Introducing the Microscopic Image Rapid Analysis (MIRA) software

I – INTRODUCTION

MIRA software is an optional representation and analysis software that is developed by Prof. Gunther Wittstock[1-5], based at the University of Oldenburg. The software offers a full range of graphical representations specially designed for area maps data. One of the most interesting feature is the ability to fit Scanning ElectroChemical Microscopy (SECM) approach curves, giving access to various physical and chemical parameters related to the experiment itself. This note introduces some of the features of the MIRA software, with a special focus on the SECM approach curves fitting tool.

II – PLOTTING DATA OBTAINED WITH M370 or M470

The data obtained with the M370 or M470 scanning workstation are compatible with MIRA.

II - 1 AREA MAPS (3D FILES)

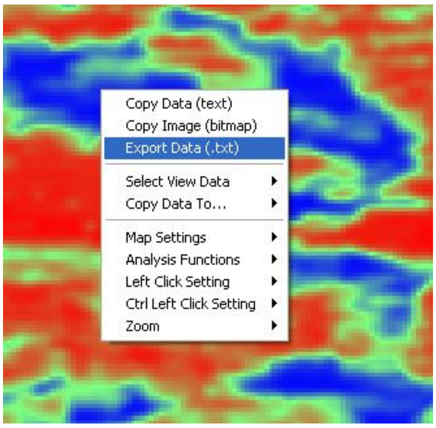

Fig. 1 : Export command an M370 or M470 data file opened in M470 software in .txt format.

First and foremost, the data acquired using M370 or M470 scanning workstation software must be exported as .txt files. This is done in the M370 or M470 software by right-clicking on the data representation window as shown in Fig. 1.

The data compatible with MIRA are the area maps of all techniques including all the different data available in ic- and ac-SECM, approach curves obtained with dc- and ac-SECM, and CVs.

When starting the MIRA software, the window seen in Fig. 2 pops up, displaying which .ini files are available. .ini files define the folder that will be opened by default, the default output folder as well as the default representation. The default paths can be changed as shown in Fig. 3a and these changes can be saved in a new .ini file as shown in Fig. 3b.

.ini files are located in MIRA\startup.

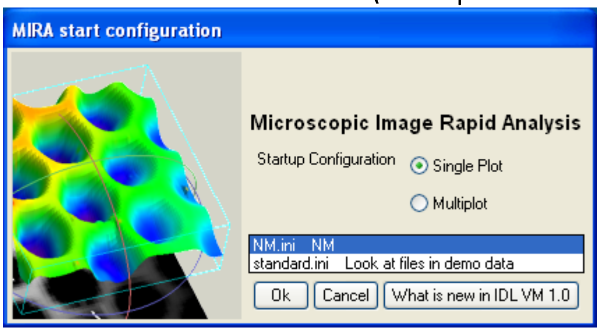

Fig. 2 : Configuration window showing the available .ini files.

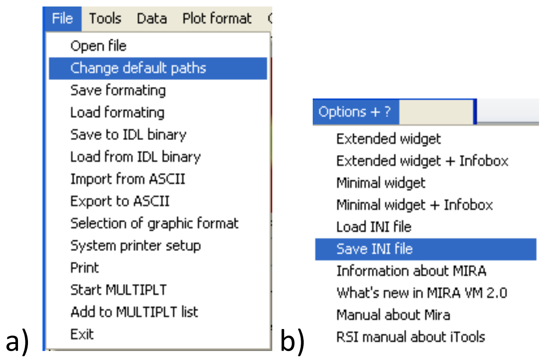

Fig. 3 : a) Changing the default paths, b) Saving the new .ini file.

MIRA software contains tools that have been developed by Prof. Wittstock and default tools written and provided by IDL (Interactive Data Language v.8.1 by Research Systems

Inc., Boulder Colorado). These imaging tools have a name which usually start with an i.

When opening a file, the window shown in Fig. 4 will appear. It shows the default representation of the opened data in a small window and all the available representations. Clicking on the “Redraw” button will open a new window showing the data.

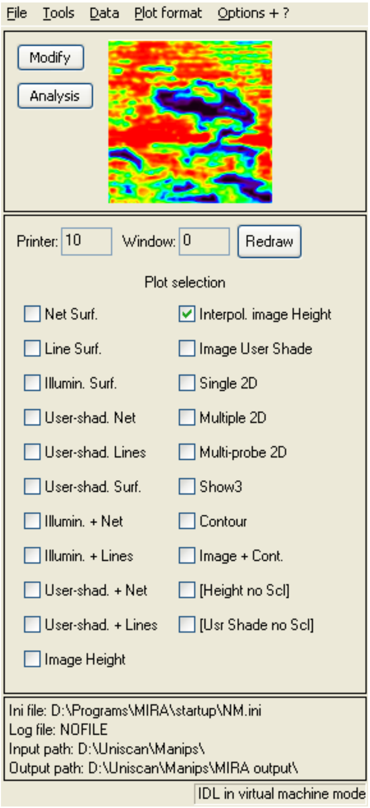

Fig. 4 : Main window.

The plotted data can also be saved as a graphical file using the “Print” command in Fig. 3a.

The parameters of the export can be changed using the “Selection of graphic format” also shown in Fig. 3a. The file will be exported into the default folder. It can be saved in various matrical formats (.jpeg, .tiff, .bmp) as well as vectorial formats (.ps, .eps).

Examples of data plots are shown in Fig. 5.

The palette used to plot the data can be changed using the following command Tools->XLoadct.

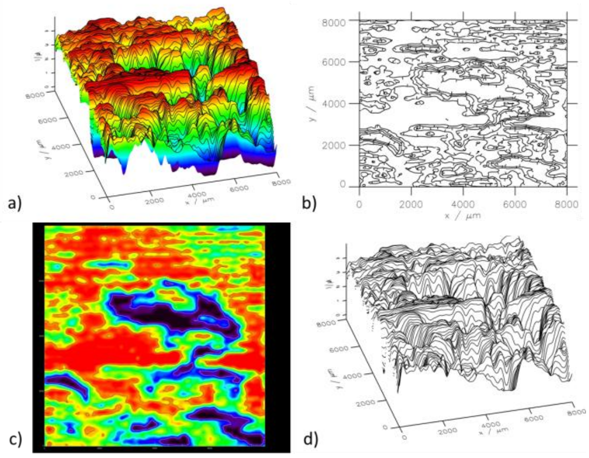

Fig. 5 : Various 3D data representations : a) User-defined 3D shade + Lines, b) Contour plot, c) 2D interpolated + contour, d) 3D lines.

II - 2 2D FILES

The MIRA software also allows to plot 2D files such as line scans, CVs and approach curves (Fig. 6).

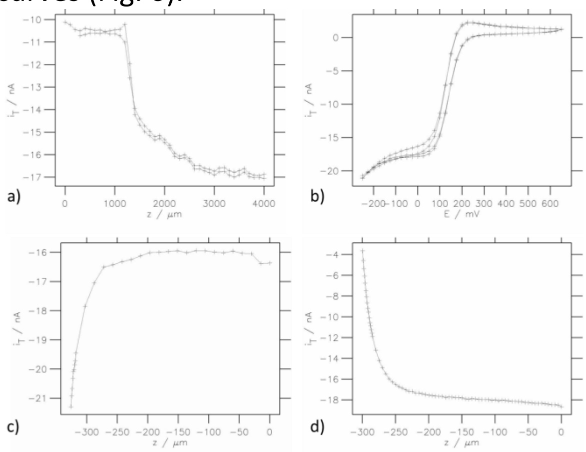

Fig. 6 : Various 2D representations : a) SECM forward-backward line scans, b) CVs, c) Approach curve on conducting region, d) Approach curve on insulating region.

III – USING THE FITTING TOOL

One of the most interesting tool of MIRA is the ability to fit dc-SECM approach curves and have access to experimental parameters and reaction kinetics.

The Curve fitting tool is accessible using the Analysis button on the left of the data display window (Fig. 7).

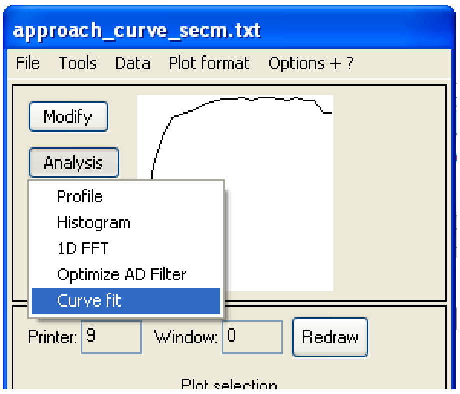

Fig. 7 : SECM approach curve fit window.

In the next window, an abundant choice of conditions will be displayed along with the analytical expression used to fit the data, the fitting parameters and the paper in which it was first described (Fig. 8).

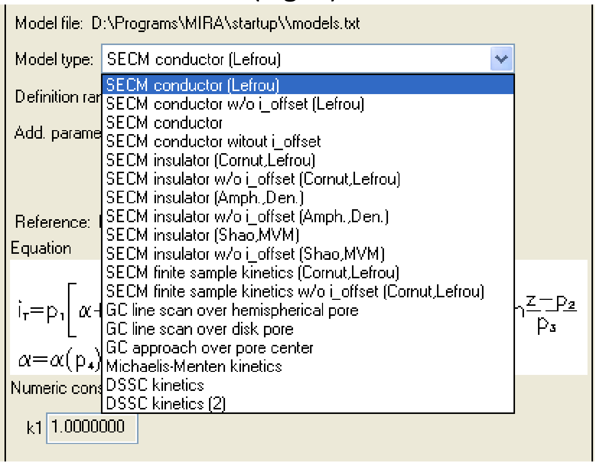

Fig. 8 : The choice of equations available to fit the approach curves.

After choosing the equation corresponding to user-specific conditions (approached material, current offset, acquaintance with the researchers), the best way to start is to click on “Guess start parameters” in the fitting commands window, and then “Start iteration” (Fig. 9). The “Guess start parameters” uses an algorithm, which analyzes the curve and tries to find starting values which are close to the final values.

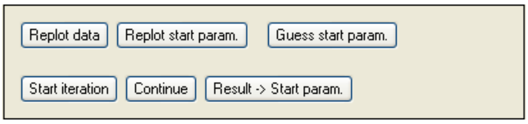

Fig. 9 : The fitting commands window

In this document, we tried to fit the approach curve located in the demo folder : MIRA\demo\DEVICES\Biologic_Uniscan\approach_curve_SECM.txt.

This approach curve was performed with a 25 µm diameter Pt probe in 10 mM $Fe(CN)_6K_3$ and 100 mM KCl on a Au electrode (SECM model sample). The probe was polarized at -0.25 V *vs.*Ag/AgCl. The probe position is at first 0 and then approaches the sample, hence the negative values of z. We used the equation named “SECM conductor w/o i_offset (Lefrou)”[6].

Clicking on “Guess Start Parameters” and then “Start iteration” with 30 iterations leads to the results shown in Fig. 10.

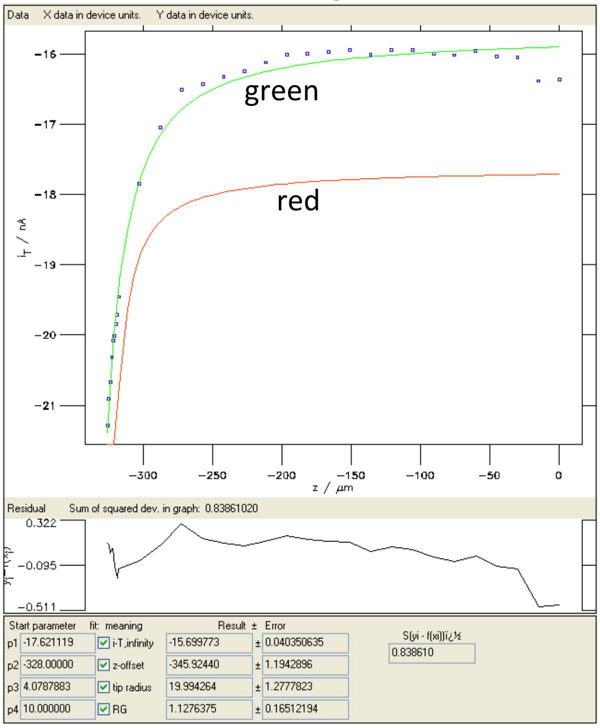

Figure 10 : The results window obtained with “SECM conductor w/o i_offset (Lefrou)” expression. In red the curve obtained using the Start parameters, in green the curve obtained after fitting.

Four parameters are obtained in this case :

. *i-T, infinity* is the current when the probe is in the bulk or at a infinite distance from the sample,

. *z-offset* is the opposite value of the distance between the probe and the sample at the beginning of the approach,

. *tip radius* is self-explanatory,

. *RG* is the ratio between the diameter of the glass sheath around the metallic electrode and the diameter of the metallic disk.
The starting values and the values after fitting are shown along with their error, as well as the residuals and the square of the sum of these residuals, also called the χ^2 parameter (considering the variance is equal to 1, as there is only one experiment done). This function χ^2 is used in the minimization process, which is based on the Gauss-Newton algorithm[7]. The lower this number, the better the fit (for the same number of points). In the example shown in Fig. 10, $\chi^2 \approx 0.839$. The residuals reach a maximum at the first points of the scan (points close to z = 0). The software allows bad points removal using the top left window, shown in Fig. 11.

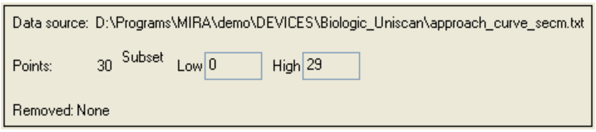

Fig. 11 : Data removal window.

Entering 2 in the "Low" box will remove the two first points in the lower values of the variable (z). Then click on the "Replot data" button shown in Fig. 9. The results of the fitting done on these new data are shown in Fig. 12.

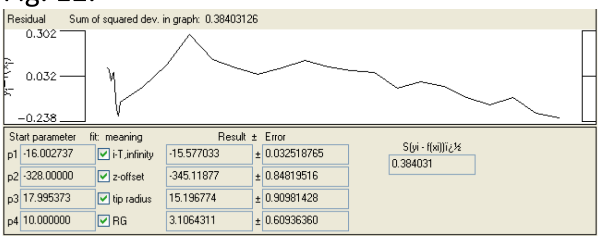

Fig. 12 : Fitting results obtained on the newer dataset obtained with "SECM conductor w/o i_offset (Lefrou)" expression.

Now, the $\chi^2 \approx 0.384$, which is expected as the number of points has been reduced but also means that the fit is of better quality. The value of the tip radius decreased and is closer to the experimental value i.e. 12.5 µm. The value of the Rg parameter increased from around 1.13 to 3.11, which is a more sensible value.

Tips : i) In the approach curve shown above, the step size was 15 µm and the scan speed 5 µm/s. It is recommended to perform approach curves with a step size smaller than 1 µm and a scan speed of 1 µm/s or less. In these conditions, the experimental values do not diverge too much from the theory and the trueness of the fitting will be increased (and the χ^2 factor decreased).

ii) Using parameters independently determined can be beneficial for the fit. For example the value of the tip radius can be precisely determined by the VCAM3 and entered in Fig. 10 in the "Start parameter" box. Then, if the box under "meaning" is unchecked, the parameter will not be taken into account in the fitting process.

IV – CONCLUSIONS

The purpose of this note is to introduce some of the various representation features of the MIRA software for 3D maps and 2D curves. A special emphasis is given on the particularly complete fitting tool of approach curves. For more detailed information, please consult the MIRA manual or contact us.

REFERENCES

1. G. Wittstock et al., Fresenius J. Anal. Chem. 2000, 367, pp. 346–351.
2. U. M. Tefashe et al., J. Phys. Chem. C., 2012, 116, pp. 4316-4323.
3. C. Nunes-Kirchner et al., Anal. Chem., 2010, 82, pp. 2626-2635.
4. W. Nogala et al., Bioelectrochem., 2008, 72, pp. 174-182.
5. G. Wittstock et al., Angew. Chem. Int. Ed. 2007, 46, pp. 1584 –1617.
6. C. Lefrou, J. Electroanal. Chem., 2006, 592, pp. 103–112.
7. Ebert,Ederer, Computeranwendungen in der Chemie. 2. Ed., VCH, Weinheim 1985, S.323.