

Kramers-Kronig test for Windows

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Note:

This program may be used free of charge for scientific research. It is not allowed to distribute the program to third parties without written consent from the author.

When results obtained with this program are presented in the scientific literature, the authors are requested to make proper reference to the original ideas behind this program:

- B.A. Boukamp, '*Electrochemical Impedance Spectroscopy in Solid State Ionics; Recent Advances*', *Solid State Ionics* **169** [1-4] 65-73 (2004).
- B.A. Boukamp, '*A Linear Kronig-Kramers Transform Test for Immittance Data Validation*', *J. Electrochem. Soc.* **142** [6] (1995) 1885-1894.

Disclaimer:

The author does not assume any legal liability or responsibility for the accuracy, completeness, or usefulness of the Kramers-Kronig transform-test program, nor for any claims evolving from the use of this program.

Introduction

Knowing the quality of your impedance data is essential for a proper CNLS-analysis. Problems generally observed are: non-stationary systems, strong non-linearity (too large signal applied) or systematic errors added by the measurement system. It is important to be able to discern between 'bad' data and an inappropriate model function for the CNLS-procedures. The Kramers-Kronig relations present a very useful tool for data checking. Data that complies with the Kramers-Kronig transformation rules must be: *causal*, i.e. the measured response is solely due to the applied (perturbation) signal, *linear*, i.e. no higher frequency response may be generated by the system and *stable*, the electrochemical cell may not change with time. Often it is the stability condition that is violated: measurements performed too quickly after e.g. a change in temperature, partial pressure or polarization, or through corrosion or aging processes. The K-K relations are very effective in testing for data corrupted by non steady state behaviour.

The Kramers-Kronig rules show the relation between the imaginary and real part of a frequency dispersion. Any real value, $Z_{re}(\omega)$, can be derived from the imaginary part:

$$Z_{re}(\omega) = R_{\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{x Z_{im}(x) - \omega Z_{im}(\omega)}{x^2 - \omega^2} dx \quad (1)$$

where $R_{\infty} = Z_{re}(\infty)$. Similarly the imaginary part, $Z_{im}(\omega)$, is obtained from the real part by:

$$Z_{im}(\omega) = \frac{2\omega}{\pi} \int_0^{\infty} \frac{Z_{re}(x) - Z_{re}(\omega)}{x^2 - \omega^2} dx \quad (2)$$

The major problem with applying the K-K rules is the need for a zero to infinite frequency range, which is an experimental impossibility. Extrapolations need the assumption of specific models and thus are less generally applicable.

A new route has recently been proposed by the author. In this method a series connection of parallel $-(RC)$ -circuits was used to model the data set, see Figure 1. The M time constants associated with the RC circuits, $\tau_k = R_k C_k$, are fixed and logarithmically spaced over the inverse ω range, with:

$$\tau_1 = \omega_1^{-1}, \quad \tau_M = \omega_N^{-1} \quad (3)$$

The subscript 1 refers to the first frequency of the data set and N to the last frequency, with $M < N$. In this case the simulated impedance is represented by:

$$Z(\omega_i) = R_{\infty} + \sum_{k=1}^M R_k \left\{ \frac{1}{1 + \omega_i^2 \tau_k^2} - j \frac{\omega_i \tau_k}{1 + \omega_i^2 \tau_k^2} \right\} \quad (4)$$

Fitting this model to the original data set only requires solving the linear set of equations in R_k -values. The basic idea is that each $-(RC)$ -circuit is Kramers-Kronig transformable, hence the entire circuit is KK-transformable. When this circuit can be fitted, within reasonable accuracy, to the data set, then the data set must be KK-transformable. Deviation from KK-compliance is most easily monitored in the residuals plot where the relative differences, $\Delta_{re,i}$ and $\Delta_{im,i}$ between the data and its KK-compliant fit are plotted versus $\log(\text{frequency})$:

$$\Delta_{re,i} = \frac{Z_{re,i} - Z_{re}(\omega_i, a_k)}{|Z(\omega_i, a_k)|}, \quad \Delta_{im,i} = \frac{Z_{im,i} - Z_{im}(\omega_i, a_k)}{|Z(\omega_i, a_k)|} \quad (5)$$

For KK-compliant data only a noise distribution around the frequency axis should be observed. A clear trace around the frequency axis indicates that the data is corrupted. (see Figure 6 below)

For further detailed information see: B.A. Boukamp, *J.Electrochem.Soc.* **142** (1995) 1885.

Starting the program

It is convenient to place either a shortcut on the Desktop or in the 'Office toolbar'. After start up the program will show the following window, Figure 2:

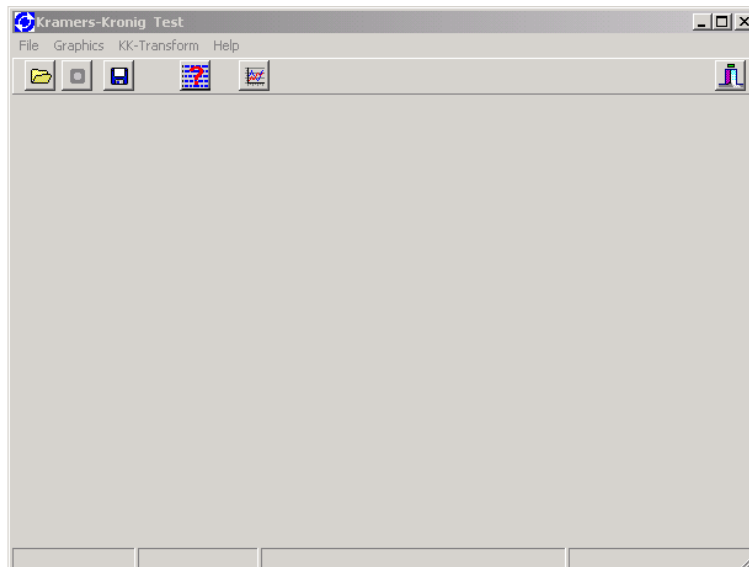


Figure 2. Opening window for the Kramers-Kronig test program.

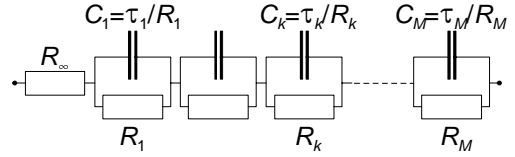


Figure 1. Arrangement of $-(RC)$ -circuits used in the Kramers-Kronig compliance test.

The top shows the program name, followed by the menu toolbar. Next is the speed-button toolbar. At the bottom information fields are shown. The large grey area is for the graphics. As soon as a data file has been read its frequency dispersion will be presented in the current representation mode, see Figure 3. Impedance is the default representation at start up.

Speed button toolbar:



Button for opening a data file (also available in the pull-down menu). This is a standard Windows procedure. Data files can be selected on predefined extensions: *.dat for general data files, *.Z or *.ZPL for Zplot data files, *.P00 for 'Boukamp compatible' data files from ECO Chemie equipment and *.CRV for data files generated by Volta Lab. equipment.

As soon as a file has been opened its frequency dispersion is presented in the currently selected format. The impedance representation is the default at start-up.



When a data file has been loaded successfully then this icon will appear on the speed button toolbar. Use this to convert the file to the standard 'EquivCrt' format. The file is automatically saved in the source directory with the extension *.DAT. After saving the data file the icon will change to:



This icon shows that the data has been saved in the 'EquivCrt' standard format, or that no data is present.



With this speed button a special combination of the original data and the Kramers-Kronig test data will be saved for use with the 'EquivCrt' program. Is also available from the pull-down menu.



This speed button displays the data header information (first 5 lines) in a window. Close the window before continuing.



Speed button to reset the graph when a break appears in the graph.



Speed button for exiting the program.

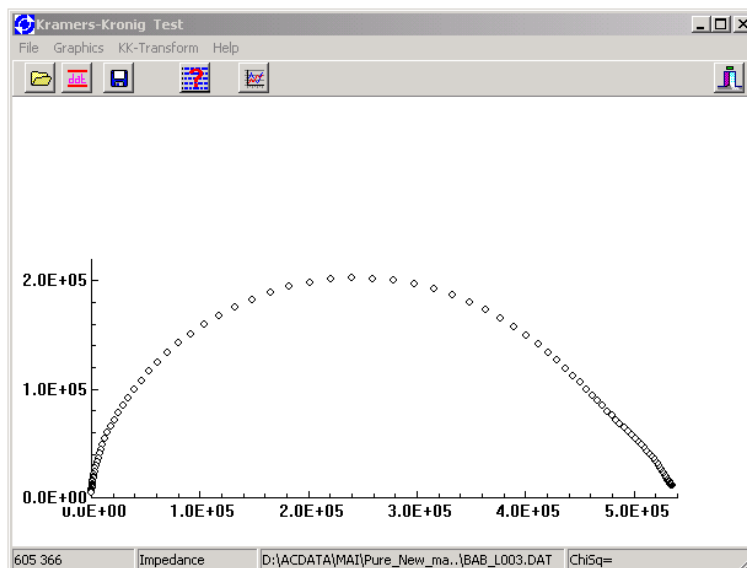


Figure 3. Program window displaying automatically scaled data in the impedance representation.

Graphical representations:

Currently only the complex plane representations (real versus imaginary) are available. These can be chosen from the graphics menu (Representation), or directly through the 'hot-key' combinations indicated between parentheses:

- Impedance (Ctrl + I)
- Admittance (Ctrl + A)
- Capacitance (Ctrl + C)
- Dielectric (Ctrl + D)
- Modulus (Ctrl + M)

The current representation is shown in the second field in the bottom bar. See Figure 2.

In the future Bode-type representations will be added.

There is a limited zoom function using the left mouse button. Draw a square in the plot area with this mouse button down. Upon release a new graphics range will be calculated and displayed. In order to restore the original full graph go to the graphics menu, or use the hot-key combination.

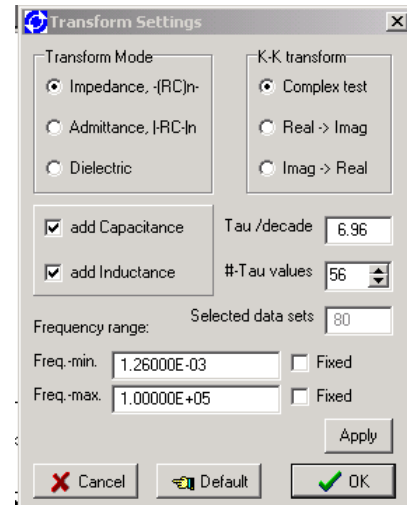



Figure 4. Window for adjusting the Kramers-Kronig test parameters. Some options are not yet available (see text).

Kramers-Kronig test settings:

The settings for the Kramers-Kronig test are placed in a separate window, accessible through the KK-transform window presented in Figure 4. For general use there is no need to change the default values. Currently only the transform test for the impedance and admittance mode are operational. Also only the 'Complex test' is available, the actual transformations will become available at a later date. For details on the procedures, see B.A. Boukamp, J.Electrochem.Soc. **142** (1995) 1885. The frequency range can be decreased in order to see if the main section of the data is free of KK-errors. This selected frequency range can be fixed for subsequent data analysis under the same conditions. The options of adding a capacitance and inductance to the test circuit are described in the previously mentioned paper. The number of time constants per decade (tau-values) can be changed, but practice has proven that approximately 7 tau-values per decade is a good number.

Non-standard data files:

Standard files are recognized by the first line in the data file. In order to read non-standard files the data format has to be specified in the 'File Properties Window' (Figure 5), which can be accessed through 'Data Settings' in the File menu. A basic data structure is assumed:

- 1) 0 – 10 Data header lines. Only the first 40 characters of the first 5 lines will be kept internally. These may be viewed using the speed-button .
- 2) Number of Data Sets. Only when the file contains the number of data sets (in a single line) directly after the 'Data Header Lines' this option must be turned on
- 3) Column heading. When a single line of column headers precedes the data, turn this option on.

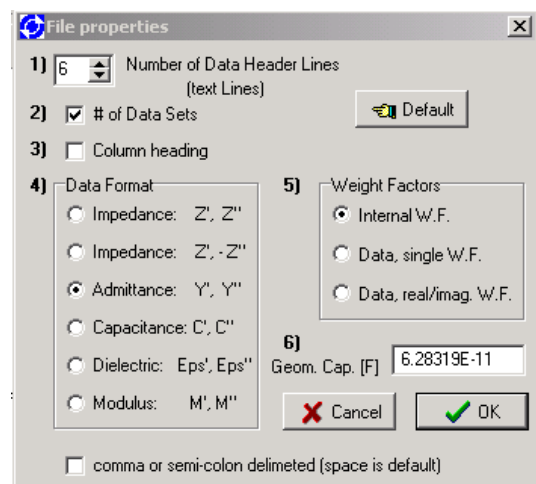


Figure 5. Window for specifying the data structure for non-standard data files.

- 4) The data is assumed to be in the order: Frequency, Real part, Imaginary part (, Weight factor real, Weight factor imag.) on a single line. The data may be separated by spaces(s) a comma or a semicolon. Use of the last two separators must be indicated at the bottom of this window. Select here the type of data representation. Impedance Z' , Z'' assumes that the imaginary part is negative for capacitive effects. For the other convention (positive imaginary part) use the second option: Z' , $-Z''$.
- 5) When the data contains weight factors, this must be indicated.
- 6) In case dielectric data is entered, or a dielectric representation is needed, the geometric capacitance of the cell must be entered (in Farad).

The default button restores the default setting: 6 lines of Data headers, number of data sets, NO column headers, Z' , Z'' representation and no weight factors.

Please note: the data may not be followed by further information as this will cause an 'I/O-read error'. The data does not need to be ordered in a specific way.

Kramers-Kronig test

The K-K test can be accessed directly with the right mouse button (the other options in this menu will be implemented in the future). The K-K test will be executed using the settings defined in the K-K Transform Settings window (see above). The K-K test can also be started from the pull down menu. The result is directly presented in the form of the relative differences plot, Figure 6. The scaling is performed automatically; the red dots present the real part differences (residuals: eq. (5)) and the blue dots the imaginary part differences. The resulting 'pseudo Chi-squared' value is shown in the right-hand field at the bottom of the main program window. A random distribution around the frequency axis indicates that the data is K-K compliant. A clear trace, as indicated in Figure 6, shows that there is non K-K behaviour. In this case it is quite small as the residuals are less than 0.5%.

The minimum range for the residuals axis is between -1% and $+1\%$. The maximum range is $\pm 100\%$. This window must be closed before continuing. The K-K transform data is presented in the complex plane plot as the small red circles, see Figure 7. Other representations may be selected; the K-K transform will be included. The measured and transformed data can be saved in one file using the data save option. This file can also be used for graphical programs.

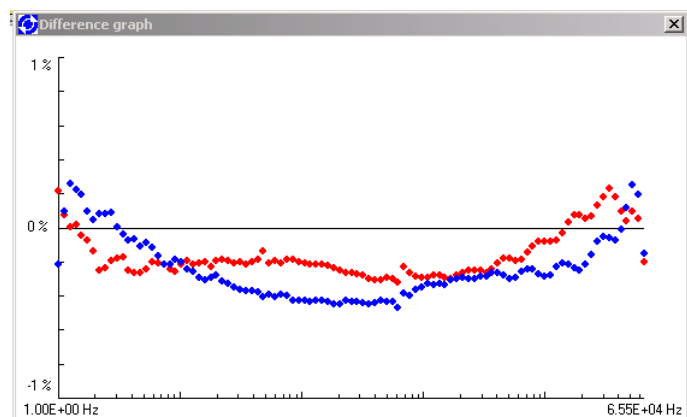


Figure 6. Display of the KK-test residuals for a KK-test of the data in Figure 2. The curvatures show that there is (minor) non-KK behaviour.

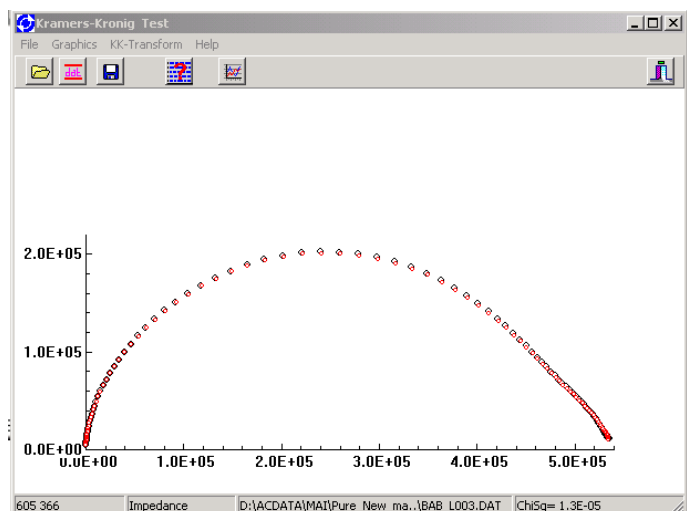


Figure 7. Display of the combination of the measured data and its KK-transform. Data from Figure 3.