned to the Free Variable metadata field afterwards.

10.12.2 THE CONDUCTIVITY WIZARD (NON-INTERACTIVE)

This wizard performs the same tasks as the Conductivity Wizard, but does so without any options. It selects default options and can be used in further functionality like RelaxIS Remote (section 20).

10.12.3 THE BATTERY WIZARD

The Battery Wizard fits typical battery spectra. These include a high frequency inductive part, up to two semicircles in the intermediate frequency range and a low frequency diffusion part. The Battery Wizard exists in two versions. The first only uses ideal circuit elements, meaning that an inductor is used for the inductive part and ideal capacitors are used for the semicircles. Only the diffusion part uses a constant-phase element. The Empiric Battery Wizard instead uses constant-phase elements also for the inductive part and the semi circles.

You don't have to enter any settings for the wizard to work. The Wizard can also be used in the RelaxIS Remote feature.

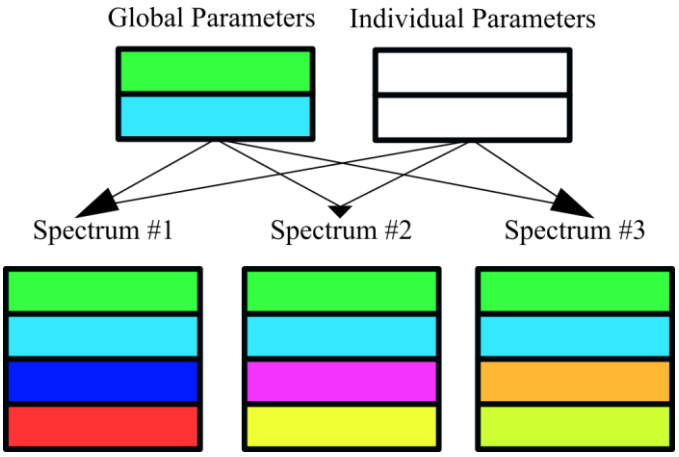
10.12.4 THE SEMICIRCLE WIZARD

This wizard is used for spectra that contain multiple semi-circles in either the Impedance, Admittance or Complex Capacitance. It can also fit a high frequency inductivity and low frequency polarization/dispersion.

On the settings page, you need to define how many semicircles in the spectrum you wish to fit. For overlapping circles, as is often the case, an automatic detection is very prone to errors, and therefore a semi-manual method of selecting the circles is used. After setting the number, you are presented with a plot of the active spectrum containing a corresponding number of green markers. Please use the mouse to drag these markers to roughly the maximum of each semicircle you wish to fit. Afterwards click **Next** to finish the wizard. If you select to evaluate more than one spectrum, the marker positions are adjusted proportional to the Z' scale, e.g. Marker 1 is interpreted as being at 36% between Z'_{min} and Z'_{max}, and the absolute Z' value will be calculated accordingly for each spectrum.

10.13 Fitting Multiple Spectra with Global Parameters

RelaxIS allows you to treat multiple spectra as a combined dataset and define a fitting model where some of the parameters are shared between all involved spectra thus produce only a single value. Other parameters can also be individual and thus take individual values for the spectra. An example would be a measurement series at the same temperature, where you expect the electrolyte conductivity to be constant for each measurement. You would then define the respective electrolyte resistor as a global parameter while other parameters such as capacitances or charge transfer resistors are individual for each spectrum.



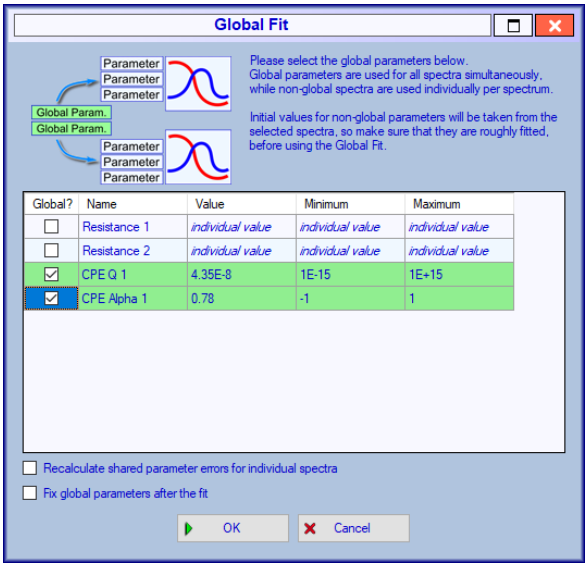
Using global parameter is not the same as using fixed values for the respective parameter. The global parameter is still an active fitting value and not a constant, it will just have the same value for each spectrum at any given time, but this value is flexible and will be adjusted for a best fit of all involved spectra.

RelaxIS offers two interfaces for performing fits with global parameters. A simplified interface that just allows you define one or multiple parameters of the currently used fitting model as global parameters and perform the fit. This is called the *Global Fit*. Furthermore, RelaxIS offers an advanced *Multi-Spectrum-Fit* procedure that is based on individual plugins which define the model. These plugins completely define the model and can not only take use the frequency as independent variables but also spectra metdatadata. This

allows, for example, to define a temperature-dependent model that calculates parameter values from an Arrhenius function and thus has the Arrhenius parameters as fit parameters for the impedance spectra. Such models are very specialized and currently only few examples of such a fitting approach are published. RelaxIS therefore currently does not contain premade Multi-Fit models, but relies on the user to implement the model as a plugin.

10.13.1 Global Parameter Fit

To perform a *Global Parameter Fit* first move the spectra to the respective model and perform a fit with non-global parameters. The reason is, that the current parameter values will be used as initial parameters for all individual parameters. The initial values for global parameters are chosen per default as the average of the respective parameter values over all spectra, but can be adjusted in the global fitting process. After performing the individual fits, click the **Global Fit** button in the Main→Fitting tab. Use the Select Spectra dialog to include the spectra you wish to combine as the global dataset.



The Global Fit interface then allows you to select one or more parameters as global parameters. The selected parameters will receive a green background and you will be able to adjust the initial values and parameter limits of them.

The option *Recalculate shared parameter errors for individual spectra* will advise RelaxIS to use the resulting value of the global fit and calculate an error for each individual spectrum from the covariance matrix again. This will give

individual error values for this parameter per spectrum. If the setting is disabled, the error value from the global fit will be applied to each spectrum. The latter is the sounder procedure, since the parameter value was indeed derived from the combined dataset and not from the individual spectra.

You can furthermore select to fix the global parameters in the parameter lists of the individual spectra.

Once you have set everything up, click the OK button to perform the fit. The fit results will be entered into the individual parameter lists of all spectra. You will notice that every spectrum has the same value for the global parameters.

10.13.2 MULTI-SPECTRUM-FIT

You don't have to assign a model or perform fits before beginning the Multi-Spectrum-Fit procedure, since it is usually completely independent of previous fits. Depending on the used model it may however use the individual fits to determine values for the initial parameters. Start the Multi-Spectrum fit using the **Multi-Spectrum-Fit** button on the Main→Fitting tab of the ribbon. Use the Select Spectra dialog to select the spectra you wish to include in the fit.

Models can define metadata that it requires the spectra to have. If spectra don't have these metadata fields filled with values they will not be usable in the fit. If none of the selected spectra has the required metadata the model will be disabled in the list of available models in the Multi-Spectrum-Fit dialog.

In the Multi-Spectrum-Fit dialog select the model you wish to use and click the **Next** Button. On the next page, you need to define initial parameters for the fit. On the top left, you see the list of shared parameters and you can set up which parameters are free or fixed, as well as their parameter values and limits.

Below you will find the list of individual spectra. Use the arrow buttons to cycle through the individual parameter values of each spectrum. This will also select which spectrum is displayed together with the current model curve in the graph on the right. You can note that individual parameters only change the model curve of one spectrum, which shared parameters change the curves of all spectra at the same time.

Below you can select a weighting mode and you also have a button to show the fit algorithm page in the settings menu. For Multi-Spectrum fits the **Automatic Thorough** fitting mode is recommended!

Before clicking **Perform fit** make sure that the initial parameters describe *all* spectra reasonably well. Then click the button to perform the fit.

The following page then shows the best fit values obtained during the fit, with the shared parameters at the top and the individual results on the bottom.

You can use the **Export** button to export either the parameter list or the plots into the TSV format. You can also use the **Store Result** button to store the result in the Result Library.

Please note:

The individual result parameters *may* contain more values than the fitted ones. The models can use the fit results to calculate additional values that may e.g. be derived from the individual fit results. An example would be that automatically the Brug-Formula is applied to calculate a capacitance value from a CPE. Which values show up is entirely up to the used model plugin. So calculated values are marked with a star (*) in front of their name.

The parameter values **cannot** be applied back to the parameter lists of the individual spectra, because the Multi-Spectrum-Fit-models are independent of any equivalent-circuit-based models.

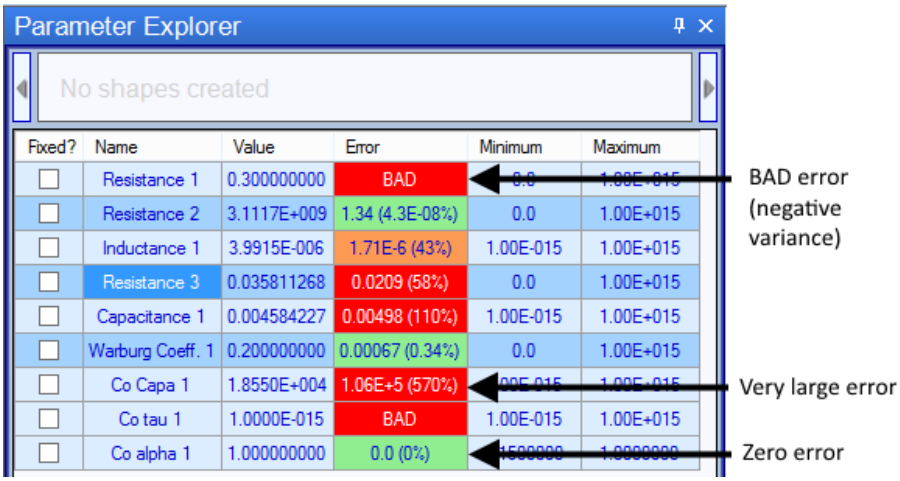
11 Evaluating the Fit Quality

After you have performed a fit, it is recommended to evaluate the quality of the fit results. For this purpose, RelaxIS offers several tools.

11.1 Parameter Errors

The fitting algorithm returns error values for the free parameters of the fit. These are standard errors calculated from the covariance matrix of the fit. You would always expect these parameters to lie in a sensible range between about 0.1% and 30% and you should be skeptical, when you experience larger parameter errors than this.

Especially when a model is unsuitable for the given data, you will find very abnormal error values, like in the following example.



BAD errors (meaning that the variance calculated for this parameter is negative, which is bad, since the error is the square root of the variance) and very large errors, but also errors that are exactly zero indicate very serious problems with the results. Usually, the model contains too many free parameters in these cases, and you should evaluate whether you can simplify the model, or fix one or more parameters in order to get a reasonable fit result.

11.2 The Fit Information Window

You can check more detailed statistics about the fit by using the Fit Information dialog. You can access this dialog using the **Fit Information**

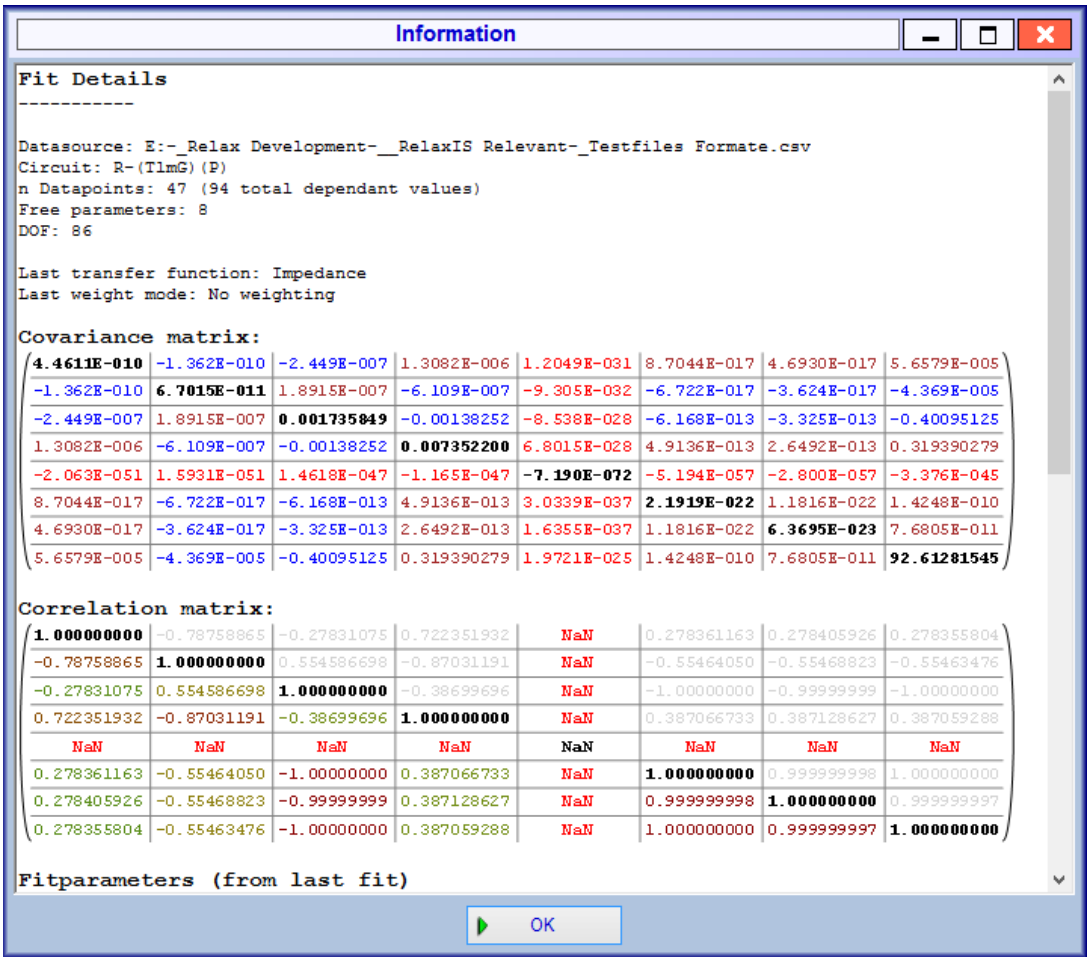
button on the **Fit Results** tab of the main ribbon bar. The dialog shows information about the data set, but also about the covariance and correlation matrix.

Both matrices can point to flawed fitting results. The covariance matrix should be a symmetrical matrix, meaning that it should be mirrored around the diagonal. RelaxIS checks the matrix and marks elements that do not mirror in bright red. You also find that parameters with a BAD error have a negative value on their diagonal position.

The correlation matrix shows how certain parameters behave in regards to each other. Values of +1 or -1 indicate that the parameters are perfectly coupled – either proportionally or anti-proportionally. That means, that if one parameter changes, the other parameter changes in the same way. The correlation matrix should be symmetric as well and is marked accordingly if it is not.

Be very cautious if you see any **NaN** values in the matrices, or find that they are not symmetric. This is usually a sign for **a very wrong and/or too complex model** for the data. The following image shows an example of a very bad covariance and correlation matrix. You can see that the covariance matrix contains negative values on its diagonal and is not completely symmetric. The correlation matrix therefore contains NaN values and shows some very large correlations between parameters. It is not advisable to trust a fit that shows this behavior.

A permanently visible Fit Information window can be shown by selecting **Create New Spectrum View→Info View** from the **Plotting** tab. This window can be docked in the main window and always shows the fit information of the currently selected spectrum. By clicking the Setup button in the menu on the left, you can select which statistics are calculated and displayed.



11.3 Fit Residual Analysis

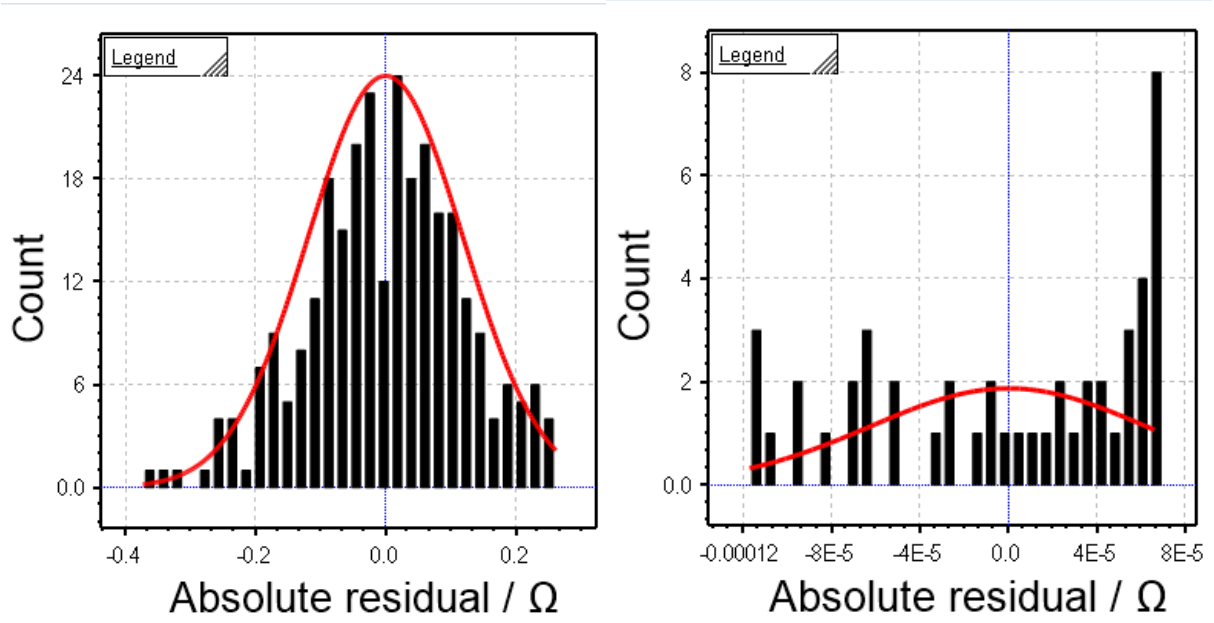
Another good approach to check the validity of a fit is to examine the fitted residuals. If a model correctly describes measured data, the deviations between model and fit should be due to normally distributed noise. After you have performed the fit, open a new Residual Analysis window using the **Create New Spectrum View→Residual View** button on the **Plotting** tab. By default, a plot of residuals of the real part are show as a function of frequency. Click the Setting button in the menu in the left part of the view to select, what is shown. At the top, you can select the diagram type, as well as the transfer function that should be used for the calculations. If *Global Selection* is chosen for the transfer function, then the currently selected one is used.

For the *Normal* diagram type, you can select a plot for the left and right axis individually. Select from which derived value the residual should be calculated, e.g. from the Real Part or the Magnitude. You can also select if the absolute or relative residual should be shown, as well as the chart type.

The Histogram and CDF Plots are only calculated for the value selected for the left axis. The Histogram shows a simple distribution of the residuals together with the curve of the normal distribution. The CDF (*cumulative distribution function*) defines the probability, that according to the given distribution, a randomly chosen value X is less than or equal to the function value x (https://en.wikipedia.org/wiki/Cumulative_distribution_function). The plot can be calculated for both the normal distribution and the residuals and can be compared well.

For the analysis, the **histogram** or **CDF** representation is recommended in order to check the residuals for normal distribution.

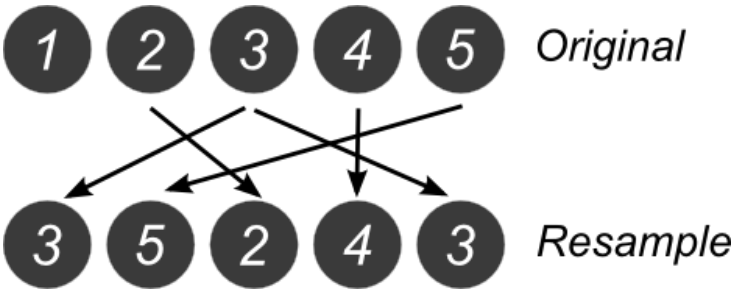
You would expect the histogram bars to form a bell-shaped curve around zero if the errors are normally distributed. You can use the shown line to visually inspect if the results match this expectation. If it does not you may want to reconsider the validity of the model for the given data. Below you can see a good example on the left, and a bad example on the right.



The residual view, by default, automatically performs a Shapiro-Wilk test for normal distribution of the data (for 95% probability). The result is shown above the axes, where ND says, that the data is normally distribution and not ND says that it is not. A more detailed report of the normality tests, can be shown by clicking the Normal Distribution Test button in the menu on the left.

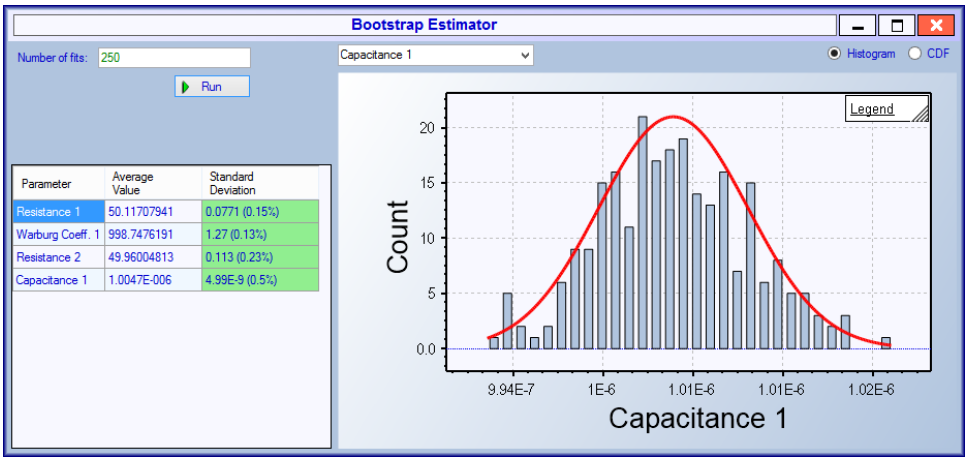
11.4 Bootstrap Error Estimation

Beside the method of calculating errors from the covariance matrix it is also possible to employ Monte-Carlo methods to get an estimate for the errors of each parameter. The Bootstrapping method uses multiple random resamplings of the data and fitting of that data to estimate the error of each parameter value.



The resampling process takes the original data and creates a new data set by randomly choosing data points with replacing from the original data set until the new data set is equally large as the original. That data set is then fitted with the initial parameters of the original data set. This procedure is repeated several hundred times and the results for each parameter are collected. From the collections both the average as well as the standard deviation can be calculated and taken as a measure for the accuracy of the parameter.

In RelaxIS you can access this functionality using the **Bootstrap Error Estimation** button on the **Fit Results** tab of the main ribbon bar. In the dialog, simply enter the number of resampling steps you want to perform and click the **Run** button. The process may take several minutes depending on the speed of your computer and the number of resamples.



Once finished the table on the left shows you the average parameter values and errors. The graph on the right allows you to see the distribution of the values extracted from the resample. Use the dropdown box on top to select the parameter you want to display values for. The values should usually be normally distributed around the average value.

You can plot the data in either a **histogram** or in a **CDF** plot, to check for a normal distribution.

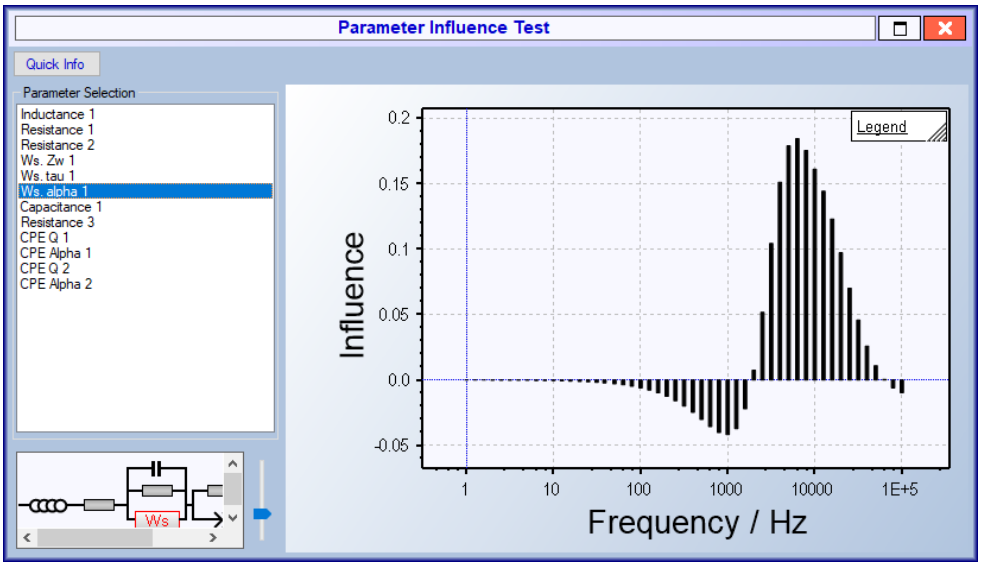
11.5 Parameter Significance Test

The Parameter Significance Test shows *for the current model with current parameter values*, at which frequencies a parameter influences the impedance magnitude. The spectrum data is not taken into account!

The test calculates the partial derivatives of the transfer functions magnitude with regard to the selected parameter for each frequency. The plotted value is scaled by the parameter value (absolute significances) or by the parameter value and magnitude of the model at the same frequency (relative significances).

In layman's terms, this means that the values of a model at a given frequency changes a lot when the parameter changes, the significance value is large and vice versa.

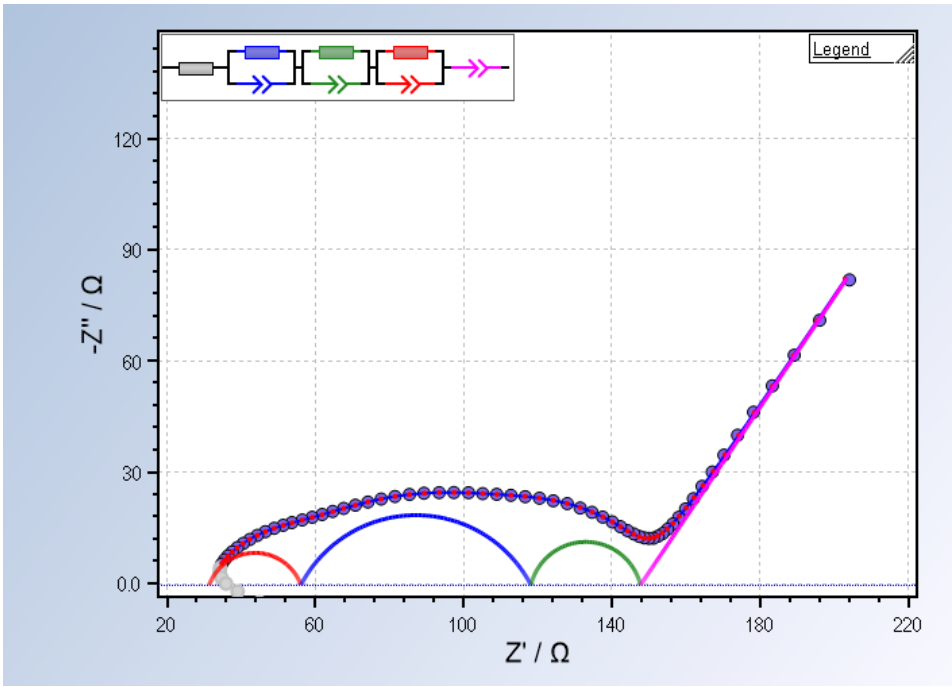
The tester uses the currently active transfer function for the calculations.



11.6 Circle Visualizer

An often-used technique to visualize the fit results of models based on (R)(C) or Havriliak-Negami fits is to draw semicircles with the various parameter values sorted by time-constant directly into the spectrum.

RelaxIS offers a Spectrum View to automatically create this display.



To display the Spectrum View select **Plotting→Create New Spectrum View→Circle View** from the main menu. The View is kept always up-to-date for the current fit values.

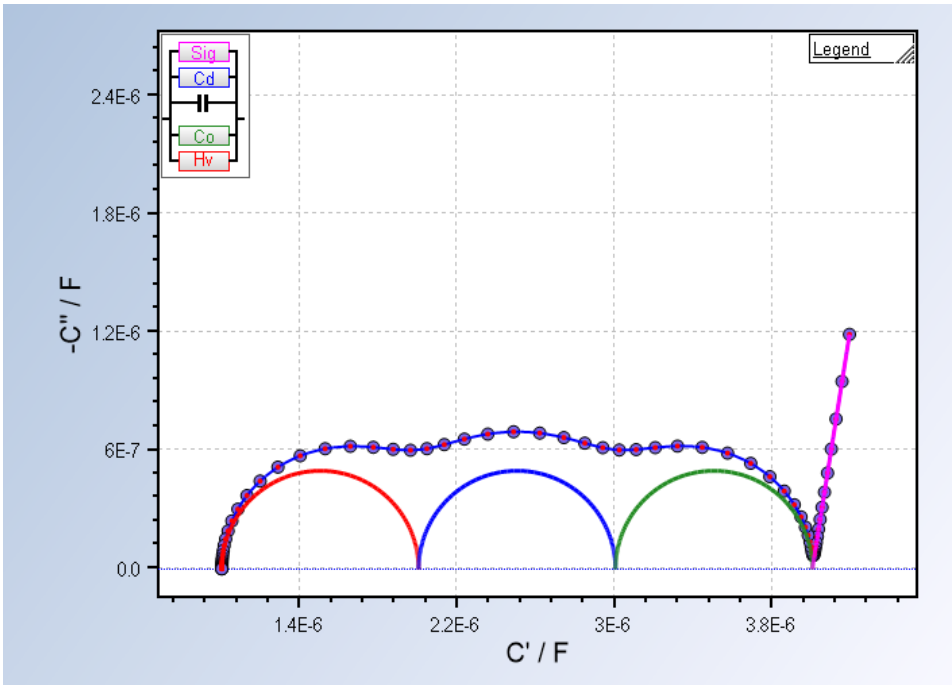
In the top-left of the plot you find a display of the current model where individual parts are marked with the colors corresponding to the shapes in the plot.

Supported models depend on the selected **transfer function**.

Elements in the **Impedance** are:

- Series resistor(s) that are added up and provide a high-frequency offset
- (R)(C) and/or (R)(P) elements which each provide a semicircle
- Series C, P or W elements, that provide a line in the low-frequency regime

- (RW)(P) and (RW)(C) elements which provide both a semicircle and a line in the low-frequency regime



In the **Complex Capacitance**:

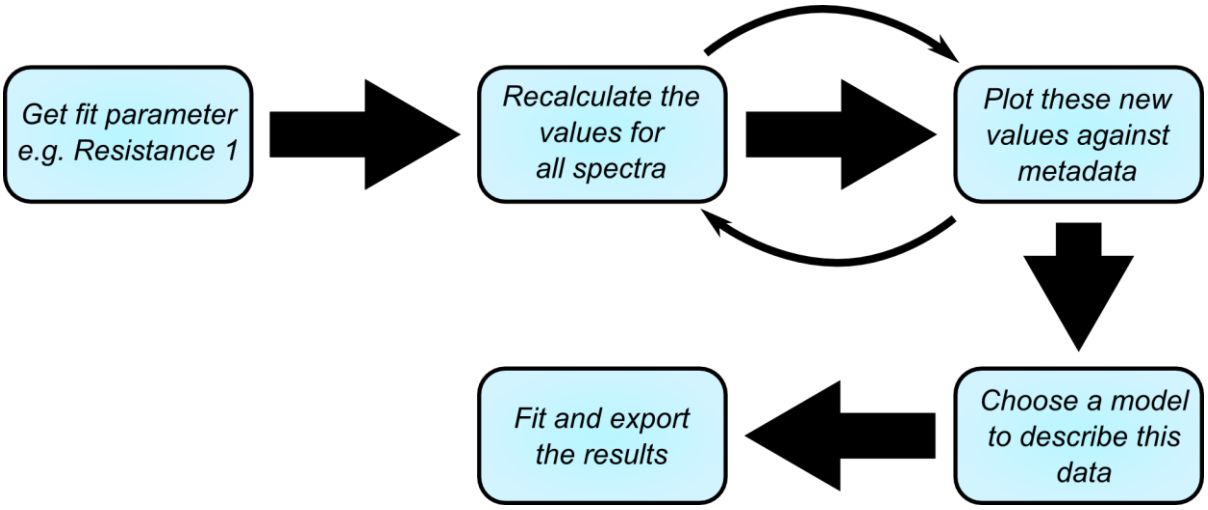
- **Parallel** (Co), (Cd), (Hv) elements provide a semicircle each
- **Parallel** (C) element(s) provide a high-frequency offset
- A **parallel** (Sig) element provides a low-frequency line

The semicircles are calculated from each specific type of element and thus provide accurate visualization of α, β factors.

You can **export the graph image** or the illustrated model from the right-click context menu of the graph.

12 Result Preview and Evaluation

The Result Preview and Evaluation feature allows you to use the fit results from your spectra to relate them with the metadata of these spectra. The parameters can be plotted against metadata variables and afterwards be further described using various fit models, like the Arrhenius model, or parabolas. A typical workflow consists of the following steps:

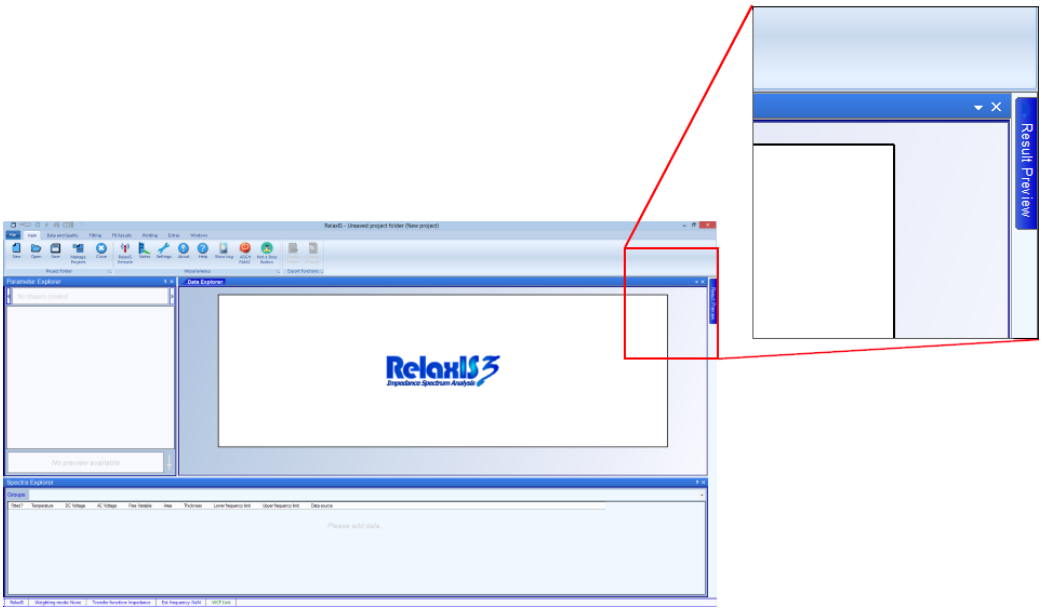


After you have fitted all spectra using the methods described in section 10, you can use the Result Preview window to plot the fit parameters against metadata.

Please note

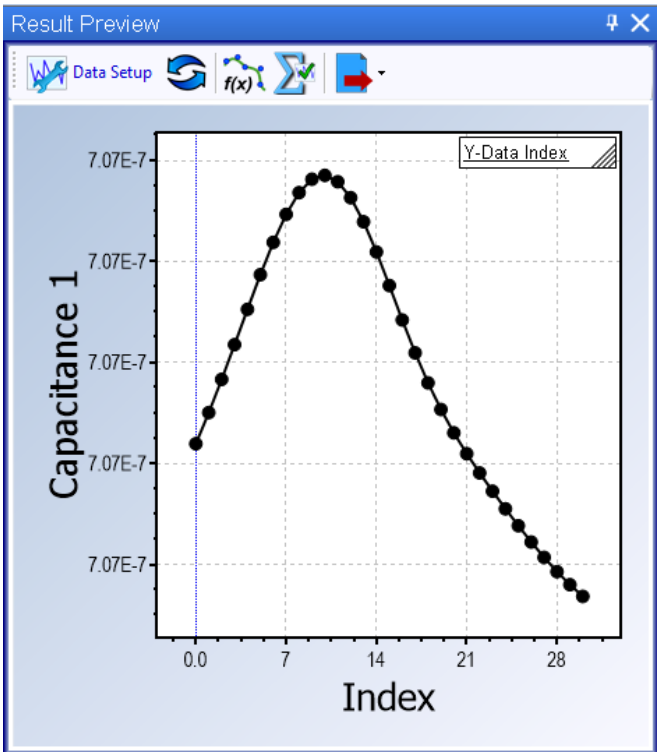
The Result Preview feature replaces the **VFT- and Arrhenius-Module** from RelaxIS 2.x. The models are implemented alongside other models in the Further Evaluation part of the Result Preview feature.

The Result Preview window – by default – is located in retracted form on the right border of the RelaxIS window.



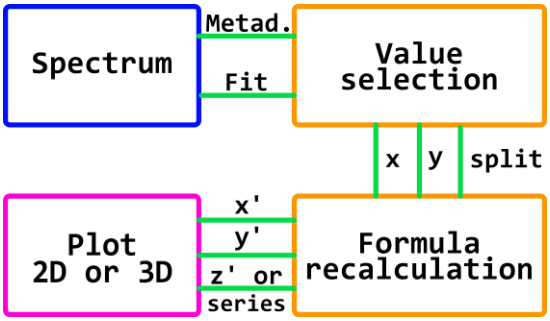
You can open it by moving your mouse onto the flag and open the window permanently by clicking the needle symbol in its title bar.

The Result Evaluation window is split into a graphing part and the tool bar at the top. The toolbar contains actions such as a setup for the displayed data, or data export options.



12.1 Settings

Data is generated from a spectrum in multiple steps. The Data Setup dialog lets you define a value selection, formulas, and plot options to generate the output you want. These settings can also be saved as templates, that you can later apply with one click.

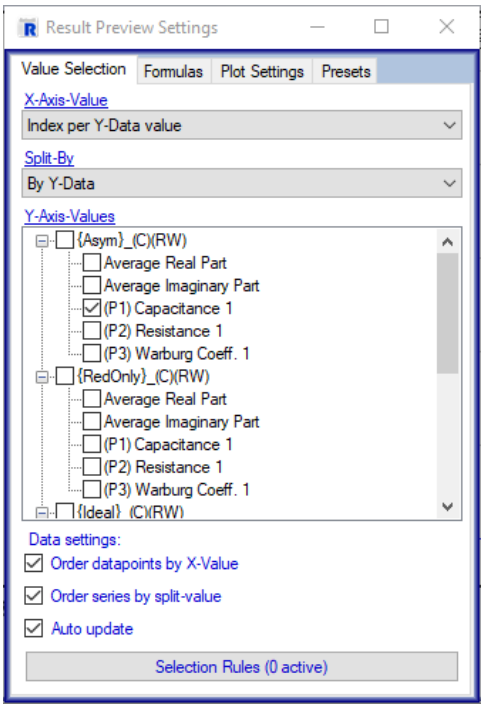


You first select raw X-, Y- and Z-data types. This selection produces one X, Y and Z number per Y-Axis-Value for each spectrum. These datapoints are then optionally recalculated by custom formulas that you can enter. Afterwards, the data is split into multiple series according to the Z-value. Datapoints with the same Z-value are sorted into the same series. The data is then plotted in either a 2D- or 3D-plot.

12.1.1 The Data Setup dialog

Click the **Data Setup** button in the toolbar to setup the data displayed on the form as well as plotting options. The button displays a floating dialog that is split into four tabs. The dialog can be left floating, or it can be docked to the main user interface for permanent visibility.

Changes made in the dialog are immediately reflected on the plotted data.



12.1.2 Value Selection

12.1.2.1 Y-Value (included data) Selection

In the Y-value selection you can choose one or multiple values per (model-) group. For each spectrum in the group (that matches selection rules) this value is selected and plotted on the graph. That means that you get one datapoint per selected Y-value per spectrum in the Result Preview plot.

To select the Y-Axis values, find the groups you wish to include and put a checkmark into the box next to the parameter. Each group also contains parameters called **Average Real- and Imaginary-part**. Selecting these will calculate the average real- or imaginary part of a spectrum in the currently selected transfer function.

Clicking the **Selection Rules** button at the bottom of the dialog allows you to define additional rules for excluding spectra from the Result Preview based on metadata. Click the Add, Delete or Clear buttons to change the list of rules. For a rule, define a metadatum, an operator and a value. Only spectra that matches all or one of the rules (depending on the selection in the dialog) are included in the result preview.

12.1.2.2 X-Axis Selection

Further, you can define what value is chosen for the X-Axis.

The available X-axis values are:

- Spectrum Index: The index of the spectrum that produced the point in the list of spectra included in the plot.
- Index per Y-Data value: The index of the datapoint counted separately per Y-Data value selection.
- Metadata: The value of the respective metadata field of the spectrum that produced the point.

If a spectrum does not contain the chosen X-value (in case Metadata is used), it is omitted from the plot. To select the X-Axis value, simply select it from the X-Axis-Value dropdown menu.

Note: The index is related to the spectrum, not to the valid datapoints. If a spectrum does not produce a valid point (i.e. invalid formula due to missing metadata) the index is skipped. Use X-formula “iP” to replace the indizes with a datapoint-based index.

12.1.2.3 Splitting data into multiple series

Next, data in the Result Preview can be split into separate series. Per default, the values from all spectra and parameters will be plotted into the same series. Use the **Split by** dropdown menu to select a value that is used to split the datapoints into separate series. The Result Preview will first select all datapoints for the defined X- and Y-parameters. It will also find a numeric **Split value** for each datapoint depending on the selection in the Split by dropdown. The Split value is also referred to as **Z-value**.

The split values are:

- No split: All points are combined into one series, split value = 0.
- By Spectrum: Points are split by the model of the source spectrum, the split value is defined as an index for each unique model.
- By Parameter name: Points are split by the source parameter name, the split value is defined as an index for each unique parameter name. **Note**:

If parameters in different models have the same name, they will be combined!

- By Y-data selection: The data is split by the source Y-data, i.e. each entry with a checkmark in the selection list. The split value is an index for each unique Y-data.
- By metadata: The data is split by the value of a metadata field of the source spectrum. The split value will be the metadata value. I.e. selecting Temperature will combine all points with T=20 into one series, with T=30 into another and so on.

If the Split value can't be determined for a source spectrum, the datapoint is omitted (i.e. if a spectrum does not have the required metadata defined).

The datapoints are then sorted into separate series by this Split value. The Split value can also be used further in formulas or in the 3D-plot as the Z-axis value.

12.1.2.4 MISCELLANEOUS DATA SETTINGS

The value selection tab further has settings to order the datapoints by X- and Split value. This is recommended, as it avoids unexpected display "artifacts" if the spectra are not in a suitable order.

Last, you can decide if you want to enable Auto Update of the plot. Here, the result preview graph is updated roughly every second. Disabling this might help if, for instance, updating the plot takes a long time and leads to stutter in the program.

12.1.3 FORMULA INPUT

As mentioned above, the value selection first produces a raw x, y and z/split value for each input spectrum. Before these are used for a plot you can recalculate the values using a formula expression. This step is optional but often useful, as you rarely evaluate fit parameters directly. One example is to recalculate a resistance into a specific conductivity.

The formula settings tab in the Settings dialog allows you to enter a formula for the x, y, y-error and z/split value independently.

Click the Help button to find a list of all variables you can use in the formulas.

For the Y-Error formula it is also possible to set it to an automatic calculation mode. Here, an error propagation calculation is performed using the Y-value formula.

Please note

The split value formula is calculated BEFORE the data is split. So, if calculating the formula results in identical split values for two series they will be combined.
X, Y, Y-Err and Z in the formulas refer to the RAW values of the datapoint before recalculation.

Clicking the dropdown in the formula input fields reveals a list of parameter indizes that can be used to refer to a particular parameter in a model. Clicking the item in the dropdown inserts the parameter symbol into the formula.

12.1.4 Plot Settings

The plot settings allow you to define various settings about how the graph is plotted. First, you can define if the axis titles should be overridden. Mark the checkbox next to an input box and enter the title you wish to display for the axis.

If the titles are not set, RelaxIS will try to infer a title automatically.

The tab-control at the bottom allows you to switch between a 2D and 3D graph. Select the tab for the plot you wish to display in order to change to graph.

For the 2D graph you can define if the legend title is chosen automatically if error bars are shown on the datapoints and if lines are shown between the datapoints. The line-settings overrides graph styles.

For the 3D graph you can define if the data series should be plotted, if lines should be drawn between datapoints, if a surface plot should be displayed and the color map for the surface.

The 3D graph will use the Split- or Z-value for its third axis.

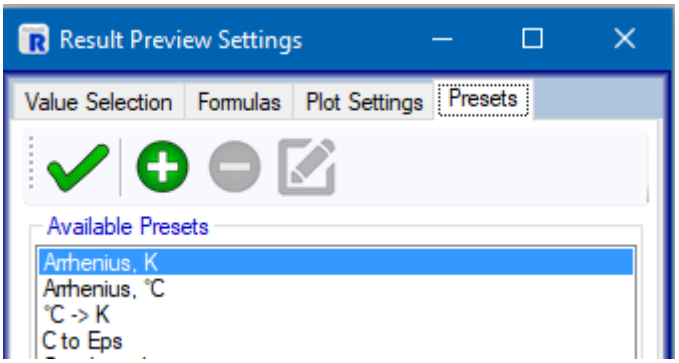
12.1.5 PRESETS

It is possible to save the formula and plot settings in a preset. The preset can then be applied with one click. The data settings are not stored, so you will still need to select the data to plot from the Data Settings tab on the settings dialog.

Please note

The value selection settings are not included in the preset. Before or after applying a preset you still need to manually select which data to include in the plot by adjusting the Value Selection tab.

To access the presets, open the **Presets** tab on the settings dialog. The tab shows a list of all available presets. RelaxIS contains a set of premade presets. Select a preset from the list and click on Apply to apply it to the settings.



To add a new preset, click the **Add new Preset** button in the toolbar. This will bring up a dialog that lets you define a preset name (for display in the list). You can also change the settings stored in the preset here (will be set to the current settings at first).

Note, that for formulas you can enter a **hashtag** # as a special symbol. When applying the preset, RelaxIS will note this symbol and not override the current formula in a field. This is helpful if you i.e. only want to change the Y formula with the preset.

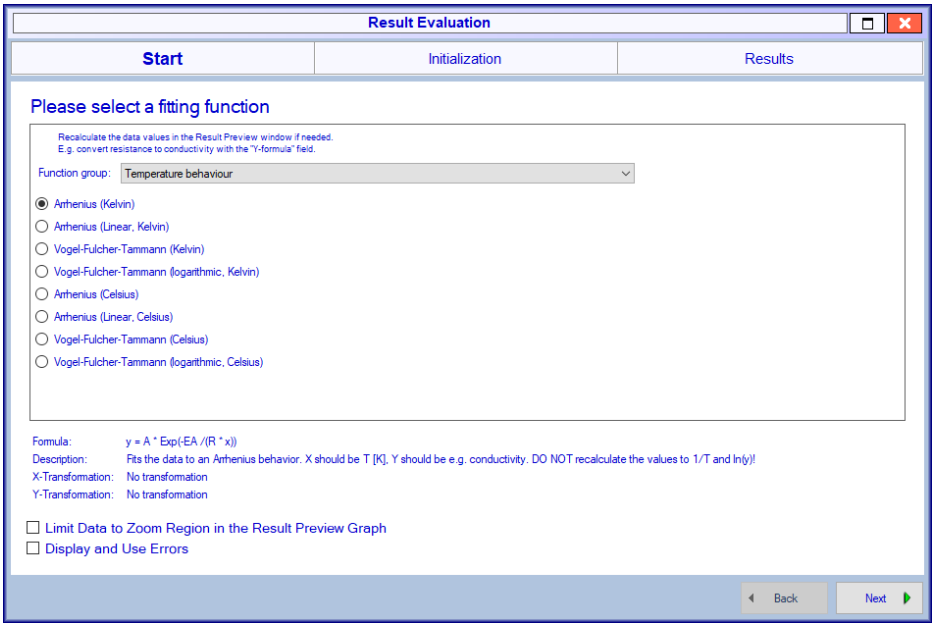
Click **OK** to save the preset. It will then be available in the dropdown and can be applied by clicking it.

The toolbar allows you to delete or edit existing presets. Note that this is only possible for custom presets. The built-in presets can't be changed or deleted.

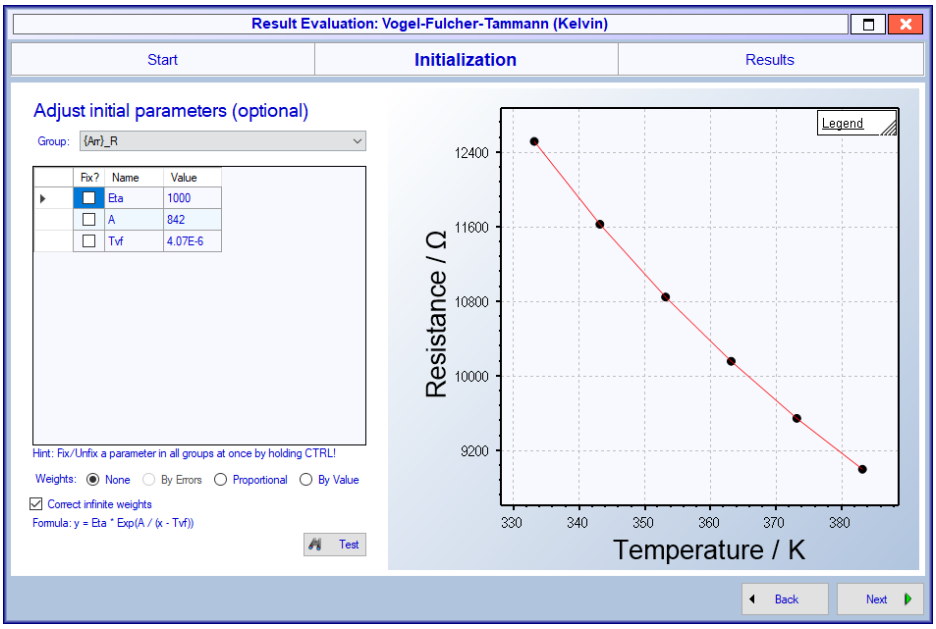
12.2 Result Evaluations: Fitting the Results With Further Models

Once you have plotted the parameters from the spectra in the way you like and possibly recalculated them, you can now use further models to fit the **currently plotted (or visible) data** to another model. Click the **Send to Evaluator** button to open the fitting dialog.

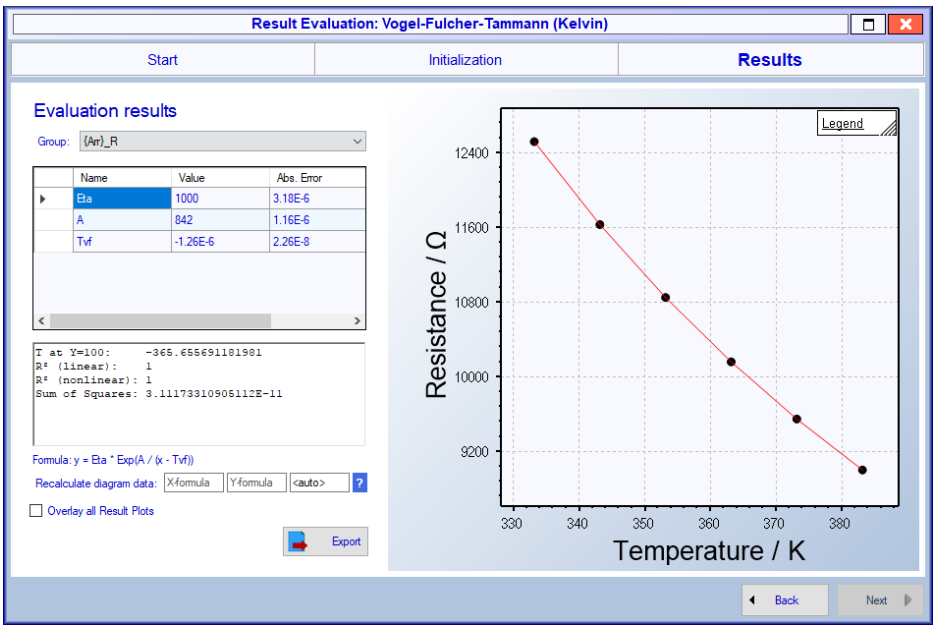
You can limit the used data to the datapoints that are currently displayed in the **Result Preview** graph (through zooming/panning) by checking the respective checkbox. You can also select, if the errors of the result preview values should be displayed and used for the fits.



1. First select a model on the first page. The models are sorted into different groups. You can find the formula the data is being fitted to below the model list, as well as a description of the model. Click the **Next** button to move to the next step. You can create your own models with the **RelaxIS SDK**. Models may include a pre-transformation of the X and Y values, that will be applied before the model parameter initialization.



2. Now set the initial parameters for the fit. All models have an automatic initialization method and should require very little initialization.
    a. If you have split the data, you can select and inspect the initial parameters for all series by using the combobox at the top.
    b. You can fix one or more parameters of the model to specific values by checking the respective box.
    c. You can test the fit by clicking the test button and observing the green result curves.
3. Click the **Perform fit** button to execute the fit.



4. The last page lets you inspect the fit results for each series and the calculated errors. You can plot all results at once by checking the "Overlay" box.
5. Some models calculate additional information. For example, the Arrhenius-model calculates the activation energy in eV. Further inferred results are listed in the textbox below the parameter table.
6. The page allows you again to recalculate the data plotted in the graph to the right. This enables for example a fit of $\sigma(T)$ data from a conductivity measurement directly to the Arrhenius- or VFT-model, and afterwards a plot in the common $\log_{10}\sigma(1000/T)$. By default, the error propagation is calculated automatically by the **<auto>** formula.
7. You can export the data into a file or the Windows clipboard. The export process is further described in section 14.

⚠ Please note

Please check the formulas used for the models exactly. For example, you shouldn't send $\log_{10}\sigma(1000/T)$ data to the VFT- or Arrhenius models, since these do not use the linearized but the exponential form. Plot $\sigma(T)$ data in the Result Preview and use it directly. This applied also for the linearized/logarithmic versions of these models, because the transformation is applied automatically during the pre-transformation step.

For all default, temperature dependent models plot the straight value, e.g. σ versus the temperature in the Result Preview. Necessary transformations will be done automatically. If your temperatures are given in Celsius, select the models named with **(Celsius)**, if your temperatures are given in Kelvin, use the models named with **(Kelvin)**.

12.3 Result Preview Pivot Statistics

This feature allows you to calculate descriptive statistics of the currently plotted data rows in the Result Preview and calculate overall means and standard deviations. It allows you, for example, to find the minima of the plotted curves, which can be copied and used for other evaluations, as metadata or in formulas.

13 PREMADE ANALYSIS TOOLS

13.1 MOTT-SCHOTTKY ANALYSIS

Mott-Schottky analysis is primarily used in semi-conductor studies and there is used to determine the donor density in the semi-conductor. This is done by measuring dc-dependent impedance spectra and determination of the capacitance of the space charge region.

This capacitance is related to the donor density via

$$\frac{1}{{C_{SC}}^2} = \frac{2}{e\varepsilon\varepsilon_0 N}\left(E - E_{FB} - \frac{k_B T}{e}\right)$$

Here C_{SC} is the capacitance of the space charge region, e is the elementary charge, ε is the semi-conductor's relative permittivity, ε_0 is the vacuum permittivity, E is the potential, E_{FB} is the flatband-potential, k_B is the Boltzman constant and T is the temperature.

A plot of $\frac{1}{{C_{SC}}^2}$ versus the potential should therefore give a straight line with slope $\frac{2}{e\varepsilon\varepsilon_0 N}$, allowing the determination of the donor density via linear fit and the flatband-potential can be derived from the linear function's root.

In RelaxIS the procedure is implemented via **Fit Results → Mott Schottky Analysis**. It can work with two types of input data: single frequency values or fit parameters. Typically, you would use an appropriate model to fit the data and get the capacitance from a suitable fit parameter. However, in some cases the capacitance is calculated directly from impedance value at a certain frequency. Here, two methods or calculating a capacitance are possible: "Cp" mode, where the complex capacitance is calculated via $\hat{C} = {}^{1}/_{i\omega\hat{Z}}$ and C_{SC} is taken as its real part, or "Cs" mode, where the capacitance is taken directly as $C_{SC} = -{}^{1}/_{\omega Z''}$.

To perform a Mott-Schottky analysis, perform the following steps:

1. Optional: Fit the data to an appropriate model, where one parameter designates the value of C_{SC}.

2. Set metadata for all spectra: **DC Voltage** in Volt and sample **Area** in m². **Please use the correct units!**
3. Start the Mott-Schottky analysis from Fit Results → Mott Schottky Analysis.
4. On the first page, select the spectra you wish to include in the analysis. Select spectra from the list on the left and click the "Add" buttons to add them to the used dataset. You can add spectra from multiple models.
5. Next, select which data should be used. You can combine parameters from multiple groups into single datasets. It is also possible to add multiple datasets. A Mott-Schottky analysis is performed for each dataset. You can choose between fit parameters, Brug calculation from a resistor and CPE or a Zarc element, and single frequencies and combine the latter freely into datasets. E.g. if spectra's frequencies vary slightly you could combine 1000 Hz, 1001 Hz and 999 Hz into a single dataset.
6. Set the Temperature in Kelvin (!) and the dielectric constant of the semiconductor. If you selected single frequencies as data, you can also select the capacitance calculation method at the bottom.

On the last page the results are displayed. By default, the linear fit is done over all datapoints. You can drag the green bars on the graph around to limit the X-range over which the linear fit is performed. Click the "Update Results" button at the top to update the linear fits.

On the right you get a list of the calculation results. N is the donor density, given in both m^{-3} and $cm^{\wedge-3}$, and E_fb is the flatband potential. Below you get the raw data used for the plots and calculation.

⚠ Please note

Please check the validity of the calculated values carefully. Mistakes in e.g. the metadata units may lead to invalid results. When in doubt, calculating one or a couple of values by hand is a good way to sanity check the results!

The "Export" button at the top allows you to export both the analysis results as well as the plot data, and you can store the whole analysis in the Result library.

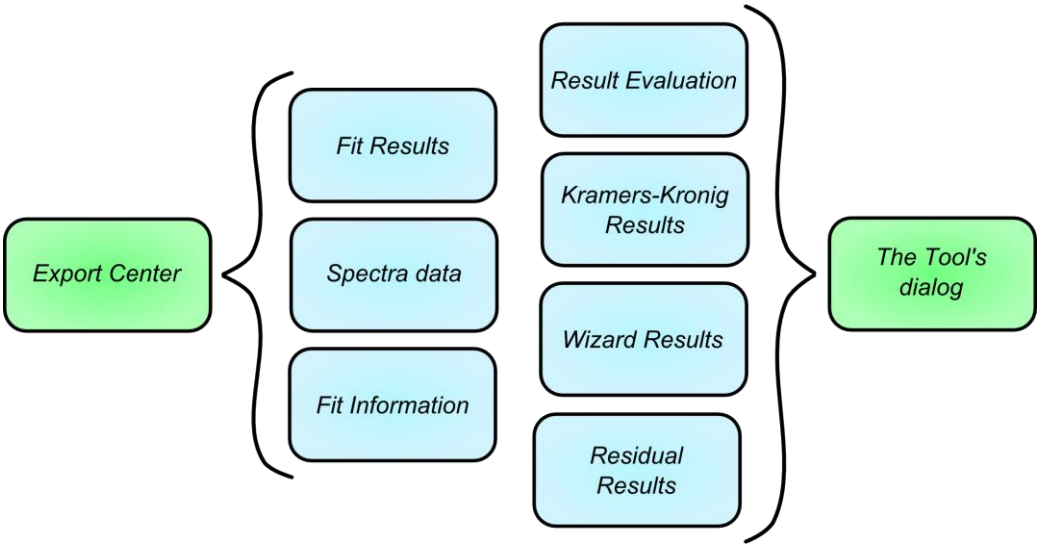
14 EXPORTING DATA

Besides exporting the images of the various graphs as explained in section 8.1.4 you can export the raw data into either a file or into the Windows clipboard as tab-delimited text. This makes it easy to work with it in various spreadsheet-based programs.

Additionally, it is possible to create reports to quickly present data in a common format. These are intended to be used for presentations or meetings and can be customized with your own designs.

14.1 THE EXPORT DIALOG

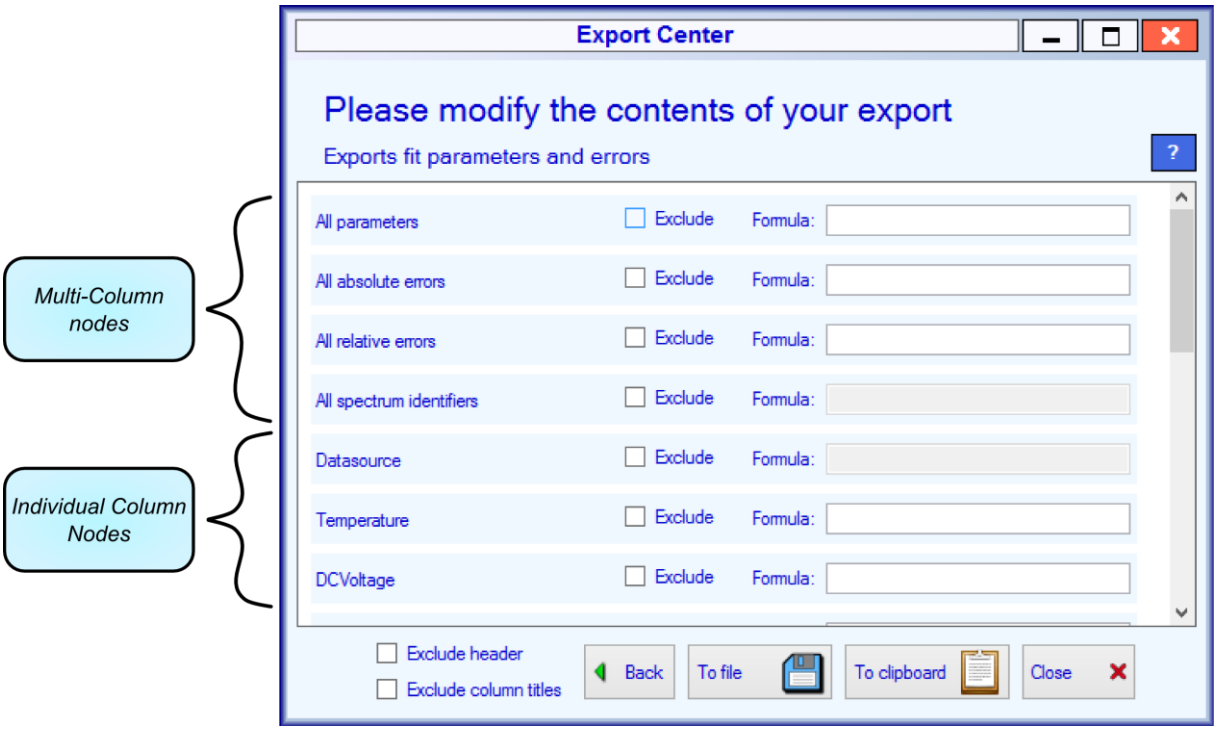
Every raw data export is performed using the Export Dialog. The dialog is usually accessed using the **Export Center** button on the **Main** tab of the ribbon bar. Depending on the data in question, the Export Dialog is sometimes opened not from the Export Center, but from individual dialogs of the different tools. In that case, you can find a button labeled **Export** on the respective tool's dialog.



In the Export Center, choose the type of export you would like to use by selecting the respective button. Then click **Next** to move to the Export Dialog.

Depending on the type of data, you may be prompted by the Spectra Selection dialog first, to choose which spectra to include in the export or it will use the currently selected spectra (direct selection mode).

The Export dialog shows you all contents that the export can contain. These are shown as nodes, where each node represents one or multiple columns.



Typically, you find nodes that can alter multiple columns at once at the top of the list, and nodes that can alter single columns below. The multi-column nodes usually begin with the word **"All"**.

⚠ Please note

The exporters adapt dynamically to the data present in your project. Some contents may not be available in some situations, for example when you have no model assigned to a spectrum.

For each node, you can designate the Exclude option as well as specify a formula. A formula can only be applied, if the column contains numeric data.

- **Exclude** causes that content to not show up in the exported data. Multi-nodes take precedence over individual nodes in this case.
- The **Formula** recalculates the data in the column. You can use the symbols found in the **?** message. Usually you can use metadata of each

spectrum here. Individual nodes take precedence over multi-nodes in this case!

The export usually contains a header of two lines of text that describes the type of export and the current date and time. Additionally, a title for each column is added in the third line of the export.

Using the **Exclude header** and **Exclude column titles** options, you can prevent these lines from being included in the output.

Once you are satisfied with the entered information, you can click the **To file** button to export the data into a text file. By clicking the **To clipboard** button, you can place the generated text in the Windows clipboard, for easy pasting into a spreadsheet program of your choice.

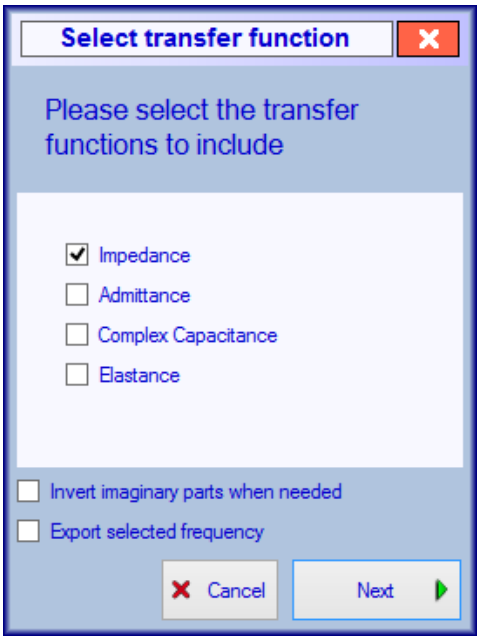
Please note

All graphs allow the export of the raw data currently shown in them, as well as the export of the graph as an image. Please refer to sections 8.1.4 and 8.1.5 for further details.

14.2 Additional Settings for Certain Exporters

Exporters may require additional settings. In this case, you are prompted with an additional dialog after you have clicked the **Next** button in the starting page of the Export Center. Enter the settings of your choice and click **OK** to move to the Export Dialog. If you want to change the settings you set, click the **Back** button on the Export Dialog and restart the procedure.

Currently the only exporter that requires additional settings is the **Spectrum Exporter** that exports the raw data of the spectra and the fitted curves.



The settings are as follows:

- The transfer functions you would like to include in the export. Multiple choices at once are possible.
- For some transfer functions like the impedance the imaginary part is usually negative. In this case you can choose to **Invert the imaginary part**. For others like the admittance this setting will be ignored.
- You can choose to export the **active frequency range only**. That way, inactive frequencies will not be included in the exported data.

15 The Result Library

The Result Library is used to save various types of evaluations in order to be able to display the exact results of the evaluation at a later time. The stored data is designed in a way to be able to display the result without any dependencies on plugins like transfer functions or models. Currently you can store the following evaluations in the library:

1. Individual spectra with fit results and plots
2. Result Preview plots
3. Result Evaluation results and plots
4. Combined Data Plots
5. DRT Evaluations
6. Kramers-Kronig Evaluations
7. Model Screening Results
8. Residual-Analysis results
9. Multi-Spectrum-Fit results
10. Parameter Influence test results
11. Bootstrap Error Estimation results

The results are stored on a per-project-basis in the EIS3 files. This means that if you use the **Manage Projects** feature to create multiple projects in a project folder, each project has an individual result library.

15.1 Storing Results in the Library

After you have done one of the evaluations mentioned above, look for the “Store” button similar to the one depicted on the right. To save the results click the Store button and enter a title and comment about the result in the dialog. Due to the amount of data required to be saved the evaluations may take significant space on your hard drive. The dialog where you enter the title and comment also shows the expected disk space required to save the data. This amount can range between a few kilobytes to several megabytes, e.g. for DRT results with many datapoints and spectra.

After entering the title and comment click OK to save the result in the library.

15.2 Displaying Saved Results

To open the Result Library, click the **Main→Result Library** button. The dialog shows the currently saved results separated into multiple groups. Select the group that contains the result you wish to display from the Dropdown Menu. Depending on the type of result you have one or multiple ways to display the data. If the data has multiple choices for display, the **Display** button in the ribbon menu of the Result Library will display a menu of choices. Click on one of the menu items to display the data. If only a single choice exists, the **Display** button will directly display the result.

15.3 Reusing Saved Settings

Depending on the type of evaluation, the settings used to obtain the result can be reused in order to perform the save evaluation again for current data. The different result types that offer this feature are:

Result Type	Reusable Setting	Explanation
Result Preview	Set formulas and values to Result Preview	The formulas, selected X, split value and Y values and options are set to the current result preview screen.
Result Evaluation	Open Result Evaluation with raw data	The stored raw data is used as fresh data in a new Result Evaluation session. This allows fitting the stored data with a different model.
	Combine raw data with current result preview	The stored raw data is combined with the currently plotted result preview plot to produce a combined dataset which is then used in a new Result Evaluation session. Gives the choice if data in the stored limits is used only.

DRT	Use settings in the DRT Dialog	Opens the DRT dialog and changes all settings to the stored values
Kramers-Kronig-Test	Use settings in the KK dialog	Opens the Kramers-Kronig-Test for the currently active spectrum with the stored settings
Residual Analysis	Open Residual View with result settings	Opens a new Residual View with the settings used in the stored result
Bootstrap Error Estimation	Use stored settings Bootstrap-dialog	Opens the Bootstrap-Error-Estimation for the currently active spectrum with the stored settings

15.4 Import and Export of Stored Results

The results are stored in XML format in the database. The XML can be saved in a text file from the result library. In order to export a stored result into a separate file select it in the result library and then click the **Export Result to XML File** button in the ribbon menu. Select a file name to save the XML to and click OK.

You can also import results into the library by clicking the **Import Result from XML File** button from the ribbon and selecting the respective file. This allows exchanging evaluation results between projects or with colleagues.

16 REPORTS

16.1 CREATING REPORTS

Reports are HTML-based summaries of the fit results and the data saved for each spectrum in the project.

Each report is created using a template. The template is a HTML-document you can view in a browser. It can contain text, images, scripts, and so on. Additionally, the templates contain certain **tags**. When you create a report from RelaxIS, those tags are replaced by information, to fill the final report with life.

By default, RelaxIS contains some templates for general tasks. They show graphs of the data together with metadata and values for the fit parameters.

To create a report, please perform the following steps:

1. Select the spectra you would like to include in the report (*optional*).
2. Click the **Create Report** button on the **Main** tab.
3. Select a template from the list and click **Select template**.
4. Use the Spectra Selection dialog to select the spectra to include in the report (or currently selected spectra are used).
5. Select a filename and location on your hard drive for the report.

The report is now created and shown in your default web browser.

The following default templates are included in RelaxIS:

Template	Description
RelaxIS General	Creates a report with one spectrum per page in color. Includes a Nyquist- and Bode-Plot, metadata and fit results.
RelaxIS General Monochrom	Creates the same report as “RelaxIS General” but uses only grayscale colors to fit better to monochrome printers.
RelaxIS Short	Creates a shorter report with two spectra per page. Includes a graph, metadata and fit results.

16.2 Creating Report Templates

Creating the actual template requires some knowledge of the **HTML** (Hypertext Markup Language) and **CSS** (Cascading Style Sheets) standards. A tutorial on these are beyond the scope of this manual. You can find multitude of tutorials about creating HTML documents and styling them using CSS on the internet.

16.2.1 Creating the Basic Template

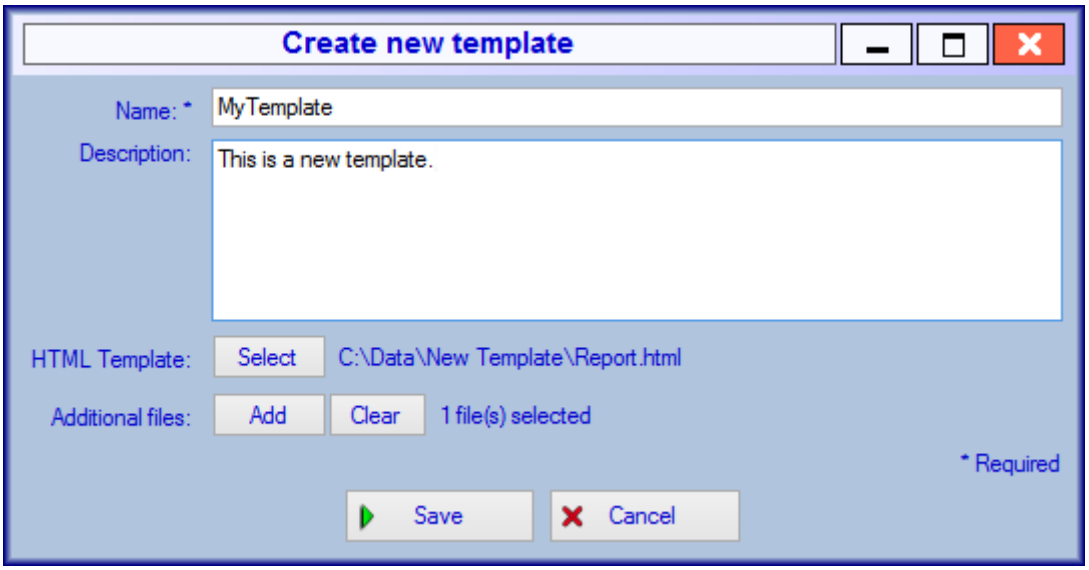
You can design your own report template. A report template consists of multiple files:

- A description in the form of an **.XML** document, that contains basic information about the template and the additional files it needs.
- An **.HTML** document that is the base layout and contains **tags** that are replaced with actual content on report creation.
- Additional files like images or stylesheets that can be included in the report.

The creation of the HTML-document will be explained below. Once you have created the HTML-file, you need to create a template from it.

The basic template structure can be created using the RelaxIS interface. On the report dialog click either the **New** or the **Clone** button. The New button creates

a blank template, while the Clone button uses the information and files from an existing template to get you started.



- The **Name** is the unique identifier for the report template. It is used to refer to it in the RelaxIS Remote feature (section 20).
- The **Description** is displayed alongside the name in the template selection dialog.
- The **HTML Template** can be selected from the hard drive using the Select button. The location is arbitrary, since the HTML document will be copied to the template location.
- **Additional files** are included in the TemplateFiles subfolder when the report is created. They can contain anything you would like to include in the report.

⚠ Please note

The TemplateFiles folder will not be unique for every report. This can lead to additional template files being overridden by ones of the same name of another template! Try to make the filenames unique to the template, for example by including the template name in the filename, e.g. use *"MyTemplate-Logo.png"* instead of just *"Logo.png"*.

Click the **Save** button afterwards to create the template and save it in your user folder.

16.2.2 Creating the HTML Template

To create the HTML template, you can use any HTML editor you like, or create the HTML code in any text editor. We recommend, for example, the free Microsoft Expression Web 4 editor.

The template is a standard HTML document, that can contain any content you like. You can include additional content like images, with the limitation that they must be placed in the **TemplateFiles** subfolder and should be linked dynamically in the HTML like

```
<img src="TemplateFiles/MyLogo.png" width="152" />
```

Content is put into the template by RelaxIS using various additional tags. The tags have a certain format:

```
{TAG-NAME|OPTION_NAME1=OPTION_VALUE|OPTION_NAME2=OPTION_VALUE|…}
```

- It always starts with the curved bracket: {
- **Tag-Name** is a unique identifier for the specific tag.
- It is followed by specific options, separated by the | character.
- Options have a certain name, are followed by an = sign and the value for the option.
- The tag closes with a curved bracket: }

The options change the behavior of the tag or define what exactly you want to show at the location. **Most options are optional!** If you leave the options out the tag will use default or automatic values for these.

The usable tags are:

- Spectrum Metadata
  - DATASOURCE
  - METADATA
  - CELLCONSTANT
- Model
  - CIRCUITSTRING

    - CIRCUITIMAGE
- Fit Information
    - PARAMETERTABLE
    - TRANSFERFUNCTION
    - WEIGHTMODE
    - SUMOFSQUARES
    - CHISQUARED
    - R2
    - DOF
- Plot Images
    - NYQUISTPLOT
    - BODEPLOT
    - BODEPHASEANGLEPLOT
- Miscellaneous
    - MATH
    - RELAXISVERSION

You can find the detailed definitions of the tags and their options in the tables on the following pages.

Tag Name:	**DATASOURCE**
Description:	The value of the *Datasource* property of the source spectrum.
Options: *No options!*	

Tag Name:	METADATA	
Description:	A single value from one of the metadata variables. The variable to display is defined by the *Variable* option.	
Options:		
Variable	*Text*	The name of the metadata variable to display. As of version 3.0.1.5 this can be one of the following: • Temperature • DCVoltage • ACVoltage • Time • Harmonic • Thickness • Area • FreeVariable • FreeVariable2
Format	*Text*	Formats the property value with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short

Tag Name:	CELLCONSTANT	
Description:	The cell constant of the spectrum calculated as *Thickness/Area*.	
Options:		
Format	*Text*	Formats the property value with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short

Tag Name:	CIRCUITIMAGE	
Description:	An image of the model assigned to the spectrum. If you append *SI* to the tag name, the images are saved into files instead of being embedded into HTML, e.g. *CIRCUITIMAGESI*.	
Options:		
Scale	*Numeric*	The scaling of the circuit image, similar to the slider in RelaxIS. *Default: 1*
Shownames	*True/False*	True shows element names in the image, False hides these. *Default: True*
MaxWidth	*Numeric/Numeric*	The maximum width and a tolerance value, separated by a slash (/). If the image is wider than Width+Tolerance the image will be split to several rows with width *Width*. E.g. *MaxWidth=150/30* *Default: No max. width*
BackColor	*Four Hex values*	The background color in the format AARRGGBB, designating the alpha, red, green and blue values in the form of hexadecimal numbers from 00-FF. *E.g. BackColor=FF00FF00* *Default: Transparent*
CSSCLASS	*Text*	The name of the CSS-class associated. The created HTML object will contain a *class="Text"* option.

Tag Name:	CIRCUITSTRING
Description:	The string representation of the model assigned to the spectrum
Options: *No options!*	

Tag Name:	PARAMETERTABLE	
Description:	The values of the parameters in the form of a table that can be designed using a column description format.	
Options:		
CSSCLASS	*Text*	The name of the CSS-class assigned to the table.
TRCLASS	*Text*	The name of the CSS-class assigned to each table row.
TDCLASS	*Text*	The name of the CSS-class assigned to each table column.
THCLASS	*Text*	The name of the CSS-class assigned to the header cells.
MaxRows	*Numeric*	The maximum number of rows, after which the table will be continued to the right of the initial table.
MaxXRep	*Numeric*	The maximum number of continuations to the right once the MaxRows rows were reached. **May override MaxRows!**
Header	*Text*	Defines the text displayed in header cells above the table columns. You should create a *header* option for each defined column in the **order of appearance** in the table.

The Column option can be repeated multiple times to define multiple columns in the table.
The general format for a column designation is

```
Column=Column-Content
```

Column-Content is an arbitrary string that may contain additional tags in the form:

```
##X[format]
```

Where X is replaced by one of the following letters designating the value to insert at this position and *format* defines the appearance of the content.

##F	*[TrueValue; FalseValue]*	Shows the Fixed state of the parameters. The format defines what is displayed when the state is true or false. *E.g. ##F[X;] displays an X when the parameter is fixed, or nothing if not.*
##N	*[]*	Shows the parameter name. No format applies (empty brackets).
##V	*[Format-String]*	Shows the parameter value with the assigned format string.
##A	*[Format-String]*	Shows the absolute parameter error with the assigned format string.

##R	*[Format-String]*	Shows the relative parameter error with the assigned format string

For example the column definition:

```
Column=##A[short] (##R[short] %)
```

Shows the absolute error followed by the relative error followed by a percentage sign in brackets, e.g. *123 (0.54 %)*

A complete example of the PARAMETERTABLE tag from the default template would be

```
{PARAMETERTABLE|cssclass=ptable|trclass=rowclass|tdclass=colclas
s|thclass=headerclass|MaxRows=14|MaxXRep=2|column=##F[X;]|column
=##N[]|column=##V[short]|column=##A[short] (##R[short]
%)|header=Fix?|header=Name|header=Value|header=Error (Relative)}
```

Tag Name:	**SUMOFSQUARES**	
Description:	The sum of squared residuals of the spectrum's current fit.	
Options:		
variable	*Text*	The name of the transfer function to calculate the value for. If not assigned, the last used transfer function for a fit of the spectrum or the current one is used. If the value is "current", the current transfer function is always used. If invalid, the current transfer function is used.
Format	*Text*	Formats the ESS value with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short

Tag Name:	CHISQUARED	
Description:	The χ^2 value of the spectrum's current fit.	
Options:		
variable	*Text*	The name of the transfer function to calculate the value for. If not assigned, the last used transfer function for a fit of the spectrum or the current one is used. If the value is "current", the current transfer function is always used. If invalid, the current transfer function is used.
Format	*Text*	Formats the χ^2 value with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short

Tag Name:	DOF
Description:	The degrees of freedom, meaning the spectrums data point count (times 2, due to real and imaginary parts counting as dependent variables individually) minus the number of unfixed parameters.
Options: *No options!*	

Tag Name:	R2	
Description:	The nonlinear coefficient of determination (R^2) of the spectrum's current fit.	
Options:		
variable	*Text*	The name of the transfer function to calculate the value for. If not assigned, the last used transfer function for a fit of the spectrum or the current one is used. If the value is "current", the current transfer function is always used. If invalid, the current transfer function is used.
Format	*Text*	Formats the R^2 value with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short

Tag Name:	TRANSFERFUNCTION
Description:	The transfer function used for the last fit of the spectrum.
Options: *No options!*	

Tag Name:	WEIGHTMODE
Description:	The weighting mode used for the last fit of the spectrum.
Options: *No options!*	

Tag Name:	NYQUISTPLOT BODEPLOT BODEPHASEANGLEPLOT	
Description:	Creates an image of one of the three plots. The Nyquist Plot plots the *imaginary vs. the real part*, the Bode Plot plots the *real- and imaginary parts vs. the frequency* and the Bode Phase Angle Plot plots the *magnitude and the phase angle vs. the frequency*. The options are the same for all plots. Please remember, that the **options are optional** and don't need to be all set! If you append *SI* to the tag name, the images are saved into files instead of being embedded into HTML, e.g. *NYQUISTPLOTSI*.	
Options:		
CSSCLASS	*Text*	The name of the CSS-class associated. The created HTML object will contain a *class="Text"* option.
Width	*Numeric*	The width of the rendered image.
Height	*Numeric*	The height of the rendered image. *Tip: Render the image in a high resolution and use the CSSCLASS together with a CSS-style to downscale the image in the HTML output.*
XMin, XMax, Y1Min, Y1Max, Y2Min, Y2Max	*Numeric*	Defines custom limits for the various axes of the graph. If undefined, the graph is automatically scaled.
XTitle, Y1Title, Y2Title	*Text*	Defines custom titles for the various axes of the graph. If undefined, automatic titles will be used.
XLog, Y1Log, Y2Log	*1* or *0*	Sets the X-, Y1- and/or Y2-axes logarithmic scaling to yes or no. If not supplied, standard values for plots are used. Allowed values are: 1 → Logarithmic scaling 0 → Normal scaling
ShowGridlines	*True* or *False*	Defines if gridlines are shown on the rendered graph (True) or not (False)
Colors	*grayscale* or *light*	If this option is set with the value *grayscale* the graph will be rendered without colors. If the value *light* is set, the graph will be colored, but will have a white background. **DEPRECATED**: It is advised to use the Style tag instead.

Style	*Text*	The name of a style template to be used for the graph. Style template names can be found by opening the Graph Style dialog (see section 8.10), and finding the name in the "Name" column.
Variable	*Text*	The name of a transfer function used to plot the data. By default, the transfer function used for the last fit is used, or (if not available) the currently selected one. If the value of this option is *current* the currently selected transfer function is used in any case. Values are case-sensitive! Refer to the appendices for default values.

Tag Name:	**RELAXISVERSION**
Description:	The current version of RelaxIS used to create the report, e.g. "3.0.1.4"
Options: *No options!*	

Tag Name:	**MATH**	
Description:	Allows performing mathematical operation by providing a formula. The formula can access metadata and fit parameter values/errors of the spectrum.	
Options:		
Format	*Text*	Formats the result of the calculation with the format string provided. Refer to https://msdn.microsoft.com/en-us/library/dwhawy9k%28v=VS.110%29.aspx. *Recommended:* format=short
Formula	*Formula (Text)*	The formula to be calculated. Access the spectrums metadata using the *T*, *DC*, *AC*, *FV*, *A*, *d* symbols and use *P1*, *P2*, … and *E1*, *E2*, … to access parameter values and errors.

Some tips and pointers for designing the templates:

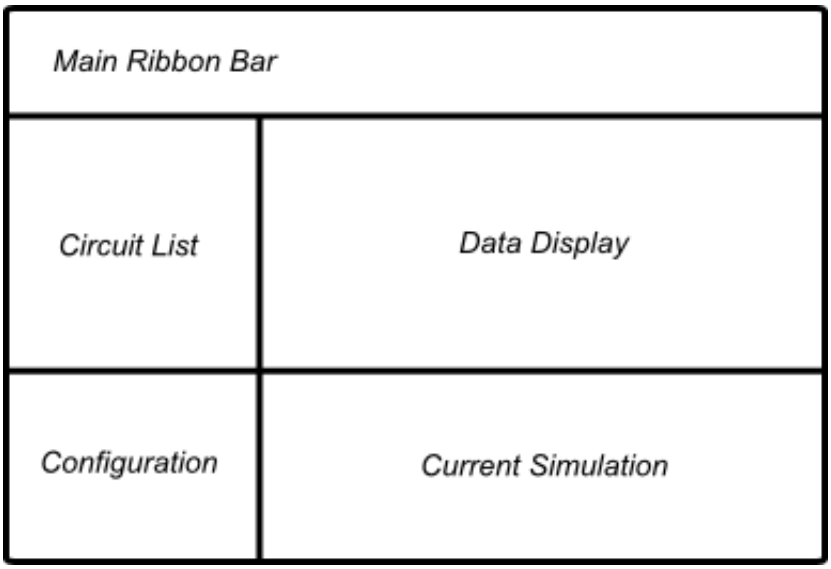
- Make extensive use of the CSSCLASS options in combination with **CSS styles** in your HTML document. That way you can set and control the appearance and size of the elements to your liking.
- Render the graphs in a high resolution and scale them down using CSS. However, don't make the resolution too large, or the graph elements may become too small once downscaled.
- **For printing the reports,** it is a good idea to place all content in a single-cell table or a `<div>`. With CSS, you can set the `page-break-after:always;` option for this section in order to place each report on individual pages.
- Embed small graphics like company logos as a Base64-String. This can allow the report to stay as a single file, without relying on external resources. This is at the cost of some disk space, because the graphic is stored for each report individually.

17 THE CIRCUIT SIMULATOR

The RelaxIS Circuit Simulator is a tool to easily calculate impedance data for any model in a free frequency range. It is mainly used for educational purposes. You can, for example, find out how certain parameters affect the impedance spectrum.

The Circuit Simulator can however also be used for evaluation purposes, for example to extrapolate a spectrum to non-measured frequencies.

You can access the Circuit Simulator from RelaxIS using the **Circuit Simulator** button on the **Extras** tab of the ribbon bar, or you can open it from the Start Menu after RelaxIS was installed.



17.1 BASIC OPERATION

The Circuit Simulator will calculate data for every circuit you have added to the circuit list and that is marked as active. You can add circuits to the list by clicking the **Add spectrum** button and using the Build Model dialog as described in section 9.1. You can **activate and deactivate** circuits by clicking the checkbox next to the circuit in the circuit list.

The parameter values used for calculating the data for each circuit can be changed by selecting the circuit in the list. The parameter values of the selected circuit are shown in the table next to the list. You can change the values to any value you like. The changes are immediately shown in the Data display.

17.2 Settings

Use the settings dialog to change relevant simulation parameters.

17.2.1 Frequency Range

You can calculate data points in a certain range. Select **Automatic Frequency Range and** enter the minimum and maximum frequency, as well as a number of datapoints to simulate. You can either enter the values into the textboxes or click and drag the bars to quickly change the values.

You can also enter specific frequencies. Select **Specific Frequencies** from the settings dialog. Afterwards you can enter a list of frequencies into the textbox. Separate frequencies with a **semicolon**.

17.2.2 Noise

You can add **normally distributed noise** to the data. Enter the standard deviation for the distribution into the textbox. Separate noise values are applied to the magnitude and phase angle of the immittance **after** the value is converted into the active transfer function. The generation of noise uses a fixed random seed, meaning that the sequence of random deviations is always identical. You can reshuffle the noise values by clicking the “Shuffle Noise” button in the Plotting menu.

Note: When noise is added in another transfer function than the impedance before sending spectra to RelaxIS the resulting amount of noise in RelaxIS may be different, because the data is sent as impedance values.

17.2.3 Further Simulation Parameters

In the further options of the settings dialog you can define which plot type to use (Nyquist, Bode, Bode/Phase Angle), which transfer function to calculate

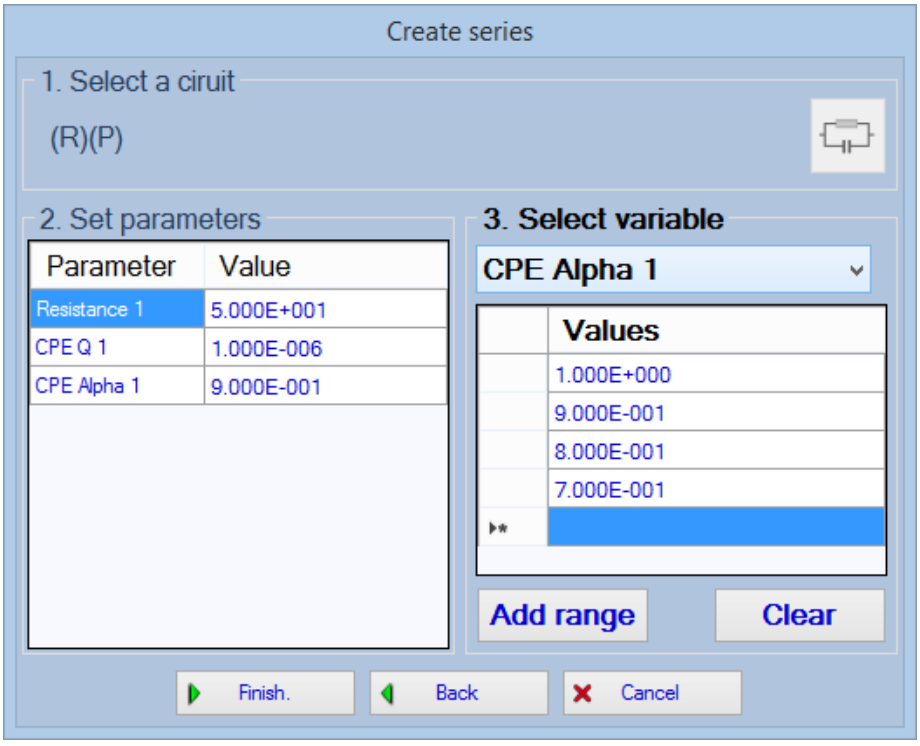
and how to plot the data. Additionally, the **Plotting** ribbon tab allows you to freely adjust what is displayed on which axis.

17.3 Adding Model Series

You can add model series that consist of the same model with varying parameter values. The Circuit Simulator contains two ways to create series. The two ways are accessed by clicking the **Add model series** button in the main menu.

17.3.1 Model Series from Value Lists

Here all parameters except one have the same value in all spectra. One of the parameters however can be assigned from a freely defined list.



First select the model to use by clicking the button at the top right. Afterwards click the **Next** button. In the next step, you need to enter the parameter values for all parameters. The one you want to vary is irrelevant in this case and is selected in the next step. Click the **Next** button once you set the parameter values.

In the next step, you need to select the parameter to vary. First select the parameter from the combobox. Afterwards you can manually enter values for

this parameter in the list below. You can delete entered parameters by clicking the row's header and using the Delete key on your keyboard.

You can also enter a range of values by clicking the **Add Range** button. Enter an upper and lower limit as well as a number of points to calculate. You can calculate the values in a linear or in a logarithmic fashion. Click the OK button to add the values to the list.

When you are done click the **Finish** button. This will add a new circuit for each entered parameter value in the circuit list.

17.3.2 Model Series from Parameter Ranges

In this mode you can define a value range for each parameter in the model and a specific method to select a value from the range for a spectrum.

First, select the model you wish to use as described above. Next, select the number of spectra you wish to generate. The parameter list will then show all parameters of the model with default value ranges. For each parameter you can select the range by specifying the start and end of the range. The *From* value does not have to be smaller than the *To* value.

In addition to the value you can also select the method to generate distinct values:

- Fixed: Each spectrum will get the *From* value.
- Linear: The parameter value will be linearly interpolated between *From* and *To* for the first to last generated spectrum.
- Logarithmic: The parameter value will be logarithmically interpolated between *From* and *To* for the first to last generated spectrum.
- Random: The parameter value is selected at random in the range between *From* and *To.*
- Log. Random: A random number *R* is generated between Log10(From) and Log10(To) and the parameter value is selected as *10^R*. Negative and 0 for *From* and *To* is accepted and will be handled.

The random number generation uses the shown random seed. That means that for the same number of spectra and same random seed (and same number of random parameters!) the same spectra will be generated. Change the seed to another positive number to generate different random numbers.

17.4 Speed Mode

Drawing the graph can take some time when many data points need to be drawn. By default, the speed mode is enabled. When you add more and more circuits to the list, at one point you will reach the number of datapoints set in the ribbon bar. At this point the Circuit Simulator will disable circuits from the bottom of the list up to keep the number of datapoints below the set limit. It is however possible to activate the circuits manually again.

Furthermore, it is possible to reduce the drawing quality of the graph to speed up the drawing. This disables for example anti-aliasing.

17.5 AC Simulation

The Circuit Simulator simulates the AC current for the active circuits based on an arbitrary AC voltage. These sine waves are displayed in the AC Voltage Simulation dialog on the main screen for a given frequency. You can set the shown frequency by dragging the bar below the graph. You can also choose to display the AC current on the same axis as the AC voltage to visualize the

relative magnitude of both, or use the secondary axis to better follow the phase shift between voltage and current.

Beside this dialog you can also open another simulation dialog by clicking the **AC Simulator** button on the main ribbon bar. Here you can directly enter an impedance value as either magnitude and phase angle or as real and imaginary part and simulate the current for this impedance value.

17.6 Exporting Data

17.6.1 Export

You can export the simulated data into an easily usable, column separated text file. This can be placed in a file on your hard drive or into the Windows clipboard. The export is based on the same Export dialog as explained in section 14.1. You can choose to export either all spectra or only the currently active spectra.

17.6.2 Send to RelaxIS

If you have a RelaxIS instance with an active project running besides the Circuit Simulator, you can directly send the simulated spectra to RelaxIS and work with them in RelaxIS like any other measured spectrum. This allows you to train yourself in the usage of the various tools, try out functions on well-defined spectra and so on. The sending uses the RelaxIS WCF Link (please see section 21). Check the **RelaxIS WCF Link** label in the RelaxIS status bar to find the currently receiving RelaxIS instance, in case you have opened RelaxIS multiple times. Only the one with the green label will receive the spectra.

18 THE RELAXIS SETUP DIALOG

Open the RelaxIS Settings dialog by clicking the **Settings** dialog on the main RelaxIS ribbon bar. The dialog allows you to set various settings and investigate which plugins are currently loaded.

18.1 GENERAL SETTINGS

In the General Settings box on this page, you can associate RelaxIS with .EIS3 files if you haven't done so during the RelaxIS installation. Buttons also allow you to open your RelaxIS user folder, or to clear the recent file list.

Comparison epsilon affects how comparisons between numbers are carried out. When floating point numbers are stored, they often contain random numbers at the last decimal places. Therefore, numbers are usually not compared 1:1 but are considered equal when their difference is smaller than the set epsilon value.

The Auto Saving box offers settings if RelaxIS should automatically create backups of your project in regular intervals. These backups are stored in your user folder, or in the original project folder if "Save in source directory" is activated. Define the time between automatic saves using the input box.

You can tell RelaxIS to show popup warning about unsaved changes as well as other common tips by activating or deactivating the settings in the Popup Tips box.

The Interface box offers options regarding the RelaxIS user interface:

- "Always use selected spectra for data-related functions": This enables **direct selection mode**, which does not use the spectrum selection dialog as often.
- Use Hotkeys exclusively…: Hotkeys, as assigned in the Hotkeys tab, are used only for the functions assigned there, thus overriding system-wide hotkeys like Ctrl-V for pasting.

- Enable Dielectrics functions: RelaxIS has some special options for working with cell independent transfer functions. Please refer to chapter 6.9. This setting enabled these functions.
- Ctrl-V imports data from clipboard in Spectra Explorer: Enable this option to override the default behavior of pasting values into the Data Explorer grid to importing spectra from the clipboard instead (default pre 3.0.15).
- Default to Cell Selection: If enabled, the Data Explorer uses cell selection per default instead of row selection (row selection was default pre 3.0.15).

18.2 STARTUP OPTIONS

You can choose to display the welcome screen on startup and if you want to check online for program updates. If you are using an online account, the settings “Close Trial Client if last instance” defines, if the Trial Client is automatically closed if the last instance of RelaxIS is closed.

The Plugin Loading box defines settings regarding loading of plugins. You can enable or disable loading of XML and or DLL/Exe files and if DLL/Exe files should be loaded first (important for duplicate plugin names).

18.3 DISPLAY OPTIONS

Graph axis number format allows you to choose whether you want to display logarithmic scales as the logarithm of the number, or as the original number.

Hide empty columns in Spectra Explorer defines, that columns without metadata in them are hidden by default.

Automatically reset main graph zoom option causes the Data Explorer main graph to reset it’s zoom level if e.g. another spectrum is selected or a fit is performed. If deselected the manual zoom is kept. Right-click the graph and select “Zoom out full” if no data is visible in the area.

Parameter Error display options define the display of parameter errors in the Parameter Explorer. You can choose to hide or show errors of fixed or out-of-

date parameters. You can also define the limit value, over which errors are shown in deep red.

Frequency Extrapolation describe the minimum and maximum displayed frequency of the extrapolation display. Please refer to section 8.8.

Click the button Reset Spectrum View Default Settings to set these settings back to their factory defaults.

Here, you can also define which metadata fields are always displayed, regardless of the option to hide empty columns.

18.4 Graph settings

The Graph Settings page allows you to change global graph layout settings that apply to all graphs in RelaxIS, such as graph titles, or legend placement. Please refer to chapter 8.1 for further information about the graph settings.

18.5 Fitting Options

Settings for the fitting algorithms are described in chapter 10.

18.6 Value Formats

On this page, you can define the formats for datasources and error display. Please refer to sections 6.2.3 and 10.2.1 for further information.

18.7 Plugins

The plugins page lists all currently loaded plugins. Plugins are written using the RelaxIS SDK and loaded on program start. You can refer to this page to find out if your plugins have been successfully loaded and the entered information are correct.

Select a plugin category from the dropdown menu and a plugin from the list. Thus, you can find the **internal name** of the plugin to use for example in the RelaxIS Remote job descriptions.

18.8 HOTKEYS

This page allows you to view and edit the hotkey assignments for various functions in RelaxIS. Hotkeys in the list with a yellow background are default hotkeys and cannot be changed. Green hotkeys are user defined and can be changed and deleted.

To add a new hotkey, use the controls at the lower part of the page. Define the keys by using the checkboxes and a key from the dropdown menu. Select the action you wish this key to execute from the larger dropdown list and the click the **Add New** button to add this key to the list.

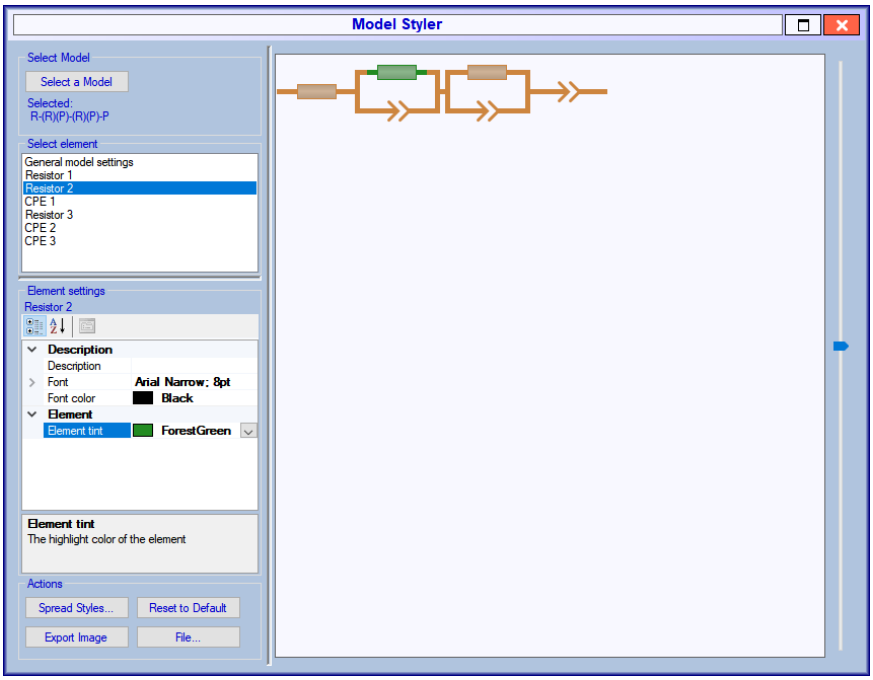
⚠ Please note

Depending on the current context of RelaxIS you are navigating in the hotkey actions may not execute correctly. This can be due to the currently active window, or the location of the input cursors, which causes the key press events to be handled by underlying Windows functions instead.

19 Additional Tools

19.1 The Model Styler

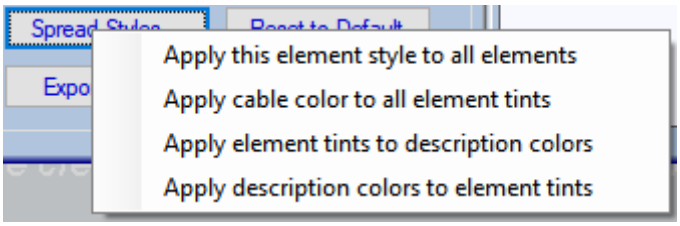
In order to create images of equivalent circuits with a more customizable style, RelaxIS includes the **Model Styler**, that can be accessed from the Extras tab of the main menu.



First, select a model by clicking the button in the top-left. This will then populate the selection box with all the circuit elements in the model, as well as a point for general style settings. Select an element in the selection box, in order to show the element's available options in the box below. For general settings, you can select the color of the connecting cables between the elements as well as their thickness.

For elements, you can select a tint color, that will highlight the element in the circuit with the selected color. Further, you can enter a description of the element. This description will be placed below the element with the selected font and color. The description may contain style elements such as `\-()` or `\+()` for sub- or superscript. Please refer to chapter 8.1.3 for details of the syntax.

The **Spread Styles** button allows you to quickly assign styles to more than one element. The options are:



- Apply this element style to all elements: All styles of the currently selected element are copied to all other elements.
- Apply cable color to all element tints: The selected cable color is applied to the element tint color of all elements.
- Apply element tints to description color: For each element individually the description color is set to the elements tint color.
- Apply description colors to element tints: For each element individually the element tint color is set to the element's description color.

The **File**… button allows you to save and load a style in a file. The style of the first element is used for storing, so the style can be applied to arbitrary models.

The image can be exported using the Export button.

19.2 Notepad

RelaxIS contains a notepad to easily catalog and save your thoughts. You can access the notepad through the **Notes** button on the main ribbon bar in RelaxIS.

Add notes to the list by clicking the **Add note** button or delete the selected note using the **Remove note** button. Click on a created note to change the title and the content of the note on the right.

19.3 Electrochemical Calculator

The Electrochemical Calculator can be accessed using the respective button on the **Extras** tab of the main ribbon bar in RelaxIS.

The calculator offers various often used formulas in electrochemical research. The functions are:

- Calculate the conductivity from a resistance and a cell constant
- Calculate the capacitance from a constant phase element using the Brugg-Formulas
- Transform a voltage into another reference frame (e.g. from NHE into Ag/AgCl-Scale).

Simply enter the respective values into the fields and read off the results from the bottom of each tab.

19.4 Fitting Benchmark

The benchmark is accessible through the **Fitting Benchmark** button on the **Extras** tab of the RelaxIS ribbon bar. On the dialog, you can click the various predefined benchmarks to perform them. The results will be shown on the respective bars. You can also run all benchmarks after another by clicking the **Run all** button.

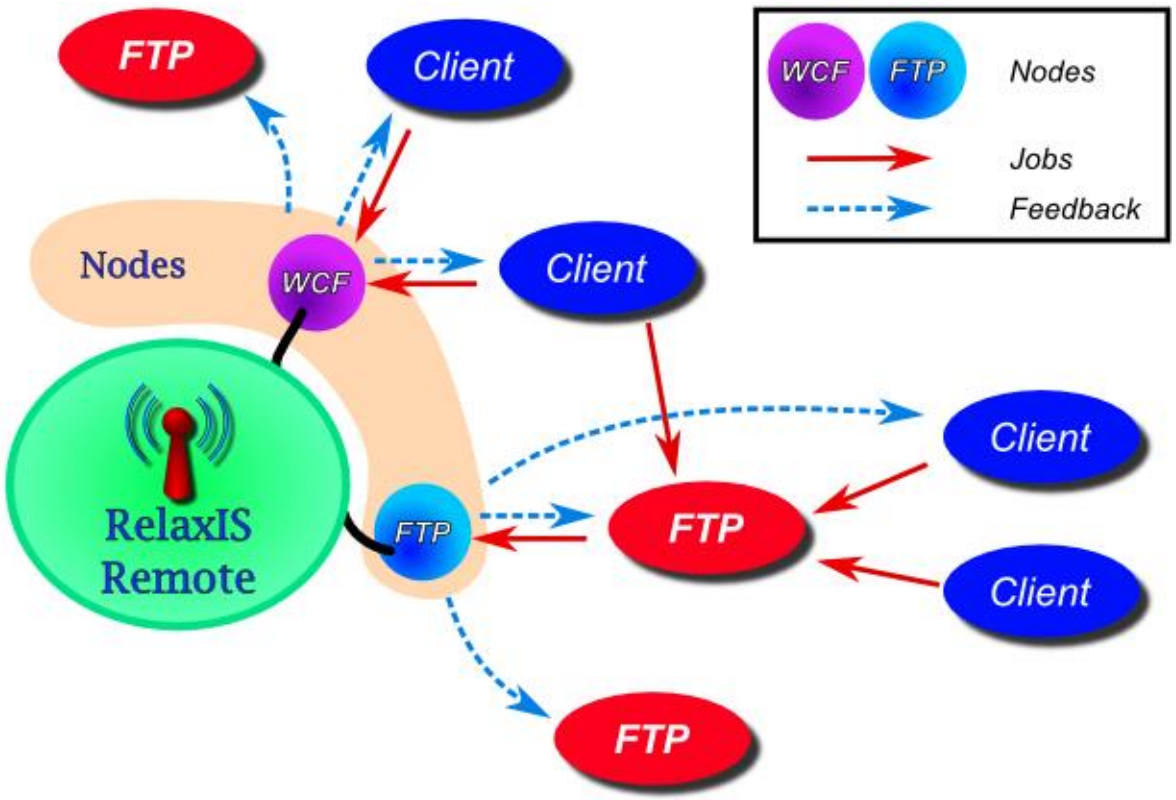
This procedure allows you to make more informed guesses about the impact of certain fitting options you can set in the RelaxIS setup dialog.

20 RELAXIS REMOTE

20.1 GENERAL DESCRIPTION

RelaxIS Remote is best described as running RelaxIS in a server mode. Clients can send data to a RelaxIS Remote Server node, let the server do the work and then retrieve the results.

You can use RelaxIS Remote to automate the evaluation of your measurements. It is intended to allow the centralization of the evaluation and storage of the data on a powerful server while the measurements are executed by simpler machines.



- **RelaxIS Remote** is the overall server mode inside of RelaxIS.
- **Nodes** are combinations of settings. A single RelaxIS instance can host multiple Nodes.

- Nodes communicate with clients either through an intermediate **FTP server** or through a Windows Communication Foundation (**WCF**) service.
- Clients do not need a running RelaxIS instance. **Clients can be anything** that can talk to either an FTP server or a WCF service.

⚠ Please note

In order to use RelaxIS Remote to its full potential you will need some knowledge about programming. That way it is very adaptable to many applications.
If you want to use RelaxIS Remote for a certain application without having the means to adapt it on your own, you can contact *rhd instruments*.

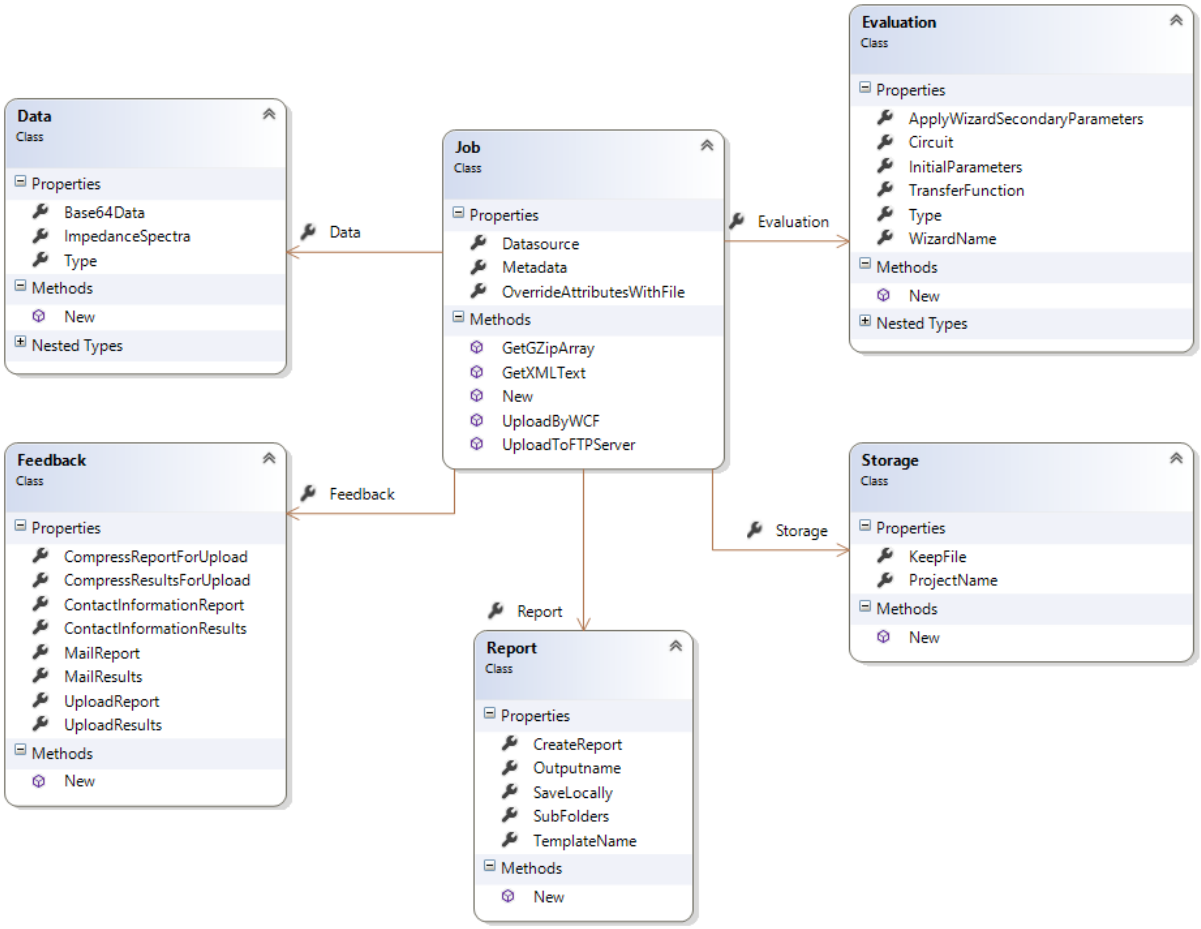
20.2 JOBS

Clients communicate with RelaxIS Remote using so called jobs. These jobs are objects containing the data and information about what RelaxIS should do with it.

The job definitions are available in the form of the `Job` type in the RelaxIS SDK (see also section 22). The SDK is a .NET DLL that not only contains the definitions but also offers methods to easily serialize the job into an .XML document and upload it to an FTP server or send it via WCF to an active WCF node.

If you want to create jobs in a different environment than the .NET Framework, you can create the appropriate .XML manually instead of serializing the created `Job` object and upload it to the respective FTP server.

You can find a detailed description of all the relevant properties in the RelaxIS SDK help files on the RelaxIS installation medium. The general structure will be described in the following paragraphs.



`Job` is the base object you need to create. The options you would like the job to perform are stored in the `Data`, `Evaluation`, `Storage`, `Feedback` and `Report` objects.

A job can contain multiple spectra. In the `Data` object, the data is stored either as binary data (e.g. from a supported binary data file) in the form of a Base64-String or as a list of `ImpedanceSpectrum_Metadata` objects. The `Type` property of the `Data` object defines which type of data is present. You can supply metadata for the spectra or it is read automatically from the binary data. In the former case the metadata is supplied as a list of `Metadata` objects, composed of an identifier like *Temperature, DCVoltage*, etc. and a value. If the `OverrideAttributesWithFile` property of the `Job` object is set to true, the metadata from the individual spectra overwrite those of the same identifier defined in the `Metadata` property of the `Job` object.

The `Evaluation` object defines which kind of evaluation should be performed on the spectra. You set the `Type` property to either perform no evaluation at

all (`NoEvaluation`), perform a single fit (`FixedEvaluation`) or Auto Fit (`AutofitQuick` or `AutofitThorough`) with a given model (`Circuit`), transfer function (`TransferFunction`) and initial parameters (`InitialParameters`) or use a certain (non-interactive) wizard to perform the evaluation (`WizardEvaluation`). `ApplyWizardSecondaryParameters` defines whether a wizard is allowed to change secondary parameters with further evaluation results.

The `Storage` object defines if and how the spectra are stored on the server. If `KeepFile` is false, the spectra will not be stored. `ProjectName` is only relevant, if the Node is running in Dedicated-Server Mode (see below in section 20.3). In that case, you can set the name of the project the spectra will be stored in. If the field is left blank, RelaxIS will automatically choose a project in the selected database.

The `Report` object defines if and which type of report should be created. The `CreateReport` property determines if a report is created at all. If false, all other options are ignored and no report is created. A value of false also prevents a report being sent via the `Feedback` object (see below). The `TemplateName` property determines which kind of report is created. It must match the name of a local report template. Otherwise the RelaxIS's general template is used. The `Outputname` property defines the filename of the created report. If left blank, a unique, random name will be chosen automatically. If defined, a short random string will be appended to avoid overwriting existing reports. The `SaveLocally` property determines if the report is saved permanently on the server. It does not prevent the report being sent via the `Feedback` object. The `Subfolders` property allows you to place the report in a certain subfolder of the server's report storage location. This allows you to organize the stored reports on the server.

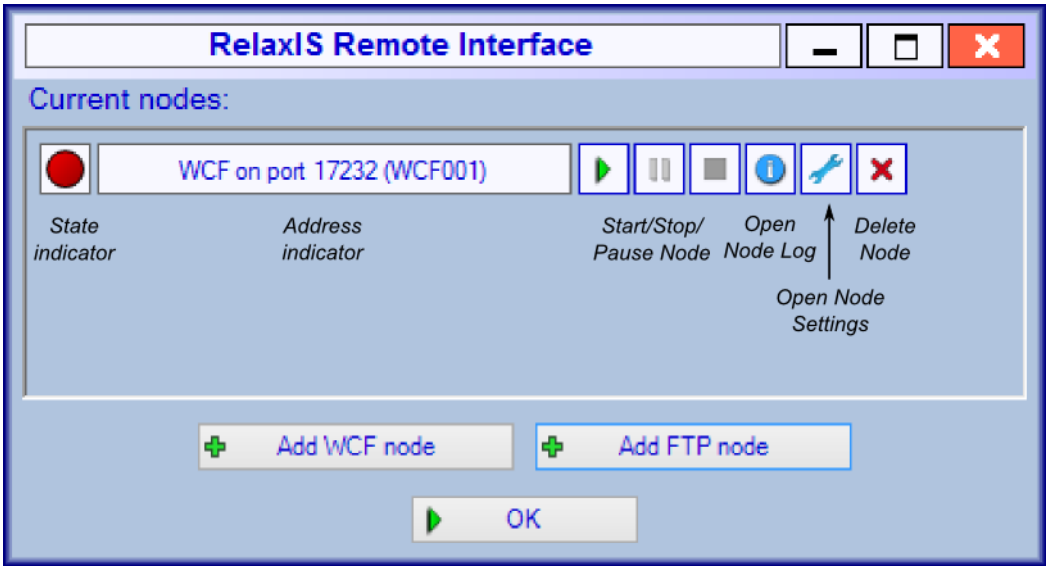
The `Feedback` object defines which kind of feedback should be generated and how that feedback is sent back to the job's sender. The feedback can contain the created report as well as the spectra and fit results in the form of a .EIS3 project folder. These can either be sent back via E-Mail or they can be uploaded to an FTP server in either compressed or uncompressed form. As mentioned

above, a report can only be sent via the feedback function if the `Report.CreateReport` property is true. The addresses to send feedback to are defined in the `ContactInformation` properties and can be different for the report and the results. These objects contain an `EMailAddress` field as well as an `FTPServerOptions` object to define how to connect to the target FTP Server.

After setting up all the desired options you can send the job to the RelaxIS node. For this you can use the `UploadToFTPServer` method in case of an FTP node, or the `UploadByWCF` method in case of a WCF node. The former takes an `FTPServerOptions` object for login information. You can let RelaxIS SDK upload the job as a compressed archive to save traffic at the cost of performance. The return of the function is the FTP status code for the operation. If successful, the code will be 226. The latter takes an address of the server running the RelaxIS Remote node as well as the identifier set up for the WCF node (see next section). It returns `Null` if the job was sent successfully, or an exception if not.

20.3 Setting Up Nodes in RelaxIS Remote

You can access the RelaxIS Remote feature using the **RelaxIS Remote** button on the **Main** tab of the ribbon. This will open the Node list that shows all currently created RelaxIS Remote nodes.



By default, an inactive WCF node is present in the list. You can add WCF or FTP nodes by using the respective buttons.

Nodes can be started or stopped using the respective buttons. Each node has a settings dialog used to configure it, as well as a log that shows statistics and messages related to the work done by the node.

⚠ Please note

In order to use FTP nodes, you need to setup an independent FTP server to work with. RelaxIS currently does not support SFTP, but SSL encrypted connections are possible.
RelaxIS does not include a server software. We can recommend the free *Filezilla Server* software.

Many options are shared by both types of nodes, some related to the connectivity however are not.

WCF Settings

- Server Options
  - Listening Port
    - WCF services are accessed using a certain network port.
  - Identifier
    - Multiple WCF nodes can be accessed using the same network port, using different identifiers. To connect the client needs to specify both port and identifier.
  - Find public IP
    - This allows you to determine the current public IP of the server in order to correctly setup the clients.

FTP Settings

- Server Options
  - Server Address
    - The address of the FTP server to use.
  - Username, Password

        - The username and password used to log into the server.
    - Use SSL
        - Defines if the connection should be SSL encrypted.
    - Passive Mode
        - Defines if the connection should be initiated using the FTP Passive Mode.
    - Keep Alive
        - Keeps the FTP connection alive during requests. This can dramatically increase the performance at the cost of a slightly more instable connection.
    - Update Interval
        - RelaxIS checks on the FTP server for new jobs at regular intervals. This is the interval at which checks proceed.
    - Test Server Settings
        - Tries to log into the given FTP server and shows the results. Allows you to troubleshoot the connection.
- Operational Options
    - Load already existing jobs from the server on start
        - When this option is set, starting the server downloads all existing jobs from the server, otherwise these are ignored.
    - Delete jobs from the server after downloading
        - When this option is set, the jobs (that are stored as files on the server) are deleted after they have been successfully downloaded.

Shared Settings

- **Operation Mode**
    - You can choose between two operational modes, that determine how the node interacts with RelaxIS.
        - **Live Mode** adds received spectra to the currently loaded project in this RelaxIS instance (if storage is defined in the job). **IMPORTANT:** A node in Live Mode can only function while a project is active. If you change or close a project while a Live Mode Node is active, that node will be stopped

and you need to manually restart it, once a project is activated.

- **Dedicated-Server Mode** adds received spectra to a preselected database (if storage is defined in the job). A node in Dedicated-Server Mode can run regardless of the state of the project.
- If you want to see the stored spectra live you can use Live-Mode. If you want to have more flexibility working with RelaxIS while nodes are active, or want to store spectra in different project folders, use Dedicated-Server Mode. **Please remember:** You are not constrained in the number of RelaxIS instances per computer you can use!

- **Operational Options**
  - **Output path (Dedicated Server)** defines the database (.EIS3) file that spectra are being stored in. Click the Select button to choose a file.
  - **New project after n files** advises the node to keep track of the number of spectra stored in a single project in the project folder. When the set number is reached a new project will be created in the database. This makes the projects more manageable. **Please note** that this does not apply when the `ProjectName` property in the `Storage` option is set to a specific project name. In that case the spectra are stored in the specified project instead of an automatically chosen one.
- Evaluation Options
  - **Suppress all evaluations** advises the node to never perform any fits on the received spectra, regardless of what is set in the `Evaluation` object of the jobs.
  - **Suppress all reports** advises the node to never create any reports, regardless of what is set in the `Report` object of the jobs.
  - **Output path (Reports)** sets the storage folder for locally stored reports. The required subfolders in the chosen folder will be

created automatically. **Please note:** If you don't set a folder, no reports can be stored!

- **Do not store reports locally** advises the node to still create reports for feedback purposes, but to discard them after sending the feedback. No reports will be stored on the server side.
- **Do not store spectra locally** advises the node to discard received spectra after sending the feedback and possibly creating a local report. The spectra will not be stored in the current project or dedicated database.

- Feedback Options
  - **Block Feedback**: These options allow you to exclude the respective feedback tasks from being performed, regardless of what is set in the jobs.
  - **E-Mail settings**: Here you need to enter connection details for the E-Mail account you want to use for sending Feedback mails. If no valid details are entered, no feedback can be mailed to the clients. You can test your settings by sending a text mail, by entering an E-Mail address and clicking the respective button.

You can save all settings for a node by clicking the **Settings→Save these settings** button in the toolbar of the Node's setup dialog. To load settings for a node, use the **Load settings** button. You can delete existing settings by using the **Delete settings** button.

21 The RelaxIS WCF Link

The RelaxIS WCF Link is a feature that allows you to access functions of RelaxIS from another program on the same computer. The communication works over so called named pipes through a Windows Communication Foundation (WCF). The accessible functions are:

- Adding spectra to RelaxIS
- Fitting a spectrum with specified models
- Calculating data for plotting models
- Querying RelaxIS for available Transfer functions and weighting modes
- Querying RelaxIS for a list of parameter names of a given model
- DRT Analysis and Reproduction

This allows you to implement fitting functionality into other applications that support the WCF framework. However, the computer needs a running instance of RelaxIS at all times.

⚠ Please note

At any given time, only a single instance of RelaxIS can have an active WCF link. The link is registered with a specific name in Windows that has to be unique. You can check the status of the WCF Link for a given RelaxIS instance in the RelaxIS status bar. A green text indicates an active link, while a red text indicates an inactive link. You can enable or disable the link by clicking on the status label.

21.1 Implementing the WCF Link into your Application

Start by referencing the `RelaxIS SDK.dll` in your .NET application. In it you find the `RelaxISWCFLink` namespace that contains all required classes and interfaces.

To call functions through the WCF service, you need to create a `RelaxISWCFProxy` object. Use the static `GetDefaultProxy` method of the `RelaxISWCFProxy` class to create a proxy with the correct settings.

Using this proxy, you can then call the functions defined in the `IRelaxISWCFLink` interface.

Please note

You can access all information about the individual functions using the SDK documentation you find on your installation medium.

22 The RelaxIS SDK and the RelaxIS SDK Code Editor

22.1 General Notes

The RelaxIS SDK allows you to easily write plugins to enhance the functionality of RelaxIS. The types of plugins you can create are:

- Circuit Elements
- Transfer Functions
- File Formats
- Wizards
- Result Evaluation Models
- Weighting Modes
- Axis Values
- Predefined Plots
- Data Manipulators

You can write the plugins yourself or use plugins other authors made.

⚠ Important Security Concern ⚠

Be very, very careful with plugins from sources you do not fully trust. The code that is executed when the plugins are loaded in RelaxIS is completely up to the author of the plugin and may be used for malicious activities on your computer!
If you can't be sure what code is contained in a plugin, **DO NOT USE IT**.

All plugins have a base class that needs to be inherited by your plugin. These base classes are defined in the `Plugins` namespace of the RelaxIS SDK.dll. You need to override several methods and properties for each plugin.

The type definitions can be examined in detail in the RelaxIS SDK help files which you can find on the installation medium.

We suggest you use an IDE like Microsoft Visual Studio to develop your plugins. RelaxIS contains a basic IDE as well, called the RelaxIS SDK Code Editor. Here you can write the code and compile it into DLLs that are then loaded in RelaxIS.

You can open the code editor from RelaxIS by clicking the **RelaxIS SDK Code Editor** button on the **Extras** tab of the main RelaxIS ribbon bar.

You can write the plugins either in the C# or the VB.NET language. After starting the editor click the **New** button. Select a template from the list and the language you want to use. Also define a name for your plugin. This name must be compliant with a .NET class name (e.g. no whitespace or special characters.

Click the **OK** button to continue.

This creates all the basic definitions needed for the respective plugin to compile successfully. Then you need to fill in the required implementations. Most properties are quite straight forward and should be clear from the comments in the code.

⚠ Please note

You are entirely responsible for the code in the plugins. It is possible that unhandled exceptions thrown by the plugin crash RelaxIS.
It is also possible that plugins cause RelaxIS to fail to start up at all.
If you experience problems, please do the following:

- In the Logs subfolder of your user folder you find log files. You can refer to these logs to find out which errors occurred.
- Always keep the .XML files with the original code of your plugins. In case of problems delete the .DLL files and **recompile** the plugin with the **newest version of the SDK**.

After writing the code you need to

- **Compile** the plugin using the
    - Check code button to check for errors

    - Compile (as) button to compile and save the plugin under a given name as a DLL in your user folder's plugin subfolder.
- **Save the plugin** code and information using the Save button. This is important to be able to recompile the code and update it to the newest SDK version.

22.2 Plugin Installation

Plugins are loaded from assemblies or SDK XML files in the %UserData%\Plugins folder when RelaxIS or the Circuit Simulator starts.

%UserData% is typically **\My Documents\RelaxIS\3.0**. You can find the user data folder from withing RelaxIS by selection Main->Settings->General Options->Open user folder.

To install a plugin:

- Close RelaxIS and the Circuit Simulator
- Copy the plugin file (.xml, .dll or .exe) into the %UserData%\Plugins folder
- Restart RelaxIS or the Circuit Simulator
- Enable the plugin during the Plugin Validation (see below)

You can check if the plugin was successfully loaded from within RelaxIS:

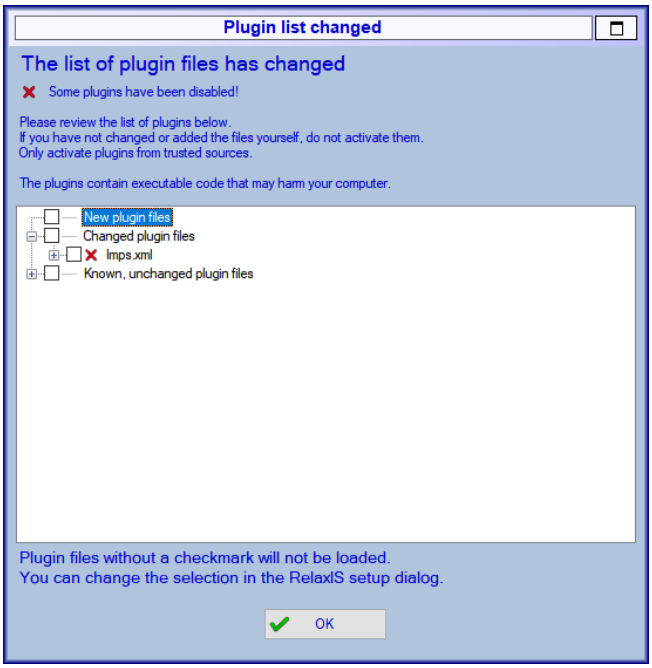
- In the menu, under Main->Show Log, you find messages starting with "(@ Plugins): Successfully loaded: …" for each plugin file
- Under Main->Settings->Plugins you find lists of all loaded plugins. Note: You also find premade plugins that are built into RelaxIS here
- After starting RelaxIS, you find a message in the bottom right of the main window, stating how many plugins were loaded in total: 

22.3 Plugin Validation

Whenever a plugin file is newly placed into the plugin directory, or when a plugin file changes you will be presented with a validation dialog before the plugins are loaded, e.g. when starting RelaxIS or the Circuit Simulator.

In this list, you have to specifically activate the plugin files that you want RelaxIS to load. Set the checkmark next to the plugin file names to activate the plugin file. These will be marked by a green checkmark instead of the red cross.

If you have not changed the plugin yourself, or copied one into the folder do not activate it. Only activate plugins from trusted sources, as they can execute arbitrary code.



To change the selection, in RelaxIS open the setup dialog by selecting **Main → Settings**. Click on Plugins, and find the buttons “Select active plugins” or “Reset active plugin file list”. The former will show the selection dialog again, while the latter completely resets the list of known plugins. This will show the selection list on the next program start.

All changes to the active plugin list will apply after the next program start. Already loaded plugins will not be unloaded during the program runtime.

22.4 Writing Plugins

22.4.1 General Notes

Plugins can be implemented as .NET Framework 4.7.2 assemblies. Please use this specific framework. Assemblies targeting i.e. .NET 5 or .NET Core are not loaded. As mentioned above, plugins can either be written in the RelaxIS SDK Code Editor and saved as XML Files or in a standalone IDE like Visual Studio or Visual Studio Code, which offer more advanced development tools.

Add a reference to the current "RelaxIS SDK.dll" to your project and inherit from the base plugin classes.

All plugins have the following properties:

Name is the internal name of the plugin that is used to refer to it. This is an important property, since some utilities such as RelaxIS Remote may refer to certain tools like transfer functions by name.

Most other string properties are simply for description purposes.

Description is a general description of what the plugin does. In addition, most plugins have additional descriptive properties, as well as the actual functionality.

The **AddLogMessage** method allows you to add custom messages to the main RelaxIS log.

After the plugin is created and initialized by RelaxIS or the CS3, the **AfterStartupInitialization** method is called once.

Some plugin types inherit from the `RelaxISOnlyPlugin` class. These plugins have a `RelaxISWCFInterface` property, that is populated by RelaxIS when the plugin is loaded. It can be used to access a RelaxIS WCF Link instance for the particular RelaxIS process that the plugin is loaded in.

There are some more complex properties that need more explanation that you'll find in the following chapters.

22.4.2 CircuitElement Plugins

These plugins implement a fitting model that can be used as a circuit element with a specific `Abbreviation` in model strings. The model receives parameter values and a frequency and returns the **impedance** as a complex number.

Implementation notes:

- The length of the arrays returned for describing names, limits and standard values need to match. These define, which parameter input RelaxIS allows for the model.
- For calculations regarding the impedance you can use the tools in the `libMath` namespace. Here you find complex number math and impedance conversion tools.
- The impedance calculation is implemented in the `CalculateImpedance` function. This is the only performance-critical function and is called often by the fit functions.
- Use the `GetTightLimits` function to calculate parameter limits for a particular spectrum. This function is used in the Auto Fit to limit the parameter ranges to smaller values for improved performance.
- The `Abbreviation` property determines the element code used in model strings. It must start with an uppercase letter and be followed only by lowercase letters or numbers.
- The `Formula` Field is only used for display purposes.

22.4.3 Wizard Plugins

Wizard plugins implement fit wizards that select a model for a spectrum. Typically, it also determines starting parameters and performs a fit. This is followed by an evaluation step that can calculate additional quantities from the fit result. Instead of parameter determination the fit wizard can also use an Auto Fit.

Implementation notes:

- The Wizard first retrieves the options to display on the dialog from the `GetOptions` method. Here you define different kinds of options like

numeric inputs or radiobuttons. These are then displayed on the Wizard Option pages. For the wizard to be used in RelaxIS Remote without interaction, no options must be needed.

- Afterwards the `RetrieveFitSetup` function is called. Here you can reference the defined options by name from the `Dictionary`. You return a fit setup with initial values and so on that is used to execute the fit.
- Last the `GetFurtherEvaluation` function is called with the fit results, that you can use to calculate further results like a conductivity from a resistance.

22.4.4 DataManipulation Plugins

Data provider plugins are the most generic type of plugin. Their function is called by the user by clicking a button on the ribbon. The button text and image can be defined by the plugin.

The plugin then receives a list of spectra and can modify each spectrum individually, i.e. change the metadata or fit parameters. It can also add new spectra to the current project.

Implementation notes:

- The overridable `AlwaysUseSelectedSpectra` property determines if the spectra selection dialog is shown (dialog selection mode) or if the currently selected spectra are used regardless.
- The plugin is executed in two steps. First, the `PerformSetup` method is called by RelaxIS with the full list of selected spectra. Afterwards, the `ManipulateSpectrum` function is called with each spectrum individually.
- Changes done on the objects in the `PerformSetup` method will not be written back to the spectra in RelaxIS. Only changes made in the individual `ManipulateSpectrum` function calls are written back.

22.4.5 FileFormat Plugins

These plugins allow you to implement additional file formats, so that the respective files can be loaded automatically without the need for the Unknown File Dialog.

Implementation notes:

- When a file is loaded, the `IdentifyFile` function is called with a `Stream` object. Read data from the stream and determine if your file format can handle this data. If so, return `true`, otherwise `false`.
- RelaxIS calls all file formats in a fixed order and the first file format that returns true in the `IdentifyFile` function is tasked with loading the data. You can move your format up in the list by overriding the `SortIndex` propery. Set it to negative values to move in front of built-in formats.
- If your `IdentifyFile` function returned true, the `GetData` function is called next by RelaxIS with a new data stream. Read spectrum data from the input and return a list of `ImpedanceSpectrum_FileFormat` objects.
- You can make use of the automatic splitting function of RelaxIS by settings the `ShouldBeAutoSplit` property of the `ImpedanceSpectrum` object to true. You can add a Metadata value with name `NDataPoints` and an integer value to tell RelaxIS to split at a specific number of points. Otherwise the automatic splitting algorithm is used.
- You can add metadata lists in the `MetadataToSplit` dictionary. These are split alongside the impedance data and averaged per split spectrum.

22.4.6 MultifitModel Plugins

These plugins define a model for the Multi Spectrum Fit feature. Such a model fits multiple impedance spectra at the same time and can take metadata values of the spectra into account.

A multi fit model has two types of parameters: a) shared parameters that only exist once and are used equally for all spectra and b) individual parameters, where one set exists for each spectrum. Hence a model with 2 shared and 3 individual sets for 10 spectra has a grand total of 2 + 10 * 3 = 32 parameters.

Implementation notes:

- Return a list of metadata names that are required for your model in the `RequiredMetadata` property. The values will be sent to the fit function during the actual fit.
- Set the transfer function that the fit should be performed in in the `TransferFunction` property.
- Implement the `GetIndividualParameters` function and return a list of individual fit parameters. Only return one set here. The function will be called once for each user-selected spectrum, allowing you to i.e. set spectrum-individual starting parameters for the individual spectrum.
- Implement the `GetSharedParameters` function and return a list of the shared fit parameters. The function receives the list of all user-selected spectra, allowing you to i.e. automatically setup the parameter start parameters.
- The `AfterInitialization` function is called by RelaxIS once the user has finished the parameter initialization. This allows you to check user inputs and possibly canceling the fit if the inputs are invalid, by setting the `Cancel` parameter to true.
- The `GetAdditionalEvaluations` function can be implemented to calculate further quantities for each fitted spectrum. The function is called with the list of fit results, split into shared and individual parameters. The individual parameters list only contains the parameters for the particular spectrum. Return a dictionary of names and values.

Implementing the `FitFunction` method:

The function implements the actual fitting model.

The `X` parameter array contains the frequency as first element and the individual spectrum index as the second element and then the metadata values requested by the `RequiredMetadata` property in the same order as defined in the property. Cast the second element to an integer to use it as an index.

The `Parameters` array contains **all** fit parameters. **IMPORTANT**: You need to select the correct set of individual parameters for your particular spectrum for

the calculation. The `GetIndividualParameterIndex` helper function can be used for this: provide it with the total number of shared and individual parameters, the index of the respective individual parameter and the index of the spectrum (from the `Parameters` array).

For example, with the example above, to select the 3rd individual parameter for the 8th spectrum, call

```
int index = GetIndividualParameterIndex(2, 3, 2, 7);
```

Note that the indizes are 0-based. The formula is simply

```
index = nShared + spectrumIndex * nIndividual + iIndividual
```

Use the parameters, frequency and metadata to calculate the result in the transfer function defined by the `TransferFunction` property and return it as a tuple.

22.4.7 PLOTPRESET PLUGIN

This plugin defines a plot preset by returning names of value provider plugins for the X, Y1 and Y2 axes of a graph. It also defines, if the axes are logarithmic and if the plot is symmetrical.

Implementation notes:

- You can find the value type names from the list of plugins in the RelaxIS Settings dialog. Open the Settings dialog and select Plugins → Value Types and find the Internal Name of the plugin.
- You can provide two value providers for each axis. If a transfer function plugin typically returns a negative imaginary part (like the impedance), the `ValueName` properties are used, otherwise the `ValueNameNonNegative` properties are used.

22.4.8 TRANSFERFUNCTION PLUGIN

This type allows you to implement a further transfer function. The plugin implements a function to recalculate the impedance into another complex value.

It is also possible to add a normalization function to recalculate the value into a geometry normalized value using an area and thickness value.

Implementation notes:

- Implement the `ConvertValue` function. It receives the frequency, Z' and Z'' values and should return the converted value as a complex number.
- Optionally implement the `NormalizeValue` function to further normalized the value. This function receives the already converted value and not the impedance. You should also assume SI units, e.g. Area in m² and thickness in m. If implemented, override the `CanBeNormalized` property to true as well.
- Implement the various text properties to provide symbol and units for display purposes, including the normalized symbol / unit if implemented.

22.4.9 RESULTEVALUATOR PLUGIN

This plugin implements a fit model used in the Result Evaluation dialog in RelaxIS. It receives X/Y data and implements the respective fit function.

Implementation notes:

- Implement the `GetParameterNames` function to return a list of the parameter names that your model uses.
- Once selected by the user, the `StartEvaluator` function is called once to allow custom setup.
- RelaxIS then calls the `PreTransform` functions. These can be overridden for data pretreatment (e.g. recalculate X values from °C to K).
- Afterwards, RelaxIS calls the `GetInitialValues` and `GetInitialFixedStates` functions, supplying the pretransformed data. You can use the data to automatically calculate initial parameters for your model. Return value arrays/lists with the same length as the list of parameter names.
- Implement the actual fit function as the `XYFunction` method. The function is called with the X value and the list of parameter values and should return the Y value.

- You can implement the `GetFurtherEvaluations` function to use the fit results to deduce further evaluations. These are returned as text fields in a dictionary.

22.4.10 WEIGHTMODE PLUGINS

These plugins implement a weighting mode used in fits. It is supplied with values in the transfer function used in the fit and should return an array of weighting factors for the real and imaginary parts.

Implementation notes:

- Implement the `CalculateWeights` method to calculate the weights for a data set. The function calculates all weights at the same time. The input data consists of an array-of-arrays, where data[0] are the frequencies, data[1] are the real parts and data[2] are the imaginary parts.
- Calculate a weight for each real and imaginary part and return them as an array-of-arrays, where result[0] is the array of real-part-weights and result[1] is the array of imaginary-part-weights.

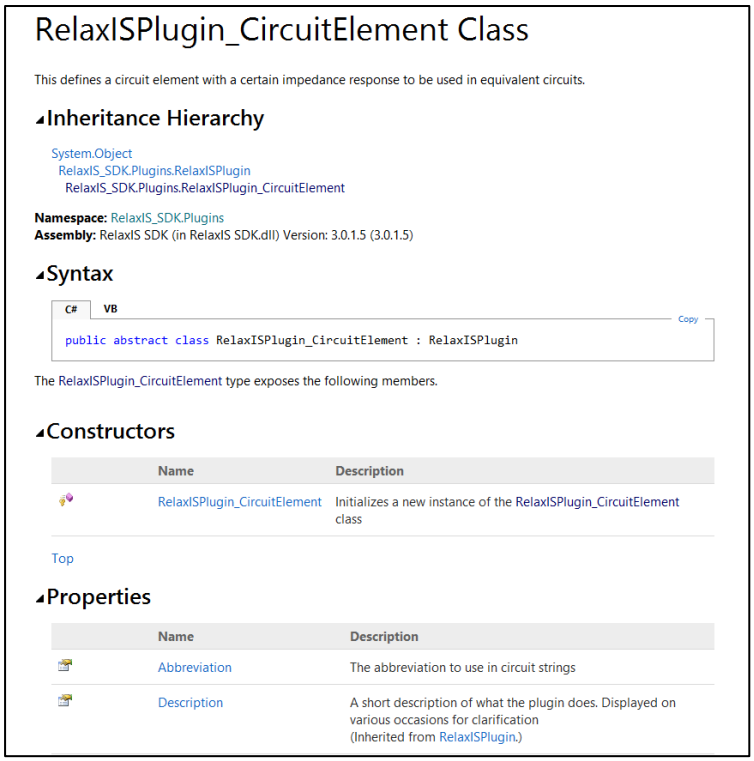
22.5 ADDITIONAL SDK DOCUMENTATION

All definitions in the RelaxIS SDK can be found in digital help documents that are installed together with RelaxIS. You can open this documentation from the RelaxIS Code Editor using the **Help → RelaxIS SDK** button on the main ribbon bar.

You can navigate the help file using the menu on the left and browse all function definitions, descriptions or parameters.

This documentation can also be found on the rhd instruments homepage as an online reference in the most up-to-date form.

The documentation contains detailed definitions and comments about the various implementable types and methods, as outlined in the example document on the right.



RelaxISPlugin_CircuitElement Class

This defines a circuit element with a certain impedance response to be used in equivalent circuits.

Inheritance Hierarchy

System.Object
  RelaxIS_SDK.Plugins.RelaxISPlugin
    RelaxIS_SDK.Plugins.RelaxISPlugin_CircuitElement

Namespace: RelaxIS_SDK.Plugins
Assembly: RelaxIS SDK (in RelaxIS SDK.dll) Version: 3.0.1.5 (3.0.1.5)

Syntax

C# VB Copy

```
public abstract class RelaxISPlugin_CircuitElement : RelaxISPlugin
```

The RelaxISPlugin_CircuitElement type exposes the following members.

Constructors

	Name	Description
	RelaxISPlugin_CircuitElement	Initializes a new instance of the RelaxISPlugin_CircuitElement class

Top

Properties

	Name	Description
	Abbreviation	The abbreviation to use in circuit strings
	Description	A short description of what the plugin does. Displayed on various occasions for clarification (Inherited from RelaxISPlugin.)

23 APPENDICES

23.1 INTRODUCTION TO ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

23.1.1 GENERAL CONCEPTS

Impedance Spectroscopy (or Dielectric Spectroscopy) is a powerful tool to derive dielectric properties of a system in a large frequency range (typically more than ten orders of magnitude). This is typically done by applying a small sinusoidal AC-voltage with a specific frequency over the sample and measuring the current response that is generated. This current response is also sinusoidal but can be shifted out of phase to the excitation voltage due to a delayed response time. From the amplitude of the AC-voltage, the amplitude of the current response and the phase angle the real and imaginary parts of the complex impedance, admittance, capacitance, permittivity and so on can be calculated which present a picture of different processes happening in the system on different timescales.

The impedance can be understood as the AC resistance. For pure resistive processes the corresponding impedance is a real number (imaginary part is zero, as well as the phase angle). For purely capacitive or inductive processes the real part of the impedance (Z') is zero and the phase angle is either -90° or +90°. Typically processes like mass transport, charge transfer between electrode and electrolyte etc. have both frequency dependent real- and imaginary parts and can be identified by their behavior.

Besides the frequency it is possible to vary other parameters. The AC voltage can be superimposed onto a DC voltage (or bias) to study potential dependent processes like electrochemical reactions or double-layer charging, or the amplitude of the AC voltage can be changed which for example can lead to the observation of higher harmonics of the AC current response.

23.1.2 IMPEDANCE DATA

The data that is stored by the measurement program needs to contain enough information to be able to calculate the frequency dependent impedance from it. This can be a combination of a number of physical quantities. The easiest

combination is frequency, real part of the impedance and imaginary part of the impedance. Another often used combination is frequency, magnitude of the impedance |Z| and phase angle. The real and imaginary parts of the impedance are then given by

$$\begin{aligned} Z' &= |Z| \cdot \sin\varphi \\ Z'' &= |Z| \cdot \cos\varphi \end{aligned} .$$

Instead of the impedance programs might use other physical quantities such as the complex permittivity, capacitance or admittance. Other quantities like the complex permittivity furthermore need geometric information about the system (the "*cell constant*") to calculate. In order to account for all these possibilities RelaxIS uses an import wizard for column based text files that is explained in detail in the respective section of this handbook. In short, the wizard allows the selection of certain combinations of values from columns of the text file and then calculates the complex impedance from these values for internal storage and use in the fitting process.

23.1.3 EQUIVALENT CIRCUITS

In order to derive physical meaning from the measured impedance spectra the common method is to use so called equivalent circuits to model the spectra and assign physical meaning to the components of these circuits. An equivalent circuit is built from classically known electrical components such as resistors, capacitors or coils that are connected by wires in parallel or in series. If an AC voltage is applied to such a circuit the current response can be measured just like the response of the sample in EIS. By changing the parameters (like the capacitance of a capacitor) and connection of the components the response of the sample can be replicated. The impedance is calculated for a given circuit by simple rules. For electrical components, the impedance $\hat{Z}$ is given by a specific formula. For example, for a resistor and for a capacitor the impedance is given by

$$\begin{aligned} \hat{Z}_R &= R \\ \hat{Z}_C &= \frac{1}{i\omega C} \end{aligned} .$$

Here R is the resistance of the resistor, C is the capacitance of the capacitor, ω is the angular frequency of the AC voltage and i is the imaginary unit. R and C are examples of fit parameters that appear in the fits. Also, it is important to note that apparently the impedance of a resistor is not a function of the frequency – it is constant for all frequencies as can easily be found experimentally. In contrast, the impedance of the capacitor is frequency dependent. For high frequencies, the impedance is very small while it rises towards lower frequencies. This is called high-pass behavior and can be explained by the charging/discharging process of the capacitor. At high frequencies, the capacitor cannot be charged very much before the polarity reverses while at low frequencies the capacitor is charged, preventing current flow through the capacitor and thus presenting an impedance.

If two impedances $\hat{Z}_1$ and $\hat{Z}_2$ are connected in series then

$$\hat{Z}_{Series} = \hat{Z}_1 + \hat{Z}_2 .$$

If the two impedances are connected in parallel then

$$\hat{Z}_{Parallel} = \frac{1}{\frac{1}{\hat{Z}_1} + \frac{1}{\hat{Z}_2}} = \frac{\hat{Z}_1 \hat{Z}_2}{\hat{Z}_1 + \hat{Z}_2} .$$

With these rules and the expressions for the impedance for various electrical and electrochemical circuit elements the overall impedance of any given circuit can be calculated iteratively for a given frequency. The circuit elements implemented in RelaxIS are listed in the Appendices.

23.2 Introduction to non-linear curve fitting

23.2.1 General concepts

Given a specific theory or model with certain parameters and a set of data one can try to adjust the parameters of the model so that it explains the given data in the best way possible. “The best way possible” is usually the case in which the sum of squared residuals is minimal. The residual of a data point is the difference between the dependent value of the data point and the calculated

dependent value of the model. In the practice of fitting equivalent circuits to measured impedance spectra the independent variable is the frequency while the real and imaginary parts of the impedance are the dependent variables. The minimization performed is

$$\min \sum_{\omega} \left(\left| \mathrm{Re}\left(\hat{Z}(\omega)_{calculated}\right) - \mathrm{Re}\left(\hat{Z}(\omega)_{measured}\right) \right|^2 + \left| \mathrm{Im}\left(\hat{Z}(\omega)_{calculated}\right) - \mathrm{Im}\left(\hat{Z}(\omega)_{measured}\right) \right|^2 \right).$$

Taking the absolutes of the differences is redundant from a mathematical standpoint but has programmatical reasons and is presented for the sake of accuracy. RelaxIS offers not only fitting of the impedance of the data but also of the complex capacitance and the admittance. While theoretically identical results should be obtained it can make a difference depending on what information are to be extracted. Reasons are given below.

In order to perform the non-linear curve fitting several algorithms have been developed over the years. Two of the most widely used algorithms are used in RelaxIS. The first algorithm is a constrained implementation of the Levenberg-Marquardt algorithm. This algorithm uses derivatives of the error function to descend along the steepest way towards the minimum of the error. It is not a simple Steepest Descend algorithm though but it incorporates some improvements that make it more robust towards certain common problems for fitting algorithms like adjusting the step width dynamically in order to force a descend on each iteration. The Levenberg-Marquardt-Algorithm (LMA) is very fast and robust in finding a minimum in the error function but is very prone to getting stuck in small local minima of the error function.

For this reason, a second algorithm was implemented into RelaxIS – the Nelder-Mead-Simplex algorithm (NMSA). This algorithm uses no derivatives but simplex transformations to iteratively find better parameters. A simplex can be thought of as an n-dimensional geometric form with n+1 edges, with n being the number of parameters. So, for a model with two parameters the geometric form would be a triangle. Each edge corresponds to a set of parameter values. In every step, the sum of squares for each edge are compared and then the triangle is transformed by a simple set of rules in order to find a better edge point with a lower sum of squares. The NMSA is very robust as well but usually

slower than the LMA. It also converges to local minima but it can be maneuvered out of these by restarting the algorithm with a fresh starting simplex around the local minimum. This makes it very powerful for fitting impedance data because, due to the complexity of the fitting models, many local minima make it hard to find the best solution.

During testing it became apparent that both algorithms have strong and weak sides. Therefore, the Automatic Fitting method was implemented into RelaxIS. Here the two algorithms are used consecutively. First the LMA is used to find a local minimum from the given starting parameters. After this the NMSA refines this fit. In this mode, no options have to be changed and the fitting usually works even from bad starting parameters.

23.2.2 Calculation of parameter errors

An important information about the fit is how error prone the fit results are. One measure for the quality of the prediction is the overall sum of squared residuals (SRR) of the model with the best fit parameters. The higher the SRR is, the worse is the prediction. However, this does not make any statement about the quality of each individual fit parameter. To find further information about these errors one can take the covariance matrix of the system into account. The covariance matrix is defined as

$$\mathbf{A} = \left(\mathbf{J}^T\mathbf{J}\right)^{-1} \approx \mathbf{H}^{-1} \ .$$

This means the covariance matrix is approximately the inverse of the Hesse-matrix as calculated from the Jacobi-Matrix. Since the Hesse-matrix contains information about the second derivatives of the error function it means that values on the diagonal of the covariance matrix are related to the curvature of the error function in regard to changes to this parameter. If the parameter value is located in a very steep valley the curvature is high and the parameter error is low, because its location is defined nicely by the minimum of the valley. If the curvature however is low, the value is not pinned down as strictly and is therefore more prone to errors. The actual errors as presented in RelaxIS furthermore take into account the degrees of freedom of the dataset in light of the used model as well as the SRR. They are therefore given by

$$E_n = \sqrt{\frac{SRR}{N-n_p} \cdot \boldsymbol{A}_{n,n}}$$

Here N is the number of data points, n_p is the number of fit parameters and $\mathbf{A}_{n,n}$ is the nth diagonal value of the covariance matrix.

Per definition the variance is the squared standard deviation. It therefore should be positive at all times. If the model does not describe the data in any reliable way (this can mean it is too complex for example) then the diagonal values of the calculated covariance matrix can happen to be negative. That makes the calculation of the standard error impossible since it would become complex due to the square root. A negative covariance furthermore has no understandable meaning. If this happens you can notice that RelaxIS calls the parameter errors 'BAD' in the current file information.

In this case you should critically evaluate, if every element of the model you have used for fitting the data is actually necessary and has a representation in your data.

23.3 Premade circuit elements in RelaxIS

All units stated below assume that the original impedance data of imported spectra are in [Ohm]. If custom files are imported with values of different units, that are then treated as impedance values in [Ohm] the units of the formulas have to be derived manually.

ω is given in Hz.

23.3.1 Resistor

- Circuit abbreviation: R
- Formula: $\hat{Z} = R$
- Parameters
    - R [Ohm]: The resistance of the resistor.

Represents a simple, ohmic resistor with a phase angle of 0°.

23.3.2 Capacitor

- Circuit abbreviation: C

- Formula: $\hat{Z} = \frac{1}{i\omega C}$
- Parameters
    - C [F]: The capacitance of the capacitor.

Represents a simple capacitor with a phase angle of -90°.

23.3.3 INDUCTOR

- Circuit abbreviation: I
- Formula: $\hat{Z} = i\omega L$
- Parameters
    - L [H]: The inductance of the inductor

Represents a simple inductor with a phase angle of +90°.

23.3.4 CONSTANT-PHASE-ELEMENT (CPE)

- Circuit abbreviation: P
- Formula: $\hat{Z} = \frac{1}{Q \cdot (i\omega)^{\alpha}}$
- Parameters
    - Q [Ss^{α}]: The CPE's admittance value.
    - α : The CPE's exponential factor.

The constant phase element describes a non-ideal capacitance. If α is 1 the CPE is an ideal capacitor with a phase angle of -90° while for lower values of α the phase angle is lowered to -(90° * α).

23.3.5 INFINITE WARBURG-IMPEDANCE

- Circuit abbreviation: W
- Formula: $\hat{Z} = \frac{A_W}{\omega^{0.5}} - i\frac{A_W}{\omega^{0.5}}$
- Parameters
    - A_W [$\Omega s^{-0.5}$]: The Warburg-coefficient.

The Infinite Warburg element describes the linear diffusion of an electroactive species to an electrode. It can be recognized by a straight line with a slope of

1 (phase angle = -45°) in the Nyquist plot. The Warburg coefficient is defined through the surface concentrations of the oxidized and reduced form of the species as well as their diffusion coefficients.

$$A_W = \frac{RT}{n^2 F^2 A\sqrt{2}}\left(\frac{1}{c_{ox}\sqrt{D_{ox}}} + \frac{1}{c_{red}\sqrt{D_{red}}}\right)$$

Here T is the temperature, R is the gas constant, n is the number of transferred electrons, F is the Faraday-constant, A is the electrode's area and c and D are the concentrations and diffusion coefficients of the respective species.

23.3.6 FINITE WARBURG-IMPEDANCE (OPEN)

- Circuit abbreviation: Wo
- Formula: $\hat{Z} = \frac{Z_W}{(i\omega\tau)^{\alpha}} \cdot Coth\left((i\omega\tau)^{\alpha}\right)$
- Parameters
  - Z_W [Ω]: The Warburg coefficient.
  - τ [s]: The time-constant parameter.
  - α : The exponential parameter (usually 0.5)

The difference between the simple Warburg element and the Warburg-Open element is that the Wo-element describes a system in which the maximum length of the diffusion is limited, which causes a depletion of the diffusing species. This can happen for example in very thin electrolyte layers or inside of pores of active electrode materials. The diffusion part is only visible for frequencies that are high enough to not allow species to reach the outer limits of the diffusion layer in time. For lower frequencies, the behavior changes to a capacitive nature.

23.3.7 FINITE WARBURG-IMPEDANCE (SHORT)

- Circuit abbreviation: Ws
- Formula: $\hat{Z} = \frac{Z_W}{(i\omega\tau)^{\alpha}} \cdot Tanh\left((i\omega\tau)^{\alpha}\right)$
- Parameters
  - Z_W [Ω]: The Warburg coefficient.

- τ [s]: The time-constant parameter.
- α : The exponential parameter (usually 0.5)

This element also describes the diffusion in a limited range from the electrode. However, the difference is that the concentration of the diffusing species is replenished to a constant level at the outer limit if diffusion layer thickness. This is the case for actively stirred solutions or more commonly with rotating disc electrodes. Here the diffusion layer thickness is defined by system parameters. For frequencies lower than the time span it takes the species to reach the outer limits of the layer the behavior changes to a parallel RC-element, meaning that the low-frequency limit is a constant Z' value.

23.3.8 GERISCHER-ELEMENT

- Circuit abbreviation: G
- Formula: $\hat{Z} = \frac{1}{Y \cdot (k + i\omega)^{0.5}}$
- Parameters
  - Y [S$s^{0.5}$]: The admittance parameter.
  - k [1/s]: The rate-constant parameter.

If the electroactive species is created with a preceding chemical reaction in the electrolyte and is then for example reduced at the electrode this element may model the impedance behavior of this system. Here k is the rate constant for the preceding reaction.

23.3.9 ZARC: (R)(P) WITH TIME CONSTANT

- Circuit abbreviation: Zarc
- Formula: $\hat{Z} = \frac{R}{1+(i\omega\tau)^{\alpha}}$
- Parameters
  - R [Ω]: The resistance (width) of the semicircle
  - Tau [s]: The time constant of the (R)(P) process
  - α : The CPE alpha parameter

The Zarc-element is equal to the (R)(P) circuit, but has the big advantage to be formulated in terms of the time-constant. This means, that the true

capacitance of the process, like the double-layer or SEI capacitance can be immediately calculated as $C = \frac{\tau}{R}$. For the usual (R)(P), the Brug-Formula must be used to get the true capacitance.

23.3.10 HAVRILIAK-NEGAMI (AND DERIVED) ELEMENT

- Circuit abbreviation: Hv/Co/Cd
- Formula: $\hat{C} = \frac{C}{\left(1+(i\omega\tau)^{\alpha}\right)^{\beta}}$
- Parameters
  - C [F]: The capacitance of the related process.
  - τ [s]: The time constant of the process.
  - α: The alpha factor of the process. If alpha is fixed to 1 the element is called the Cole-Davidson-element.
  - β: The beta factor of the process. If beta is fixed to 1 the element is called the Cole-Cole-element.
  - If both alpha and beta are fixed to 1 the element describes the Debye-relaxation.

Unlike the other circuit elements these elements describe capacitive relaxation processes in the system. The timescale of the process is described by the time constant while its capacitive contribution is described by C. Alpha and beta describe non-ideal behavior of the process.

A Hv-element leads to a semicircle in the complex capacitance plane and can be used to derive information about capacitive processes on different timescales in systems where capacitive behavior is the prevailing characteristic.

The Debye-relaxation can also be described with a series connection of a resistor and a capacitor with $\tau = R \cdot C$.

For dielectric fits, consider placing a capacitor (C) element and a conductivity term (Sig) in **parallel** to the Hv/Co/Cd elements to describe further processes such as an ε_∞ contribution.

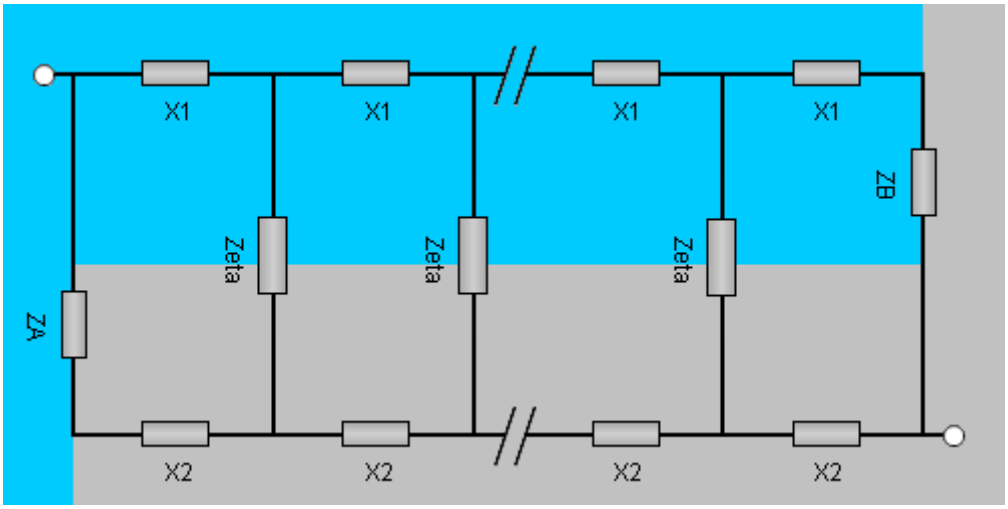
23.3.11 Dielectric Conductivity Term

- Circuit abbreviation: Sig
- Formula: $\hat{C}(\omega) = \frac{\sigma}{(i\omega)^{\alpha}} \rightarrow \hat{Z}(\omega) = \frac{(i\omega)^{\alpha-1}}{\sigma}$
- Parameters
  - σ [$Ss^{1-\alpha}$]: The conductivity associated with this term.
  - α : A non-ideality factor in the conductivity term.

The conductivity term is often used in combination with Havriliak-Negami-Fits of dielectric systems and is used to describe the (low) conductivity of the system. It typically manifests itself in the low-frequency regime of the spectrum as a straight line with an angle determined by the α parameter.

23.3.12 Transmission-Line-Models: General Description

Transmission-Line-Models are used in electrochemistry to describe porous electrode surfaces. The general model is depicted in the following image and contains impedances for the outer boundary, ZA, the inner boundary ZB, the electrolyte path, X1, the solid path, X2, and the interface, Zeta.



The individual elements don't have to be simple resistors but can be modeled with more complex subcircuits.

The models are typically written in terms of infinitesimal contributions of the individual elements X1, X2 and Zeta, integrated over the length of the pore, L,

which is important when units of the model elements are discussed. In RelaxIS, the L parameter per default is set to 1 and fixed.

The impedance of this network was given by Bisquert (Phys. Chem. Chem. Phys., 2000, 2, 4185-4192):

$$
\begin{aligned}
Z = \frac{1}{\chi_1 + \chi_2} \Bigg[& \lambda(\chi_1 + \chi_2) S_\lambda \\
& + (Z_\mathrm{A} + Z_\mathrm{B}) C_\lambda + \frac{1}{\lambda(\chi_1 + \chi_2)} Z_\mathrm{A} Z_\mathrm{B} S_\lambda \Bigg]^{-1} \\
& \times \Bigg\{ L\lambda\chi_1\chi_2(\chi_1 + \chi_2) S_\lambda + \chi_1[\lambda\chi_1 S_\lambda + L\chi_2 C_\lambda] Z_\mathrm{A} \\
& + \chi_2[\lambda\chi_2 S_\lambda + L\chi_1 C_\lambda] Z_\mathrm{B} + \frac{1}{\chi_1 + \chi_2} \\
& \times \left[2\chi_1\chi_2 + (\chi_1^2 + \chi_2^2) C_\lambda + \frac{L}{\lambda} \chi_1\chi_2 S_\lambda \right] Z_\mathrm{A} Z_\mathrm{B} \Bigg\} ,
\end{aligned}
$$

$\lambda = \sqrt{\zeta/(\chi_1 + \chi_2)}$, $C_\lambda = \cosh(L/\lambda)$, $S_\lambda = \sinh(L/\lambda)$.

Different Transmission-Line-Models now typically make assumptions about parts of this model in order to simplify the mathematical description. The most common assumption is that the electronic conductivity in the solid is much larger than the ionic conductivity, and hence X2 is simply assumed to be a short circuit. For the interface typically either blocking or non-blocking conditions are assumed, resulting in the description with a simple capacitor (or CPE), or with a Zarc-Element, (R)(CPE), respectively.

Another mathematical description for the TLM does not use infinitesimal subcircuits and instead models each distinct component by connecting a specified number of loops. This is analogous to creating the model in RelaxIS using distinct components and assuming that their parameter values are identical. With high number of loops the two approaches converge when normalized correctly. However, since the limit should be considered anyways, it is more practical to model real samples using the first kind of model that already considers $n \to \infty$.

23.3.13 TRANSMISSION-LINE-MODEL-ELEMENT (OPEN TERMINUS)

- Circuit abbreviation: Tlmo
- Formula (e.g. n=3):

$$Z(\omega) = R + \left(C^{-1} + \left(R + \left(C^{-1} + \left(R + \left(C^{-1} + (R + C)^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \quad \text{with } n = 3,\ C = \frac{1}{Q(i\omega)^{\alpha}}$$

- Parameters
  - R [Ω]: The ionic resistance inside of the pore
  - Q [Ss^{α}]: The admittances of the CPEs describing the double layer in the circuit.
  - α : The exponential factors of the CPEs in the circuit.
  - n: The number of loops in the model

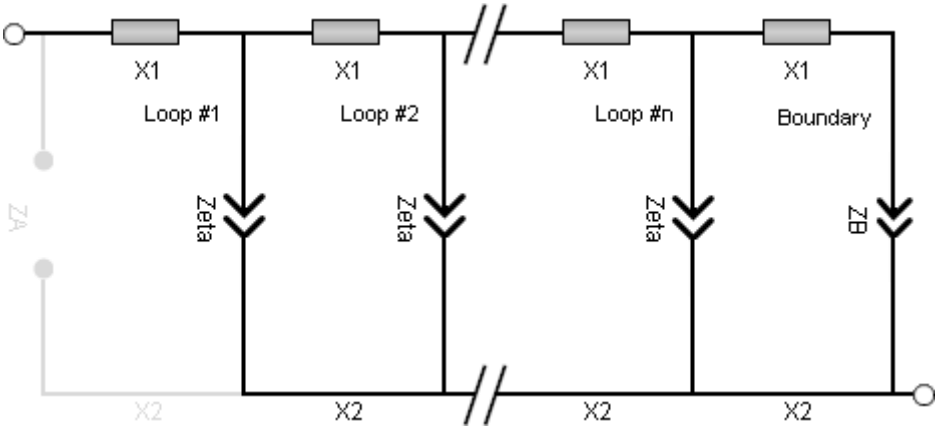
⚠ Please note

This model is typically not used for fitting. The continuous TLMs - see below - are more suitable to describe actual samples. It is implemented primarily for educational means.

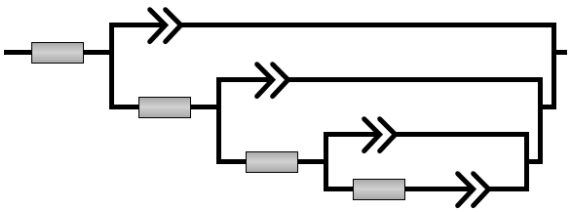
Assumptions:

- Blocking conditions
- $R_{ion} >> R_{elec.}$
- Capacitive boundary at inner end of the pore
- Capacitive behavior of inner boundary the same as for the pore

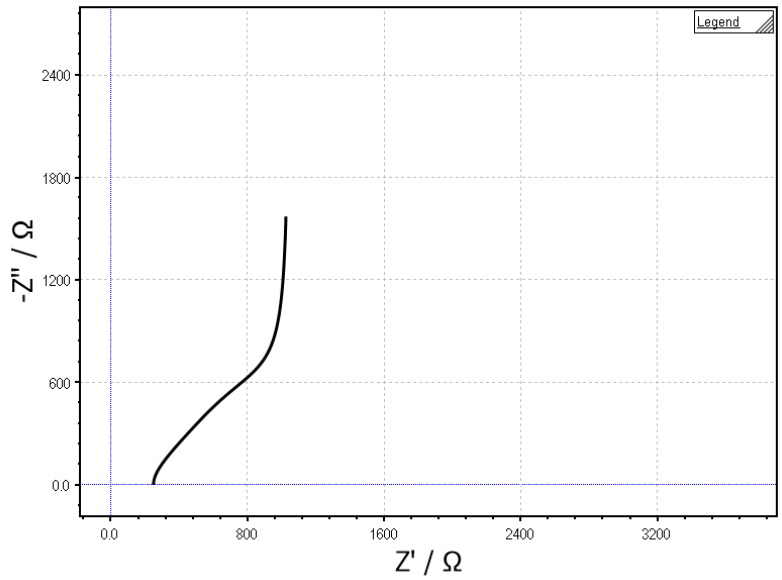
The resulting model can be visualized analogous to the complete model above:



The model could also be transferred to a normal RelaxIS model:



A typical model curve is shown in the next figure. It can be seen, that the model shows capacitive behavior at low frequencies.



23.3.14 TRANSMISSION-LINE-MODEL-ELEMENT (SHORT TERMINUS)

- Circuit abbreviation: Tlms
- Formula (e.g. n=3):

$$Z(\omega) = R + \left(C^{-1} + \left(R + \left(C^{-1} + \left(R + \left(C^{-1} + R^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \right)^{-1} \quad \text{with } n = 3,\ C = \frac{1}{Q(i\omega)^{\alpha}}$$

- Parameters
  - R [Ω]: The ionic resistance inside of the pore
  - Q [Ss^{α}]: The admittances of the CPEs describing the double layer in the circuit.
  - α : The exponential factors of the CPEs in the circuit.
  - n: The number of loops in the model

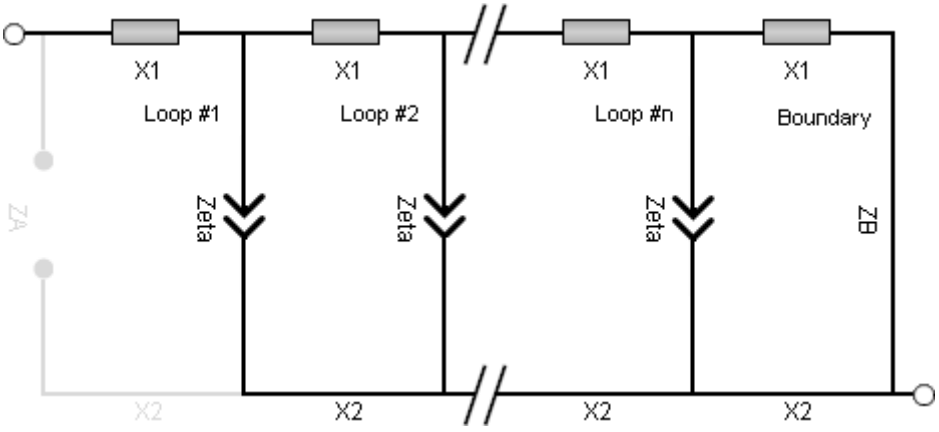
⚠ Please note

This model should usually not be used for fitting without fixing the n-Parameter. It is not primarily implemented for fitting purposes but for educational means.

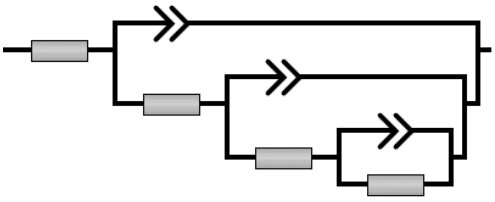
Assumptions:

- Blocking conditions
- $R_{ion} >> R_{elec.}$
- Non-reflecting (absorbing) boundary at inner end of the pore

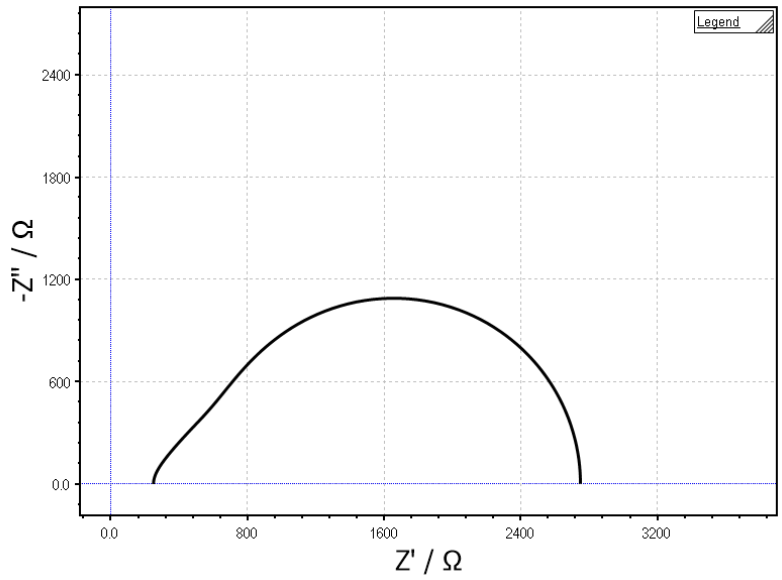
The resulting model can be visualized analogous to the complete model above:



This model can also be created as a classical RelaxIS model, e.g. for n=3:



Contrary to the Tlmo, the Tlms shows resistive behavior at low frequencies due to the short circuited inner boundary:



23.3.15 BISQUERT TRANSMISSION LINE (OPEN)

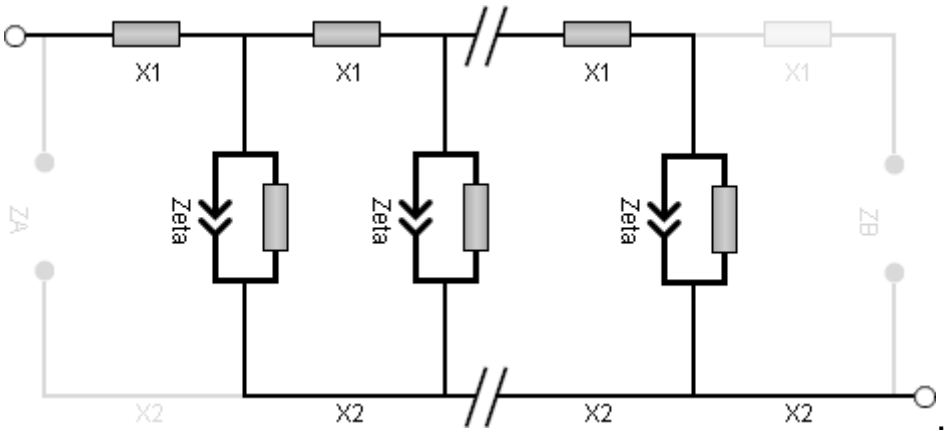
- Circuit abbreviation: Bo
- Formula:

$$Z(\omega) = \sqrt{R_{ion} \cdot \zeta}\,\coth\left(L\sqrt{\frac{R_{ion}}{\zeta}}\right) \quad \text{with} \quad \zeta = \left(\frac{1}{R_{ct}} + Q(i\omega)^{\alpha}\right)^{-1}$$

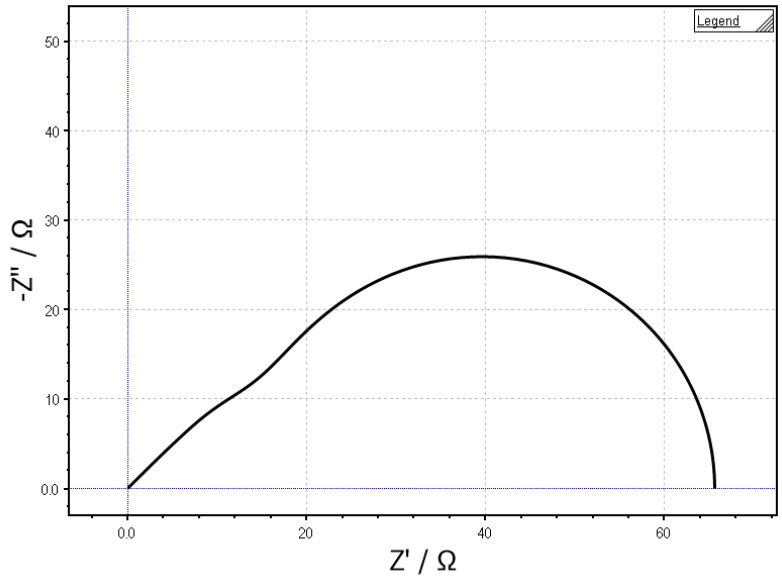
- Parameters
  - R_{ion}: The ionic conductivity contribution
  - R_{ct}: The charge transfer resistance at the interface
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [R_{ct}] = Ohm*m
  - [Q] = S*s^a/m
  - [alpha] = 1
  - [L] = m

The Bisquert TLMs describe systems with a non-blocking interface, which introduces an additional charge transfer resistor. This is of interest when

describing e.g. dye-sensitized solar cells. The “open” model assumes a reflecting (open) inner boundary. Hence, the model can be depicted as:



The plot of the model shows a Warburg-like behavior at high frequencies, and a semicircle towards a low-frequency limiting value. The function is similar, but not equal to the Warburg Short element discussed above.



Example spectrum of the Bisquert-Open transmission line.

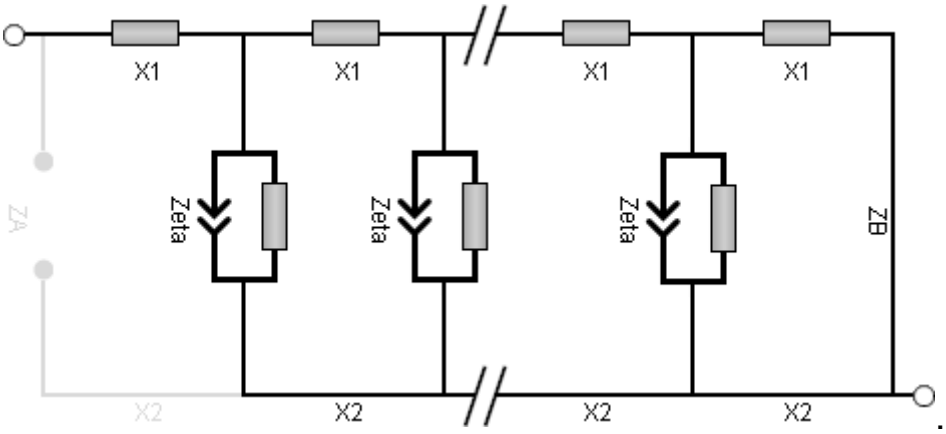
23.3.16 BISQUERT TRANSMISSION LINE (SHORT)

- Circuit abbreviation: Bs
- Formula:

$$Z(\omega) = \sqrt{R_{ion} \cdot \zeta}\,\tanh\left(L\sqrt{\frac{R_{ion}}{\zeta}}\right) \quad \text{with} \quad \zeta = \left(\frac{1}{R_{ct}} + Q(i\omega)^{\alpha}\right)^{-1}$$

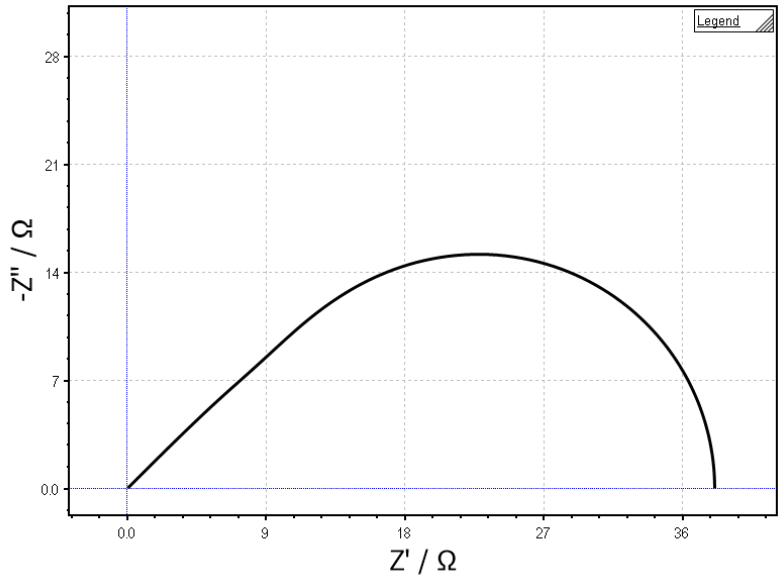
- Parameters
  - R_{ion}: The ionic conductivity contribution
  - R_{ct}: The charge transfer resistance at the interface
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [R_{ct}] = Ohm*m
  - [Q] = S*s^a/m
  - [alpha] = 1
  - [L] = m

The Bisquert TLMs describe systems with a non-blocking interface, which introduces an additional charge transfer resistor. This is of interest when describing e.g. dye-sensitized solar cells. The “short” model assumes an absorbing (short) inner boundary. Hence, the model can be depicted as:



The plot of the model shows a Warburg-like behavior at high frequencies, and a semicircle towards a low-frequency limiting value. Compared with the

Bisquert Open model it lacks the distinct “bump” at intermediate frequencies. The function is similar, but not equal to the Warburg Short element discussed above.



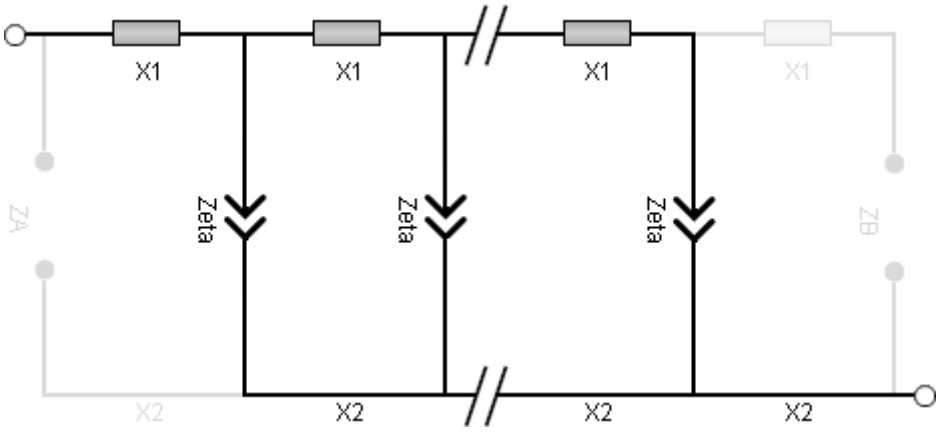
23.3.17 SIMPLIFIED, BLOCKING TRANSMISSION LINE MODEL (OPEN)

- Circuit abbreviation: Tlmqo
- Formula:

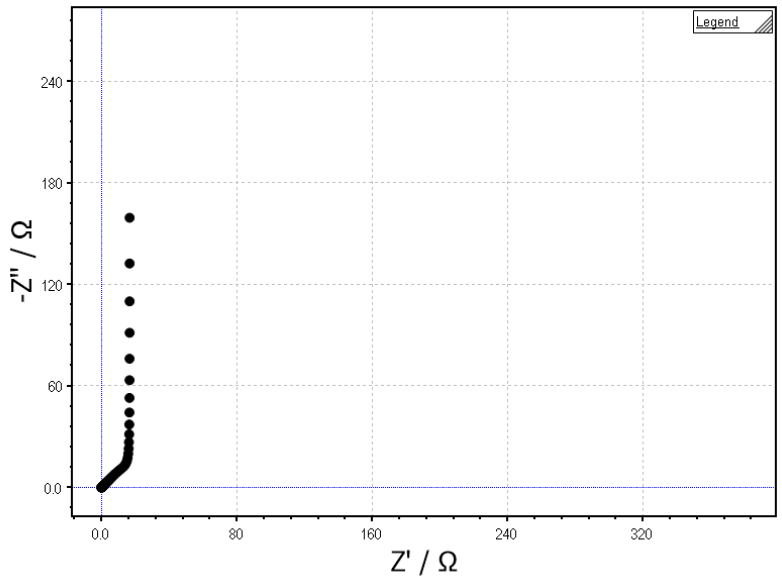
$$Z(\omega) = \sqrt{\frac{R_{ion}}{Q(i\omega)^{\alpha}}} \coth\left(L\sqrt{R_{ion}Q(i\omega)^{\alpha}}\right)$$

- Parameters:
  - R_{ion}: The ionic conductivity contribution
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [Q] = S*s^a/m
  - [alpha] = 1
  - [L] = m

This TLM is the blocking analogue to the Bisquert (Open) model. The charge transfer resistance is assumed to be infinite and is thus removed from the model. The inner boundary is modeled as an open circuit:



The plot therefore does not go to a limiting value and instead shows capacitive behavior at low frequencies. The plot and model are identical to the Warburg Open model but assumes different parameter values due to the different mathematical and theoretical formulation.



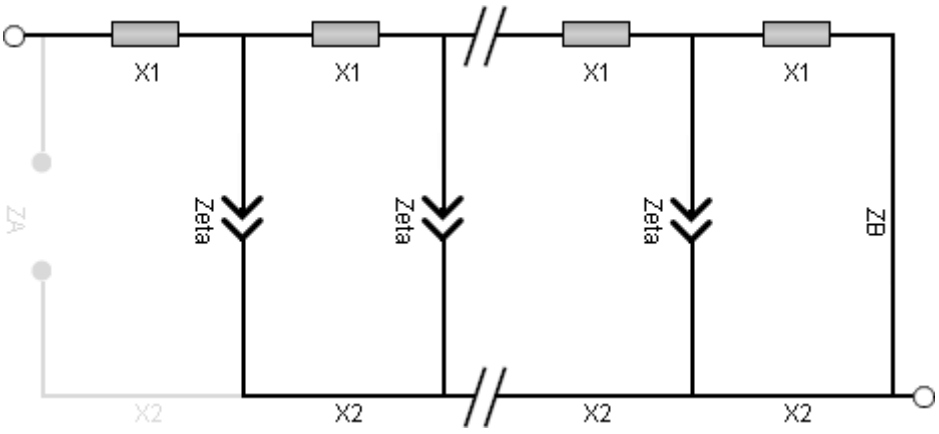
23.3.18 SIMPLIFIED, BLOCKING TRANSMISSION LINE MODEL (SHORT)

- Circuit abbreviation: Tlmqs
- Formula:

$$Z(\omega) = \sqrt{\frac{R_{ion}}{Q(i\omega)^{\alpha}}} \tanh\left(L\sqrt{R_{ion}Q(i\omega)^{\alpha}}\right)$$

- Parameters:
  - R_{ion}: The ionic conductivity contribution
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [Q] = S*s^a/m
  - [alpha] = 1
  - [L] = m

This TLMs is the blocking analogue to the Bisquert (Short) model. The charge transfer resistance is assumed to be infinite and is thus removed from the model. The inner boundary is modeled as absorbing (short):



Due to the inner boundary, the plot tends towards a limiting value. The plot and model are identical to the Warburg Short model but assumes different parameter values due to the different mathematical and theoretical formulation.

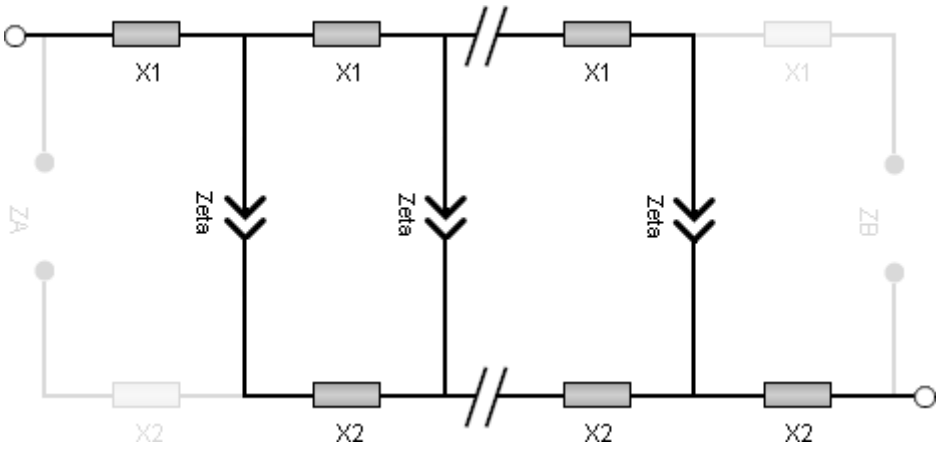
23.3.19 EXTENDED, BLOCKING TRANSMISSION LINE MODEL (OPEN)

- Circuit abbreviation: Tlmeb
- Formula:

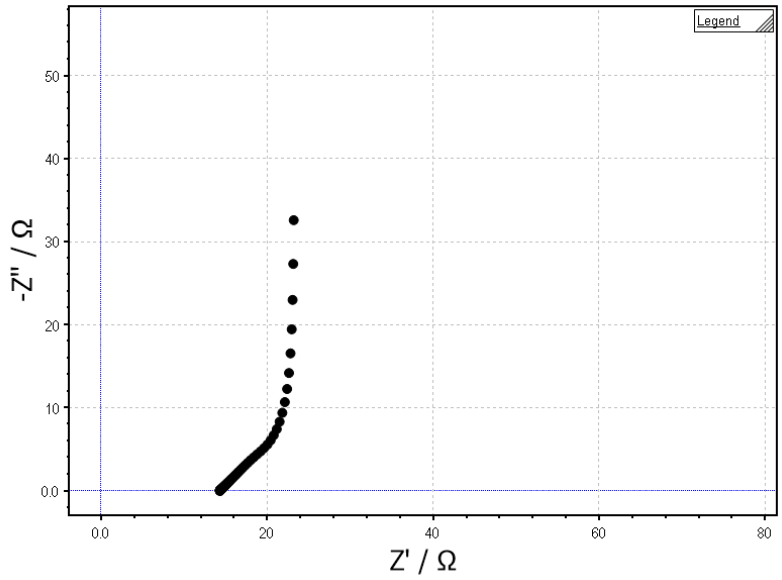
$$Z(\omega) = T \cdot \frac{\lambda\chi_1^{\,2} + 2\lambda\chi_1\chi_2 C^{-1} + L\chi_1\chi_2 T^{-1} + \lambda\chi_2^{\,2}}{\chi_1 + \chi_2} \quad \text{with} \quad \lambda = \sqrt{\zeta / (\chi_1 + \chi_2)},\ C = Cosh(L/\lambda),\ T = Coth(L/\lambda)$$

  ζ is the impedance of the CPE. This is a derivative of Bisquerts general expression shown above, optimized for numeric calculation.
- Parameters:
  - R_{ion}: The ionic conductivity contribution
  - $R_{elec.}$: The electronic conductivity contribution
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [Q] = S*s^a/m
  - [alpha] = 1
  - [R_{elec}] = Ohm/m
  - [L] = m

This TLM is analogous to the simplified blocking TLM but includes the contribution from a limited conductivity in the solid by introducing additional resistance in the second path.



The plot is equally similar but does not start at the origin point and instead goes toward $R_\infty = \frac{1}{R_{ion}^{-1}+R_{elec.}^{-1}}$.



23.3.20 Extended, Non-Blocking Transmission line Model (Open)

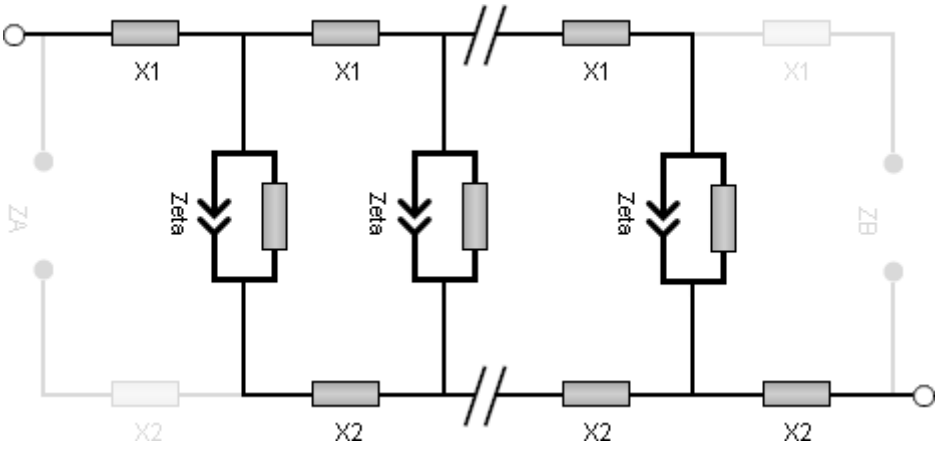
- Circuit abbreviation: Tlmenb
- Formula:

$$Z(\omega) = T \cdot \frac{\lambda\chi_1^{\,2} + 2\lambda\chi_1\chi_2 C^{-1} + L\chi_1\chi_2 T^{-1} + \lambda\chi_2^{\,2}}{\chi_1 + \chi_2} \quad \text{with} \quad \lambda = \sqrt{\zeta / (\chi_1 + \chi_2)},\ C = Cosh(L/\lambda),\ T = Coth(L/\lambda)$$

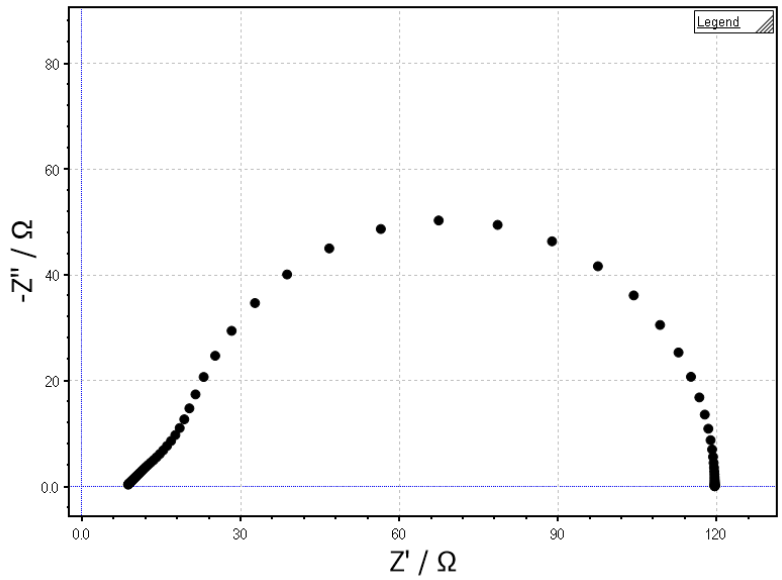
  ζ is the impedance of a Zarc element, (R)(P). This is a derivative of Bisquerts general expression shown above, optimized for numeric calculation.
- Parameters:
  - R_{ion}: The ionic conductivity contribution
  - $R_{elec.}$: The electronic conductivity contribution
  - R_{ct}: The charge-transfer resistance of the interface
  - Q: The CPE Q parameter of the interfacial capacitance
  - alpha: The α parameter of the interfacial capacitance
  - L: The length of the pore (default: fixed)
- Parameter Units
  - [R_{ion}] = Ohm/m
  - [R_{ct}] = Ohm*m
  - [Q] = S*s^a/m

- [alpha] = 1
- [R_{elec}] = Ohm/m
- [L] = m

This TLM is analogous to the simplified non-blocking TLM but includes the contribution from a limited conductivity in the solid by introducing additional resistance in the second path.



The plot is equally similar but does not start at the origin point and instead goes toward $R_{\infty} = \frac{1}{R_{ion}^{-1}+R_{elec.}^{-1}}$.



23.3.21 User-Defined-Transmission-Line-Model

- Circuit abbreviation: Tlmx[ZA,X1,Zeta,X2,ZB]
- Formula: *see Bisquerts full formula above*
- Parameters:
  - *Variable, depending on defined subcircuits*
- Parameter Units:
  - *Need to be inferred on an individual basis*

The Tlmx allows you to freely define a TLM by defining the subcircuits of the model. The subcircuits are placed in a specific order inside of the squared brackets. The impedances are then calculated and combined to the full TLM description by RelaxIS.

With the exception of Tlmo and Tlms, the piecewise TLMs, all other pre-defined TLMs can be replicated by the Tlmx.

For more information regarding the usage of the Tlmx, please refer to 9.1.2.

23.4 Names of the Implemented Plugins

The internal names of the plugins are the ones you need when you refer to them in the RelaxIS Remote or RelaxIS WCF features. Please use the names in the *Name* columns in the following tables.

Please note that the names sometimes contain single spaces!

23.4.1 Transfer Functions

Plugin	Definition	Name	Normalizes to
Impedance		`Impedance`	Specific impedance
Admittance	$\hat{Y} = \frac{1}{\hat{Z}}$	`Admittance`	Complex Conductivity
Complex Capacitance	$\hat{C} = \frac{1}{i\omega\hat{Z}}$	`Complex Capacitance`	Complex Permittivity
Elastance	$\hat{E} = \frac{1}{\hat{C}}$	`Elastance`	Modulus

23.4.2 WEIGHTING MODES

Plugin	Name
No weighting	`No Weighting`
Proportional weighting	`Proportional Weighting`
Log10²(Frequency)	`Logarithmic Weighting`
Favor low frequencies	`Low Frequency Weighting`
Favor high frequencies	`High Frequency Weighting`
Low freq. modulus	`Low Frequency Modulus Weighting`
High freq. modulus	`High Frequency Modulus Weighting`

23.4.3 AXIS VALUES

Plugin	Name
Frequency	`Frequency`
Angular Frequency	`Angular frequency`
Real Part	`Real part`
Imaginary Part	`Imaginary part`
Negative Imag. Part	`Negative imaginary part`
Magnitude	`Magnitude`
Phase Angle	`Phase angle`
Phase Angle (of Impedance)	`Phase angle Impedance`
Tan(Delta)	`Tan(Delta)`
Tan(Delta) dielectric	`Tan(Delta) dielectric`
No Value	`Empty` (It is recommended to use the `RelaxISPlugin_AxisValue.EmptyValueName` constant)

23.4.4 WIZARDS

Plugin	Name
Battery Wizard	`Battery Non-Interactive`
Battery Wizard (empiric)	`Battery, Empiric Non-Interactive`
Conductivity Wizard	`Conductivity Interactive`

Conductivity Wizard (non-interactive)	`Conductivity Non-Interactive`

23.5 Formula Symbols of the Built-In Metadata Fields

In most formulas the metadata of effected spectra can be accessed using certain symbols. Please use the symbols given in the table below.

Please note, that all symbols are case-sensitive!

Field	Symbol	Report Tag Name
Temperature	`T`	`Temperature`
Time	`TM`	`DCVoltage`
DC Voltage	`DC`	`ACVoltage`
AC Voltage	`AC`	`Time`
Current	`J`	`Current`
Concentration	`C`	`Concentration`
Harmonic	`H`	`Harmonic`
Area	`A`	`Thickness`
Thickness	`d`	`Area`
Free Variable	`FV`	`FreeVariable`
Free Variable 2	`FV2`	`FreeVariable2`

23.6 Available Mathematical Functions

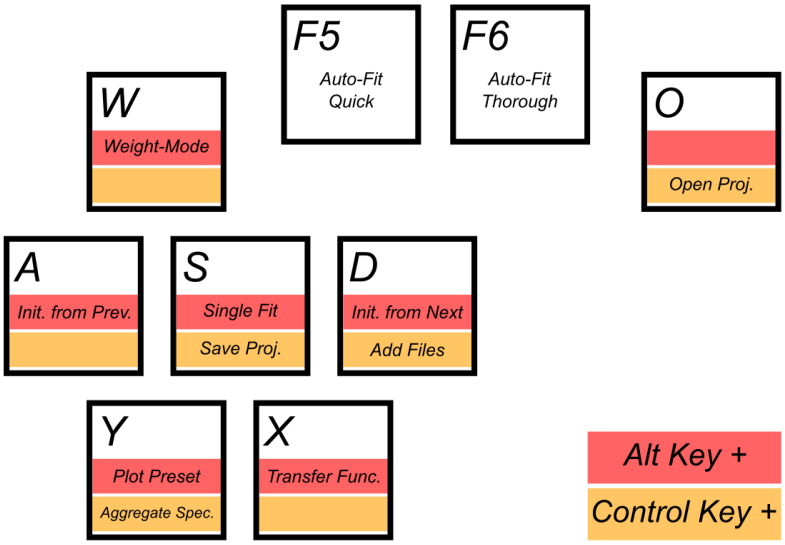
You can use various functions whenever you are entering formulas, for example for recalculating the values of the Result Preview dialog.

The functions always have the format: `Keyword(Value)`, and are NOT case-sensitive. Some functions can have multiple keywords. If you miss a function, please contact rhd instruments.

Function	Keyword
Exponential	`exp()`
Sinus	`sin()`
Kosinus	`cos()`

Tangens	`tan()`
Base-10 Logarithm	`log() lg() log10()`
Natural Logarithm	`ln() logn()`
Square-Root	`sqrt()`
Absolute value	`abs()`

23.7 HOTKEYS



Further hotkeys can be added in the **Setup** dialog. The hotkeys above cannot be changed, but you can add new hotkeys for various functions to your liking.

24 CONTACT AND TECHNICAL SUPPORT

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