Nonlinear frequency response analysis (NFRA)

ZAHNER

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1 Introduction

Non-linear Frequency Response Analysis (NFRA) is an extension of the Electrochemical Impedance Spectroscopy (EIS). In EIS, small excitation amplitude is applied to remain in the linear range, whereas in NFRA large excitation amplitude is used to simultaneously examine linear and nonlinear aspects of the processes present.

The following describes the situation from the viewpoint of the potentiostatic technique. Analogous complementary considerations are valid for the galvanostatic technique. In EIS and NFRA, the excitation signal is described by

$$\tilde{V} = \hat{V} \cdot e^{j\omega t} \tag{1}$$

Here, $\tilde{V}$ is the voltage sinewave excitation signal in time. $\hat{V}$ is the amplitude of the sinewave, t is the time and ω is the angular frequency of the excitation signal. For EIS, the response signal is described by

$$\tilde{I} = \hat{I} \cdot e^{j(\omega t+\varphi)} \tag{2}$$

Here, $\tilde{I}$ is the current sinewave response signal in time. $\hat{I}$ is the amplitude of the current sinewave and φ is the phase shift between the excitation and the response signal. In EIS, the amplitude of the excitation is kept small to fulfill the prerequisite of linearity. As $Z = \frac{\tilde{U}}{\tilde{I}}$ (analogous to $V = IR$), the impedance is calculated by dividing eq. 1 by eq. 2:

$$\text{Impedance} = \frac{\hat{V}}{\hat{I}} e^{-j\varphi} \tag{3}$$

In NFRA, a larger excitation amplitude than in EIS is used, which explicitly exceeds the linear range. This causes a non-linear response signal, consisting of multiple frequencies, where each of them is described by some equation (4), with the order number *o*=1, 2, 3...

$$\tilde{I} = \hat{I}_o \cdot e^{j(o\omega t+\varphi_o)} \tag{4}$$

$$\tilde{I} = \underbrace{\hat{I}_F \cdot e^{j(\omega t+\varphi_F)}}_{\text{fundamental response}} + \underbrace{\sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o\omega t+\varphi_o)}}_{\text{Harmonic response}} \tag{5}$$

In equation (5), the composite response signal is divided into two parts. The first term stands for the fundamental response signal with the same frequency as the frequency of the excitation signal (fundamental frequency, *o*=1) and the second part is the harmonic content with frequencies as integer multiples of the fundamental frequency (*o*=2, 3..., ending at an order number n dependent on the significance, see later remarks). For a detailed introduction to NFRA, please refer to

the manuscript NFRA – an introduction. Like in EIS, in NFRA, the impedance can be calculated from the fundamental response. The impedances measured with EIS (linear regime) and NFRA (non-linear regime) for the same test object will differ slightly or more, dependent on the grade of overdrive (i.e., non-linear contributions).

For the NFRA, it is essential that the potentiostat can carry out online discrete Fourier transformation (DFT, favorable fast Fourier transform FFT) of the excitation and the response signals. This analysis principle is realized in Zahner potentiostats since 1981. The harmonic content is provided for output and further analysis.

2 NFRA Calibration

As a prerequisite for accurate NFRA measurements, calibration of the ZENNIUM series potentiostat is recommended. During the calibration, an NFRA response of a well-known system is measured. Later on, the measured response is compared with the expected response, and calibration tables, individual for each instrument are created.

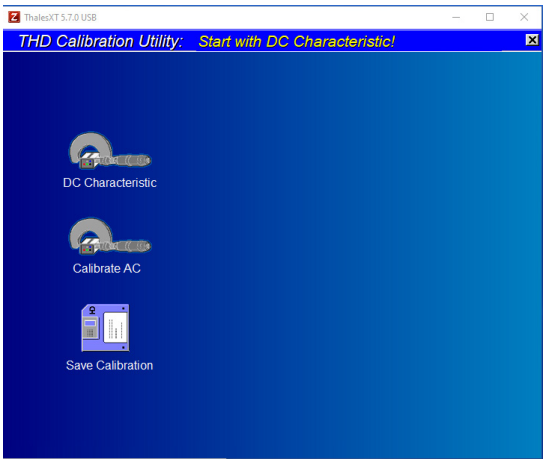
The IoZ option in the testbox represents two Schottky diodes in anti-parallel connection with respect to each other. It is used for the NFRA calibration. As the Schottky diodes are temperature sensitive, keep the testbox and the ZENNIUM series potentiostat at a constant temperature during calibration. If possible, use a temperature-controlled chamber or room. Please allow 30 minutes of warm-up time for the ZENNIUM series potentiostat before starting the calibration process.

It is recommended to repeat the calibration procedure after every six months.

2.1 Calibration process

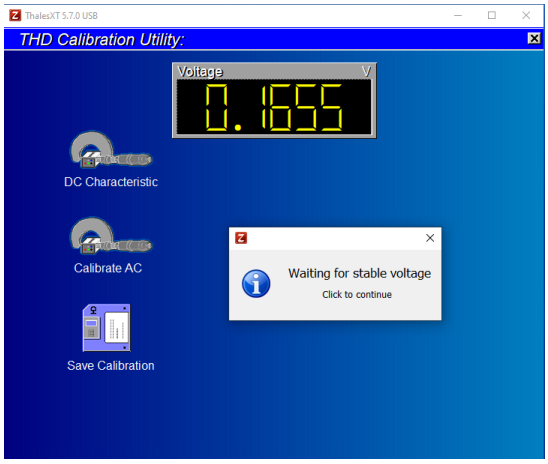
To start the NFRA calibration, click on the "EXE" icon in the Thales window and load the thd_cal.rtm file from the folder c:\thales\examples\applications.

Loading the thd_cal.rtm file will open the "THD Calibration Utility" window. Click on "DC Characteristic". This will open a "Voltage" display data box (shown on the next page). Observe the voltage value and once the voltage value stabilizes, you may click anywhere on the software window to shorten the procedure. During the stabilization phase, the voltage drift is monitored. If you miss clicking, the procedure continues automatically after sufficient stability.



In the next step, an I/E measurement, characterizing the DC transfer function of the diodes, will start. From the experimental I/E data the NFRA response to be

expected is derived by calculating the response function for a sinusoidal excitation followed by a Fourier transform. After the I/E measurement, click on “Calibrate AC”. The AC calibration requires 14 minutes for completion.



After completion of the AC calibration, click on “Save Calibration”. This will save the NFRA calibration file. An NFRA calibration file “**cal_thd.bin**” will be saved in folder c:\thales\hardware\im6\XXXXX. Here the XXXXX is the serial number of the calibrated ZENNIUM series potentiostat.

3 Setting up NFRA

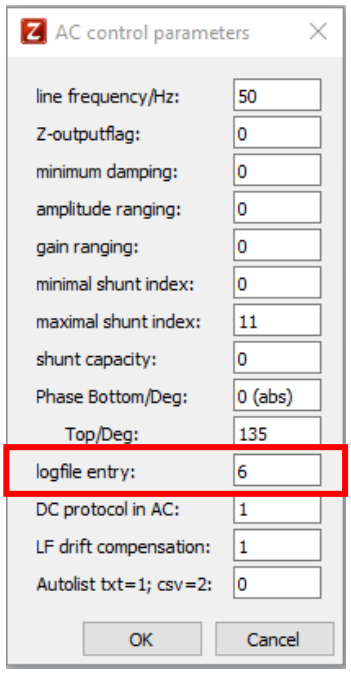
For NFRA measurements, the Thales software should be properly set up. Only after appropriate settings, the instruments is ready for NFRA and the Thales software can save the harmonics data recorded during the AC measurements.

For properly setting up the Thales software for the NFRA measurement, click on

1. EIS icon in Thales main window (classic mode)
2. Setup (Hippo icon)
3. Edit actual settings
4. “more” option in the sub window of “**AC – more**”.

This will open the “AC control parameters” data box (shown on right). Here insert 6 for **log file entry**.

5. Click “OK”.



Setting **logfile entry** to 6 will command the Thales software to record the data of the harmonics during the NFRA measurements. Further information about other possible logfile entry flags is provided in EIS manual.

For optimal EIS measurement accuracy, the “logfile entry” should be set back to “logfile entry” value that is NOT 6 or 7 (e.g. to zero). This will not only switch off the storage of the harmonics in the saving procedure, but also the adjustment of the anti-aliasing filters, optimized for best NFRA accuracy will be changed back to optimal EIS accuracy.

4 NFRA data output

Once the instrument is calibrated and the Thales software flag “logfile entry” is properly set, an NFRA measurement can be started. After the NFRA measurement, which looks identical to a linear EIS measurement, the data can be exported graphically or as ASCII text and/or saved binary. Like with any other recording format in Thales, the full set of information is only present in the binary format “filename.ism”. Please refer to the manual for EIS for details.

In the case of NFRA, besides the traditional *.ism file an additional *.thd file is saved. The *.thd file contains amplitude and phase information of harmonics of excitation as well as for the response signals plus additional data like noise and Faraday rectification.

If the Autolist Flag (see the last line in the chapter “Setting up NFRA”) is set in the AC control parameters, an ASCII data file.txt and/or an ASCII data file.csv is further stored in the saving operation. The same data list may be created and exported manually using the operation “Export data list” promptly after the measurement.

It must be mentioned here, that all these immediate ASCII data lists do not exhibit the maximum accuracy possible for NFRA. The reason for that is the role, which the distortion plays, already present in the excitation signal. No electronics may act perfectly, and so the excitation sine wave may have not zero, but a typical content of 10^{-4} to 10^{-3} distortion already in the signal. In the case of small object-assigned harmonic content (what is typical for small overdrive and higher frequency) this distortion may override the harmonic content, the user is interested in. The error propagation of this Excitation Total Harmonic Distortion (XTHD) to the response signal cannot be considered exactly during the measurement, because the necessary information is still missing about the impedance at all harmonic frequencies appearing.

Therefore, a special routine is available to cancel the influence of the XTHD in the data offline. This will be treated in detail later in this manual.

4.1 Data list formats

In the following figures, the appearance of the data list output is displayed. The listing starts with a section, identical to the output available after a conventional EIS measurement.

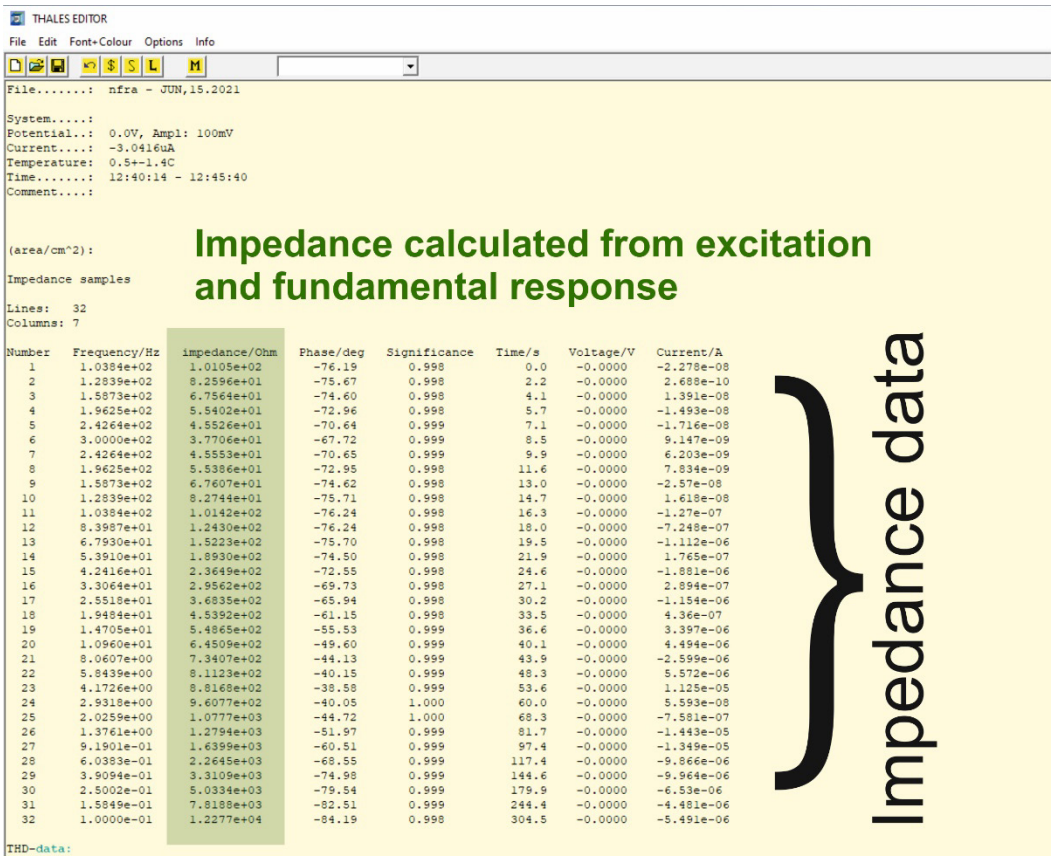


Fig. 1: Section of the general impedance data containing frequency, impedance, phase, applied bias voltage and applied bias current. It appears identical to the data list output of a linear EIS measurement.

The next section (Fig. 2) follows the listing of the harmonics 2 to 10, normalized to the amplitude of the fundamental, which one appears in this representation as always equal to one and must therefore not be displayed. Three blocks appear, containing the results for the response signal considering a tentative (scalar) correction for the XTHD interference, followed by the data for the excitation signal and then by the harmonics table of the raw response signal. Lastly, a list of the harmonics 2 to 5 of the normalized response is repeated, now in complex polar notation in order to give the user access to the sign and phase information. The second value for each harmonic is here the phase angle in radians.

The count of the harmonics is restricted here to the harmonics 2 to 5. This takes into account that the fully calibrated transfer function for the harmonics is only guaranteed up to harmonic #5. This is in accordance with the recommendations of NFRA pioneers like [1] – we also do not recommend the consideration of higher-order harmonics due to their missing significance and decreasing precision.

The last two columns of the harmonics table optionally list a noise and a DC value. The noise column value is measured during the AC data acquisition in a reserved

time slot, where the excitation signal from the frequency generator is intentionally shut down to zero for a while. The noise value is in V_{rms} or A_{rms}, dependent on galvanostatic or potentiostatic mode. The reserved data acquisition time and sample count changes with the measurement frequency. This is equivalent to an effective bandwidth change during the recording procedure so that the RMS values recorded belong to different bandwidth at a different frequency. Therefore, you should not overstress the significance of this parameter.

The data acquisition of the noise value is restricted to the frequency range, where the instrument uses DC coupling. The current software version 5.8.3 and newer uses the DC coupling technique for frequencies ≤ 1 kHz, if the NFRA flag is set. In older software versions, this limit was ≤ 77 Hz in potentiostatic and ≤ 1 KHz in galvanostatic mode. Outside of this range, the value in the noise column is set to zero.

The second optional column lists a DC value. It appears in the current software version 5.8.3 and newer. The same considerations as for the noise above, regarding the availability over the frequency range are valid. The DC value is representative for the effective bias shift due to the Faradaic rectification effect [2]. It is calculated from the zero-order FFT result value. Its validity is again restricted to the frequency range, where DC coupling is used. The physical unit is in V_{DC} or A_{DC} dependent on galvanostatic or potentiostatic mode.

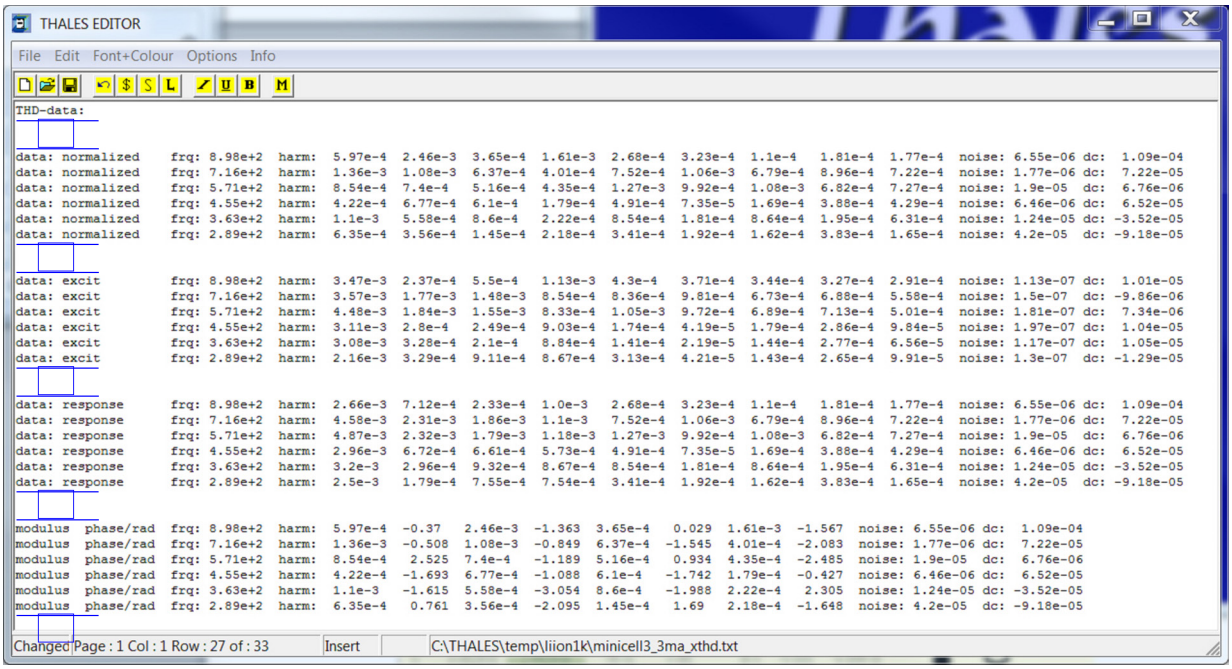


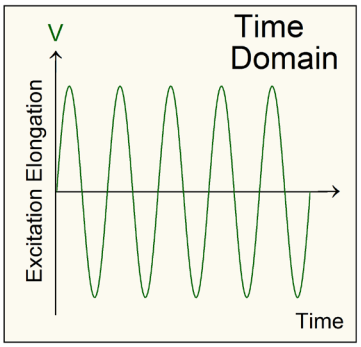
Fig. 2: First block: Relative amplitudes list (normalized to the absolute amplitude of the fundamental) of the harmonics 2 to 10 of the response signal, after a tentative compensation of the XTDH. Second block: Relative amplitudes of the harmonics 2 to 10 of the excitation signal. Third block: Relative amplitudes of the harmonics 2 to 10 of the raw response signal. Last block: Relative amplitudes of the harmonics 2 to 5 in complex polar representation. The columns “noise” and “dc” may appear or not, dependent on the software version.

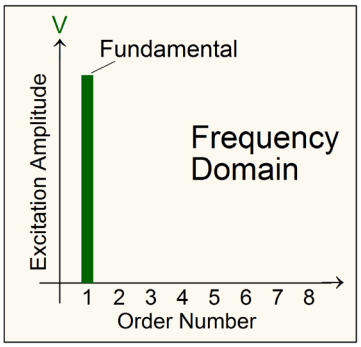
5 NFRA data conditioning

As mentioned above, XTHD, (distortion, already present in the excitation signal) affects the accuracy of the harmonics of interest, evaluated from the response signal. This is explained in the following.

Here are the NFRA signals shown in the case of perfect sinusoidal excitation (in green):

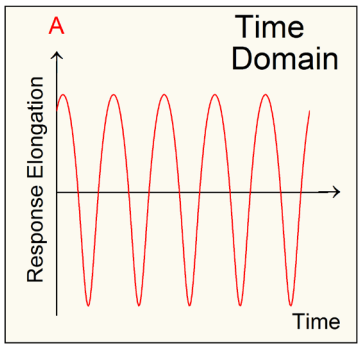
$$V = \hat{V} \cdot e^{j\omega t}$$

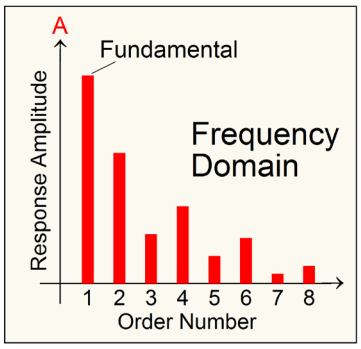




The response signal (in red) contains, besides the fundamental (left side upper term), the harmonics of interest (left side lower summation term):

$$I = \hat{I}_F \cdot e^{j(\omega t + \varphi_F)} + \sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o \cdot \omega t + \varphi_o)}$$



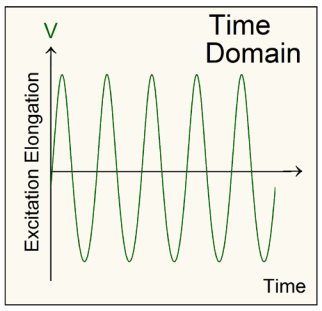


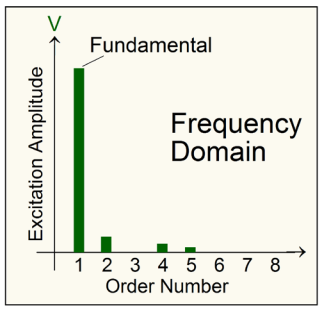
$j\omega$: complex frequency of the fundamental
o : harmonic order resp. frequency factor
$\varphi_{F,\,o}$: phase shift of the fundamental or harmonics of the response signal, caused by the objects impedance

In NFRA, if the harmonic amplitudes appear relatively high (about some percent of the fundamental) the error contribution due to the XTHD may be neglected. The numeric values of the response harmonics in the table section “normalized” and “modulus and phase” are then sufficiently accurate compared to the maximum available accuracy. In the case of the small object assigned non-linear contributions, the XTHD error may falsify the results significantly. This situation is sketched in the following.

In the case of an already distorted excitation signal, (in green), a second term besides the fundamental sine, must be considered in the formula of the excitation signal (right sum term). In the diagram of the frequency domain then appear additional, more or less clearly expressed lines for the harmonics.

$$V = \hat{V} \cdot e^{j\omega t} + \sum_{o=2}^{n} \hat{V}_o \cdot e^{j(o \cdot \omega t)}$$

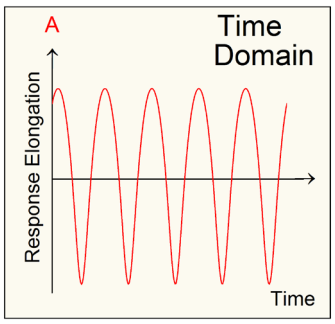


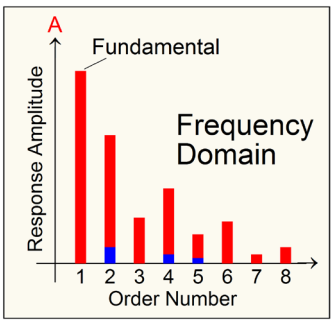


The corresponding response signal (in red) contains now, besides the fundamental (left term), and the harmonics of interest (right term) a new excitation distortion term (in blue). It falsifies the result in a way, not considerable during the online measurement procedure (visualized in the blue line parts in the right picture).

$$I = \hat{I}_F \cdot e^{j(\omega t + \varphi_F)} + \sum_{o=2}^{n} \hat{I}_o \cdot e^{j(o \cdot \omega t + \varphi_o)}$$

$$+ \sum_{o=2}^{n} \hat{V}_o \cdot e^{j \cdot o \cdot \omega t} / Z_o$$





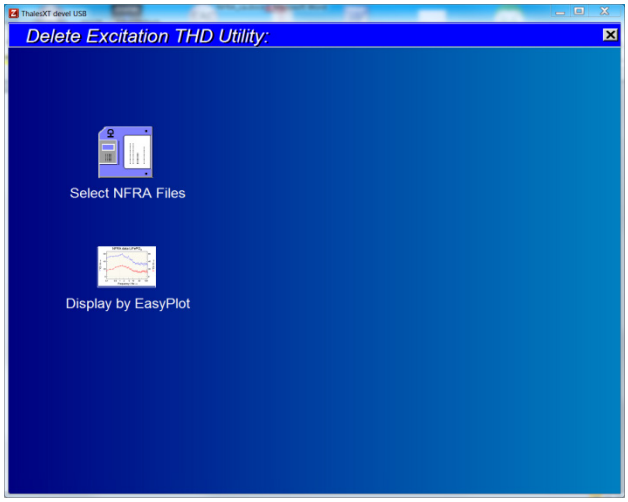
Z_o : object impedance at the frequency of the harmonics

5.1 Delete Excitation THD Utility

The blue term asks for the impedance values Z_o at all frequencies $o \cdot \omega_i$, which are neither present during the recording nor after the complete sweep through all ω_i. A special offline routine is therefore necessary in order to reconstruct the missing impedance values Z_o and calculate the excitation distortion share, present in the harmonic response.

This can be done with the routine “del_excit_thd”, available in the Thales EXE pool.

To start the “del_excit_thd” application, click on the “**EXE**” icon in the Thales window and load the **del_excit_thd.rtm** file from the folder c:\thales\examples\applications.

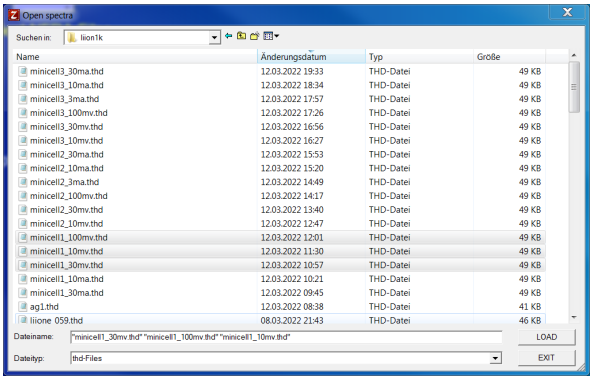


Loading the del_excit_thd file will open the “Delete Excitation THD Utility” window.

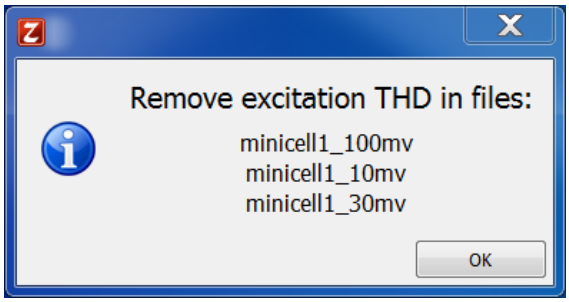
Click on “Select NFRA Files”.

A file open dialog will appear, offering

data files.thd, present in the current folder.



You may then mark one or several files for conditioning. A message window appears, informing you of the files selected. Quit with “ok”, if you agree to continue.



One or a set of text data files will be created, using the original file name, modified with an extension “_xthd” in the data source directory.

Here, the text blocks described above (Fig. 1, Fig. 2) will be repeated, but now with fine corrected data for the normalized response harmonics. Note, that frequencies above the limit of accurate calibration will be omitted now.

The text blocks in Fig. 1 and Fig. 2 have a format not really friendly for the analysis with a table calculation program. The historic reason for that is that in the first years of NFRA support by Zahner, THD-data were only accessible via the logfile entries in Z-TRACE. These entries are line-oriented, one line for every frequency point. In the case of NFRA this led to a format, where informative strings like “noise:” or “harm:” appeared illustrating every line, but complicating the automatic analysis of complete tables. Therefore the “del_excit_thd” application now adds an additional text block, organized in a straight “csv” way (Fig. 3), in order to ease future analysis.

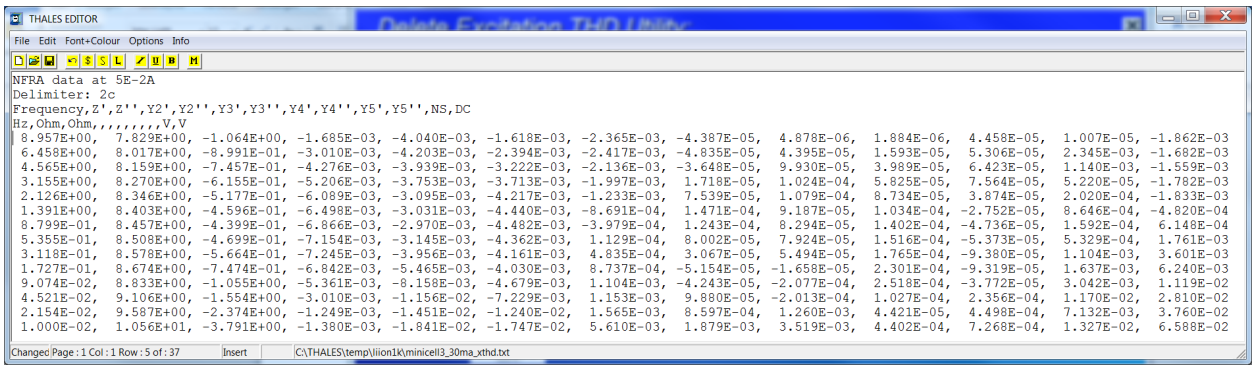


Fig. 3: Additional CSV block appearing after the application of the “del_excit_thd” program at the end of the text table file_xthd.txt: Frequency, complex impedance and relative amplitudes of the harmonic components 2 to 5 in complex real- and imaginary value representation plus the columns for noise “NS” and Faradaic rectification “DC”. Besides the impedance in the list, the excitation amplitude is displayed in the header in order to enable the calculation of the harmonic amplitudes in physical units.

5.2 XTHD compensation algorithm

The strategy, how the correction is calculated in the “del_excit_thd” program is sketched in the following, starting with Fig. 4.

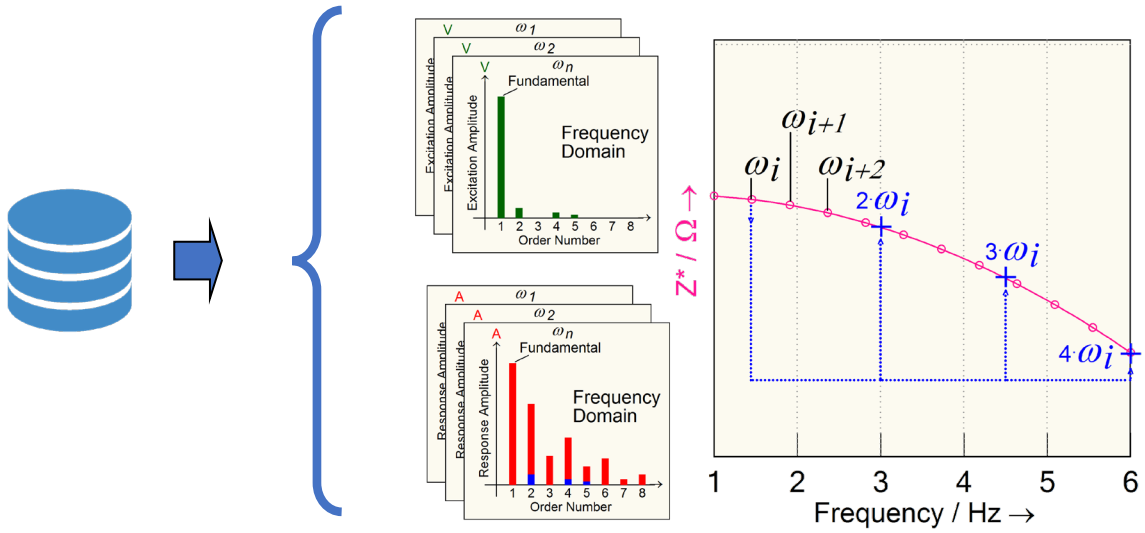


Fig. 4: The original frequency, impedance and harmonics list will be imported from storage and sent to SIM. For every measured frequency ω_i <1 KHz and $<\omega_{max}/5$ the impedance $Z_{2\cdot\omega}$, $Z_{3\cdot\omega}$, $Z_{4\cdot\omega}$ and $Z_{5\cdot\omega}$ is calculated by means of the smoothing/interpolation feature of the SIM software. So the blue-colored excitation distortion term in Fig. 5 can be calculated.

$$-\sum_{o=2}^{n}\hat{V}_o \cdot e^{j\cdot o\cdot\omega t} / Z_o$$

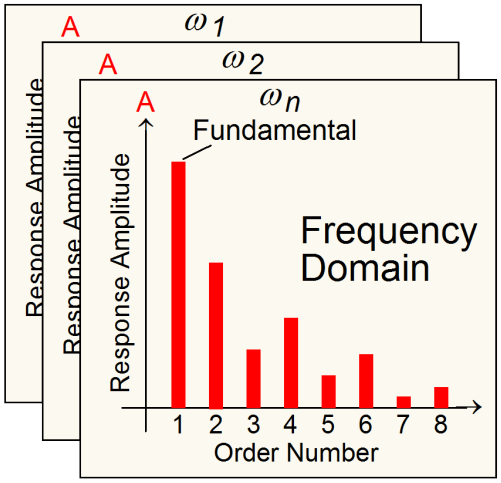


Fig. 5: Considering the phase information, the excitation distortion term is now subtracted from the raw harmonic amplitudes. This leads to accurate object-assigned response harmonics, no longer affected by the XTHD.

Excitation Components

Order	real part	imag part
1	0	1
2	-0.1	0.1
3	0	.004
4	.-5.5e-3	5.6e-3
5	0	1.1e-3

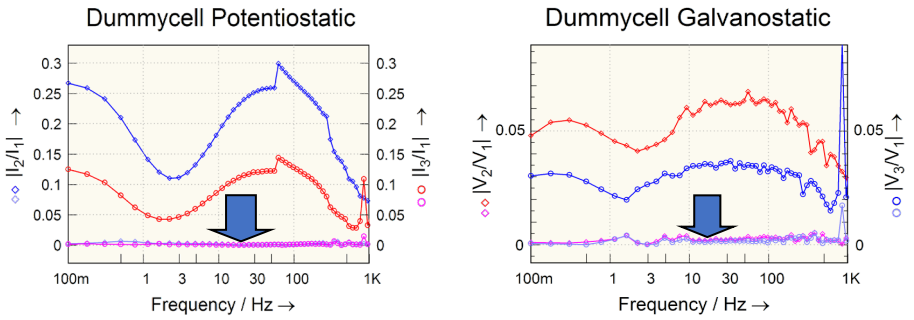


Fig. 6: On a linear system (dummy cell), the suppression of the XTHD is demonstrated. In the left table, the content of harmonics of the XTHD is displayed. The sine generator was re-programmed accordingly. The resulting 2nd and 3rd order harmonics (blue and red) in both potentiostatic (middle) and galvanostatic (right) modes are shown in the raw data. In contradiction to the result, their nominal values should tend to zero due to the linearity of the object. The light-blue and pink curves show the corresponding harmonics after the application of the "del_excit_thd" program, now appearing close to the theoretical value of zero (dark blue arrows).

6 NFRA data visualization by EasyPlot

The additional button "Display by EasyPlot" in the del_excit_thd application offers a shortcut to a tiny table calculation display program named "EasyPlot". Use "EasyPlot", if you want to immediately see graphs from your NFRA data with minimum set-up overhead. EasyPlot is designed to directly support the immediate graphic output/export of all ASCII-text based data list outputs of the Thales software. EasyPlot is accessible via the EXE-mechanism by loading from the c:\thales\examples\applications folder. The access works analogously as described above for "del_excit_thd" and "thd_cal".

The menu of EasyPlot will appear as shown in Fig.7.

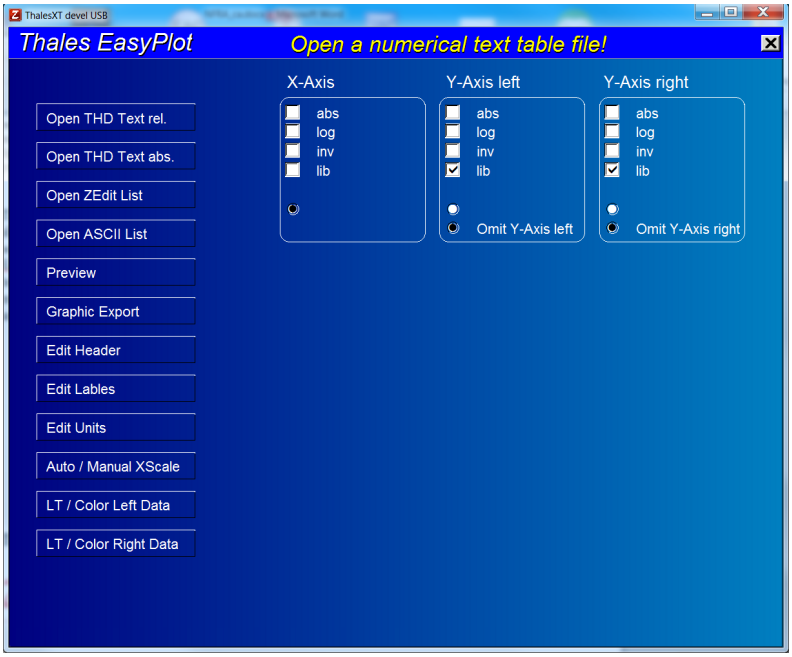


Fig. 7: EasyPlot pops up and asks the user to open an ASCII-based numeric text table file.

You can preselect the table type by using four different types of files to open. Details will be given in the specific manual of EasyPlot, but small hints will also be displayed, if you touch the buttons with the mouse pointer. Here we will restrict aspects due to the NFRA application. The most straightforward way is to use the first button. You open for instance a data list like shown in Fig. 1 or Fig. 2. EasyPlot will offer you now the possibility to select for the X-axis, the Y-axis left and the right Y-axis a column for display in a two-dimensional diagram. In the example of Fig. 8, the frequency is chosen in a logarithmic scale for the X-axis. The signal columns response harmonic #2, Y2, and the Faradaic Rectification value, DC, are chosen for the left resp. right Y-axis.

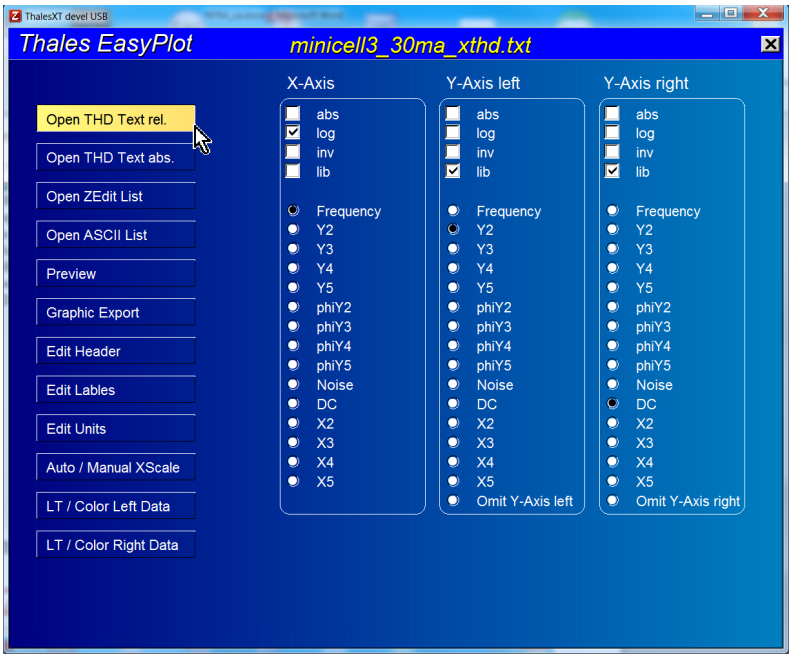


Fig. 8: If you use the first button “Open THD Text rel.”, you may open immediately files.txt of NFRA harmonic tables like output after an NFRA measurement or after the post-processing of a file.thd by means of “del_excit_thd”, like files_xthd.txt. The results for the harmonics Y2-5 are normalized to the fundamental and are therefore dimensionless.

If you choose now “Preview”, you will get an impression, how the graphic export data will look like. In Fig. 9 you see the result, if the additional LT/ Color settings “curve”, “symbols” and “smooth” are set accordingly.

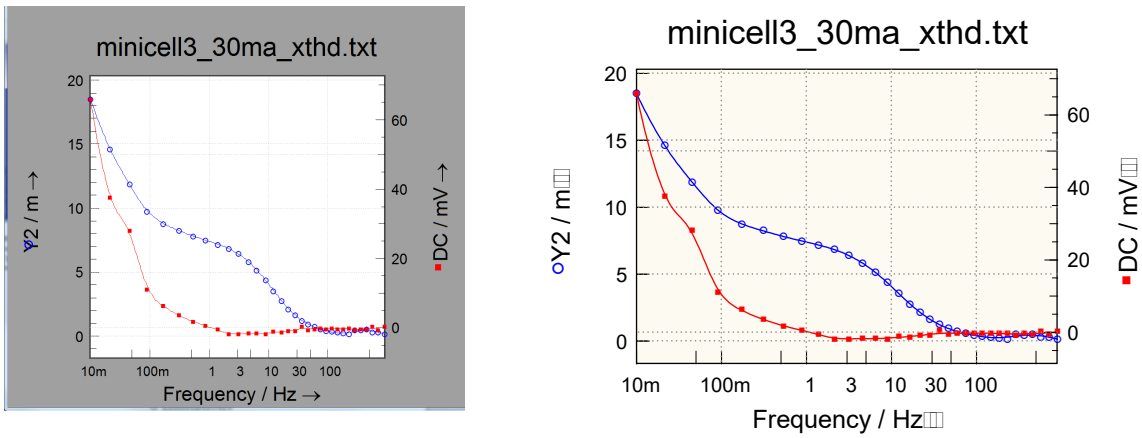


Fig. 9: Preview of the Y2-trace (in blue) and the Faradaic Rectification DC (in red) on the left-hand side. On the right-hand side, you can see the result, if you use the “Graphic Export” function.

EasyPlot supports also the display of the harmonic data in absolute physical units. For that, you must use the second button “Open THD Text abs.” and open the same type of file. The list of available table data is shown in Fig. 10.

Fig. 10: After using “Open THD Text abs.” you will get the list of possible data columns for display no longer normalized to the fundamental, but now in physical units V or A, dependent on the measurement type potentiostatic or galvanostatic. In this mode also the fundamental Y1 is listed.

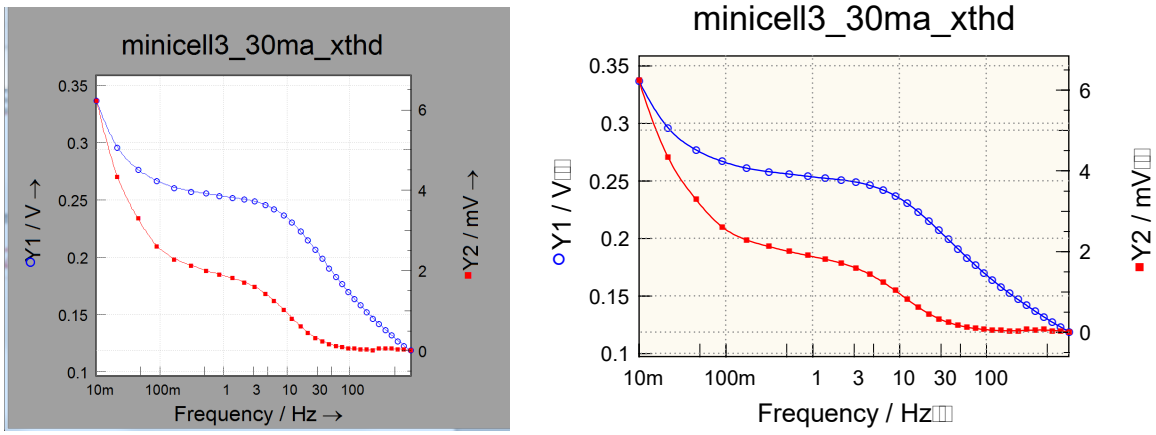


Fig. 11: Preview of the Y1-trace (in blue) and Y2-trace (in red) on the left-hand side, now in physical units of V. On the right-hand side, you can see the result, if you use the “Graphic Export” function.

It is also possible to read in text table files like the csv-type trailer appearing after the “del_excit_thd” application, shown in Fig. 3. For that, you have to shorten the total text to the part shown in Fig. 3, save it and open it using the button “Open ASCII List”. With this entry, csv-type lists are directly analyzed.

7 Limitations

Artifacts during EIS measurement can induce harmonics similar to the ones induced by a large excitation signal. Such artefacts, affecting the accuracy of the NFRA are typically caused by external distortion signals like line frequency interference and by temporal instabilities. Zahner high-end potentiostats can eliminate the effect of linear time drift during the measurement, but not spontaneous spikes, scatter and noise. Be sure, that the latter effects are small enough to keep sufficient accuracy for NFRA. You may, for instance, perform an NFRA measurement, but intentionally keep the excitation signal in the linear regime. When you compare the NFRA result with the result under a higher excitation signal, you may get an impression of the significance of your NFRA data.

The amplitudes of harmonics are very sensitive to the absolute amplitude of the excitation signal. For good reproducibility and comparability, the potentiostat must produce an accurately calibrated excitation signal. The ZENNIUM X, ZENNIUM PRO & ZENNIUM XC potentiostats are most suitable for the NFRA measurement. In comparison, Zahner's older generation comprising ZENNIUM and IM6 potentiostats do not generate perfectly exact excitation signals regarding the absolute amplitude and provide therefore less accuracy for NFRA measurements.

The interpretation of NFRA harmonic data should be limited to a maximum fundamental frequency of less than about 1 kHz. The response of electrochemical test objects at higher frequencies is dominated by the linear properties of the ohmic series resistance and the inductance contribution. The harmonics detected in this frequency range are not related to the electrochemistry, but only to instrumentation limitations. Besides, in electrochemical objects with their generally continuous I/V characteristics, the amplitudes of the higher harmonics decrease typically with the square of the harmonic order. The fully calibrated data output for the harmonics is therefore limited to the 4^{th} harmonic #5, respectively the fundamental frequency $f_f \cdot 5$.

8 References

[1] D.D. Macdonald, Transient Techniques in Electrochemistry, Plenum Press, New York, (1977), 249.

[2] D.D. Macdonald, Transient Techniques in Electrochemistry, Plenum Press, New York, (1977), 7.6, 270.