

# Manual SECMx, version 11

Last change 13 May 2009

# 1 Setting up the hardware and software

## 1.1 Main steps

1) If your system works with an AD card: Install the Plug-In AD/DA card DAS1602/16 from Plug-In company connect the break out box and run InstalCall.

Assign the board number 1 to the board.

Calibrate the AD channel and the DA channels according to the instructions from Plug-In.

2) If your system works with a Märzhäuser positioning system: Please set up the Märzhäuser positioning system and the Corvus control box according to the instructions of Märzhäuser. Test the functionality of the system with the program provided by Märzhäuser

Make at least the following checks

a) Do all axis move?

b) If you request a movement of 1000  $\mu\text{m}$ , is the measured translation 1.0 mm?

c) Can you read the absolute position of the x and y motors? (z motor does not has an encoder)

3) If your system works with an IVIUM potentiostat: Install and connect the IVIUM bipotentiostat and install IviumSoft as described by the materials obtained from IVIUM company.

4) If your system works with a ZABER tilt table: Install and connect the ZABER tilt table and install the software as described by the materials obtained from ZABER company. You may need to install an USB to serial converter. Test the tilt table with the software from ZABER.

5) If you have a shear force system: The shear-force mode runs on a second PC that comes with the shear force system and is preinstalled. It does not require further installation.

6) If all components are functionally individually, you can progress to install the SECMx program that runs the SECM instrument.

Execute the program SECMxSetup.exe.

The program will unpack all necessary files and place them in a directory, for instance to c:\programs\SECMx\. [There you need to make further settings during the first start of the software.](#)

In case some problems occur, the most important settings are listed and explained below.

## 1.2 Required files

The directory MUST contain the files in red and may contain more files depending on the hardware:

```

borlndmm.dll
cbw32.dll
cc3260.dll
cc3260mt.dll
dclusr.bpi, dclusr.bpk, dclusr.cpp, dclusr.lib, dclusr.res,
dclusr60.bpl
devices.ini
devices_all.ini
devices_dummy.ini
drv_das1602_16.dll
drv_dummy_adda.dll
drv_dummy_motors.dll
drv_e665_pi620_1cd.dll
drv_gen_ana_in.dll
drv_gen_ana_out.dll
drv_gen_bipot.dll
drv_ivium_bipot.dll
drv_maerzh.dll
drv_ports.dll
drv_zaber.dll
IVIUM_remdriver.dll
PlxApi.dll
rt160.bpl
SECMxApp.exe
users.ini
vcl60.bpl
Wp2Comm.dll

```

The directory may contain more files that are required for driving other hardware. You should keep them, in case you want to use different configurations in the future.

The files have the following function

borlndmm.dll, cc3260.dll, rtl.bpl, vcl.bpl	Borland utility
cbw32.dll	Plug-In DLL for AD card
devices_xxxx.ini	INI file that defines the devices connected and the last valid settings, that will change during operation
drv_das1602_16.dll	Driver for the AD card
drv_e665_pi620_1cd.dll.dll	Diver for the Physikinstrumente piezo motor
drv_maerzh.dll	Driver for the Märzhäuser system
drv_ivium_bipotentiostat.dll	Driver for IVIUM compact stat with bipot option (requires IviumSoft to be started before SECMx is started)
drv_ports.dll	Driver for serial ports and USB connections
drv_zaber.dll	Driver for Zaber tilt table
IVIUM_remdriver.dll	Additional file required for IVIUM compact stat
PlxApi.dll	?
SECMxApp.exe	Main control program
users.ini	Ini files for user
Wp2Comm.dll	Additional file for Märzhäuser positioning system

There are some more files which can be of interest

drv_dummy_motors.dll	Driver that emulates a positioning system
drv_dummy_adda.dll	Driver that emulates an AD/DA card
drv_dummy_tilt.dll	Driver that emulates a tilt table.

These drivers can be used to track errors in hardware and software. They emulate devices without performing any external action. This can be used also in order to practice with the software or to check the behavior of the software. For normal operation they are not required.

### 1.3 *The file device.ini*

The file device.ini contains the connected devices and the last settings. These become the default settings if the software is restarted. In this way users will automatically return to their preferred instrument configuration.

Normally, you do not need and you should not edit this file. However, if errors occurs (for instance after power supply interruption during operation) it might be necessary to reset the entire instrument into the starting configuration.

The file should look like this. (Exact content varies with hardware)

```
[GENERAL]
nDevices=9

[Device#0]
DllName=drv_ports.dll
Name=Ports

[Device#1]
DllName=drv_das1602_16.dll
Name=DAS1602/16
BoardNumber=1

[Device#2]
DllName=drv_ivium_bipot.dll
Name=Ivium bipot

[Device#3]
DllName=drv_maerzh.dll
Name=Maerzhaeuser-XYZ

[Device#4]
DllName=drv_e665_pi620_1CD.dll
Name=PI E665->P620-Z

[Device#5]
DllName=drv_gen_bipot.dll
Name=Gen. Bipot

[Device#6]
DllName=drv_gen_ana_out.dll
Name=Analog acceptor

[Device#7]
DllName=drv_gen_ana_in.dll
Name=Analog input

[Device#8]
DllName=drv_zaber.dll
Name=Zaber tilt table
```

It is certainly a good idea to keep versions of the original device\_xxx.ini files under a different name. For instance you can copy device.ini to device.001 BEFORE you start SECMx for the first time.

## 1.4 The file users.ini

The file users.ini contains the user names and the ini files used for this user. This allows different users to have different preferences for the instrument settings. For instance. The installation program generates a file that contains three users (typical configuration, all devices, only virtual devices). The data path point to Windows path that exist on each machine. You may want to change these files to make it specific to certain users. If you use older installations you may copy the ini files from that installation to the new installation. In the inifiles `devices_xxx.ini`, please delete all lines except, `Name=`, `DllName=` and `BoardNumber=` as shown in section 1.3. After the first start, you need to go to the corresponding windows to make the appropriate settings for the connections of the instruments.

**DO NOT USE** the files `user_alfons.ini`, `user_barbara.ini` or any other StdIni file **from a previous version**. The installation path should initially not contain any `user_xxx.ini` file. These files are created during operation and contain the last settings of the experiments. Because the way of storing changes between versions, they cannot be used from older versions.

```
[GENERAL]
nUsers = 5

[User#0]
Name = Alfons
StdIni = C:\Program Files\SECMx_11\user_alfons.ini
DevIni = C:\Program Files\SECMx_11\devices_all.ini
DefPath = C:\SECM_DATA\Alfons\

[User#1]
Name = Barbara
StdIni = C:\Program Files\SECMx_11\user_barbara.ini
DevIni = C:\Program Files\SECMx_11\devices_all.ini
DefPath = C:\SECM_DATA\Barbara\

[User#2]
Name = Guest
StdIni = C:\Program Files\SECMx_11\user_guest.ini
DevIni = C:\Program Files\SECMx_11\devices_all.ini
DefPath = C:\SECM_DATA\Guest\
```

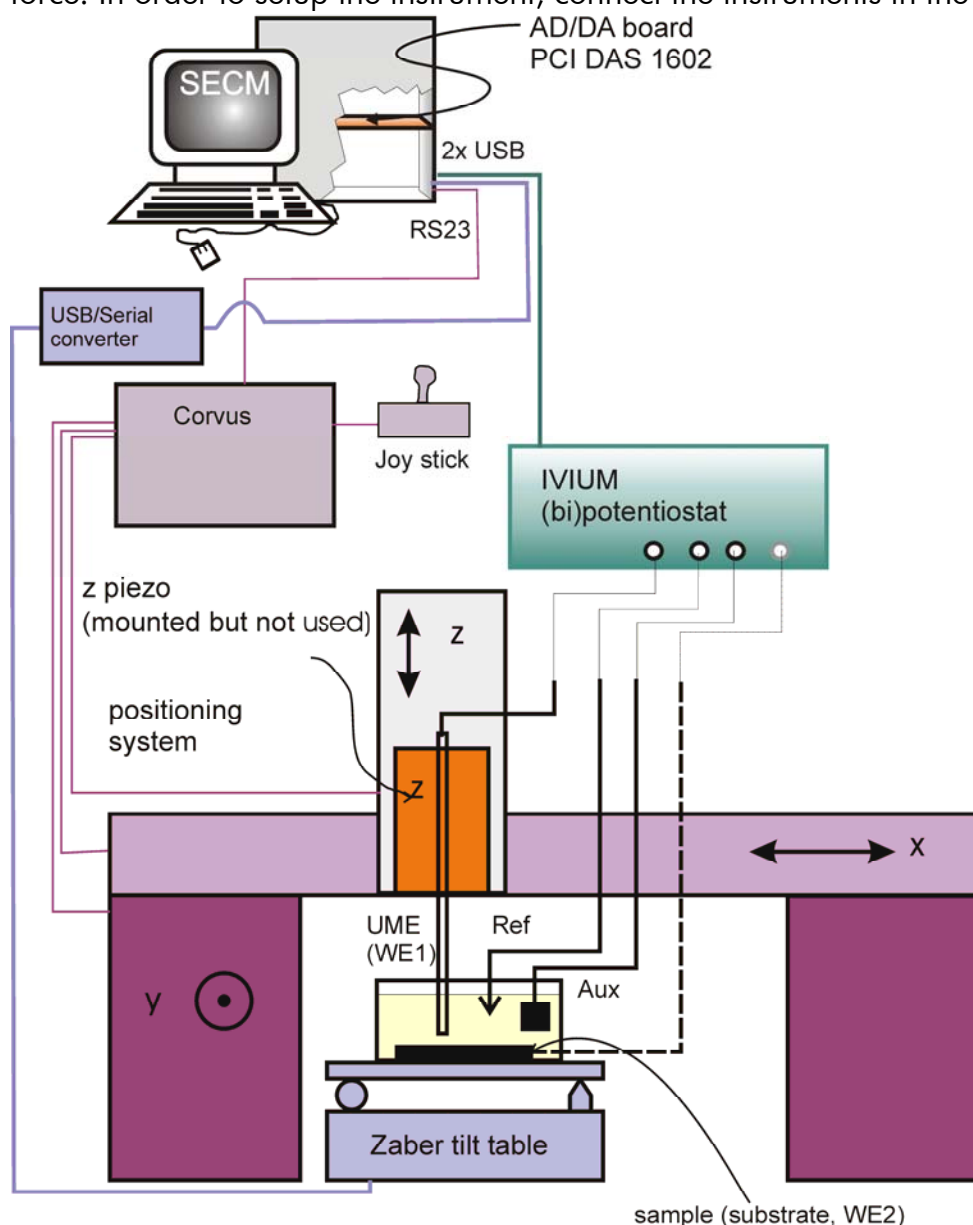
The file user.ini has to be edited when a new user is added (the red parts were added/changed to have the new user "Guest").

With these preparations you are ready to start SECMx.

## 2 Operation without using the shear-force distance control

### 2.1 Setup

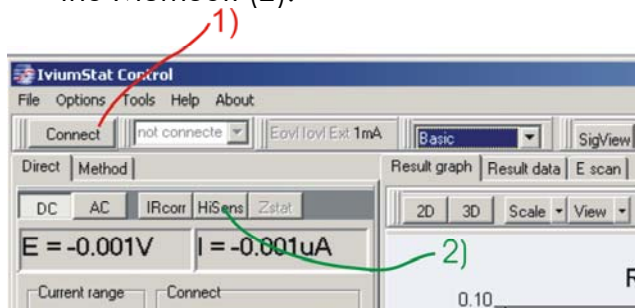
The normal operation of the SECM is without the shear force option. It is strongly recommended that your first work without shear force. Once you are familiar with the SECM principles and the operation of this hardware you may advance to use the shear force. In order to setup the instrument, connect the instruments in the following way.



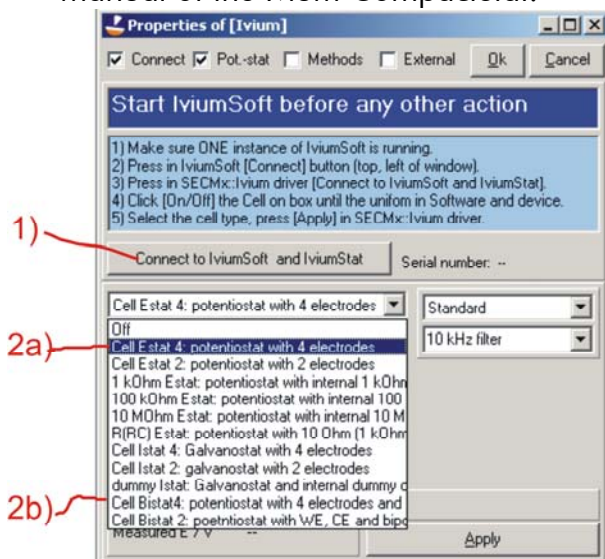
After connecting the microelectrode as WE1 to the potentiostat, fill the electrolyte solution with a mediator into the cell.

## 2.2 Step by Step to an Image

- 1) Start the IviumSoft software, press **Connect** (1), select the high sensitivity option in the IviumSoft (2).

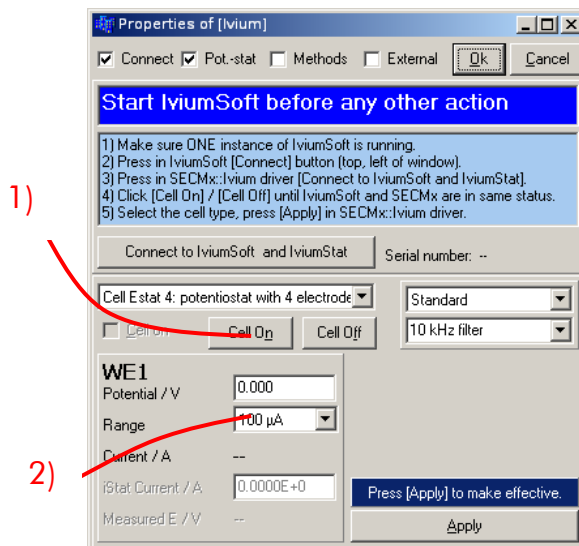


- 2) Start the SECMx software, select the appropriate user profile.
- 3) If during the loading process the window of the Ivium driver pops up, press **Connect**. (1). Select the cell type you need. In most cases you will use the monopotentiostat option (2a). If you want to use the bipotentiostat select (2b). The electrode you want to use for potential programs from the IviumSoft should be WE1 (in most cases this will be the microelectrode). For more details see the manual of the Ivium CompactStat.

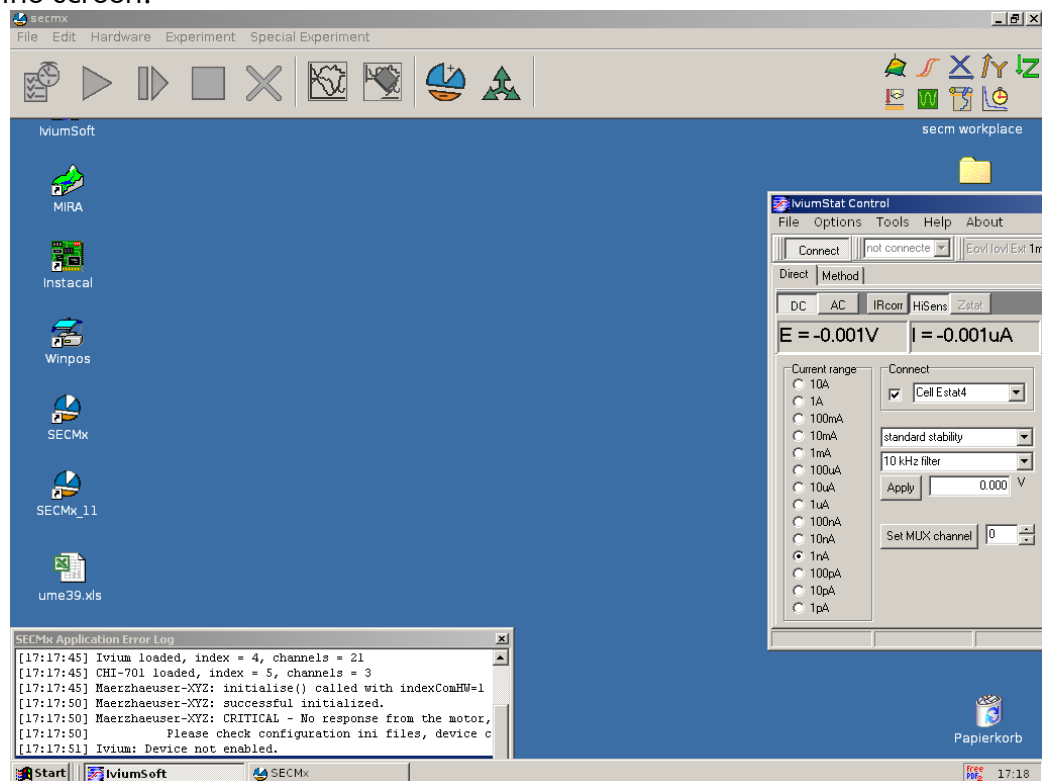


- 4) Switch on the electrochemical cell (1). Check that the corresponding option control in the IviumSoft will also switch. Then select the current range (2). Select the filter and the potential at which no reaction occurs. Press **Apply** and the **Ok**.





- 5) Now the loading process of the software is completed and you see the surface. Adjust the screen. It is recommended that you have the control panel of IviumSoft somehow visible on the screen. SECMx main window will occupy the entire upper range of the screen.

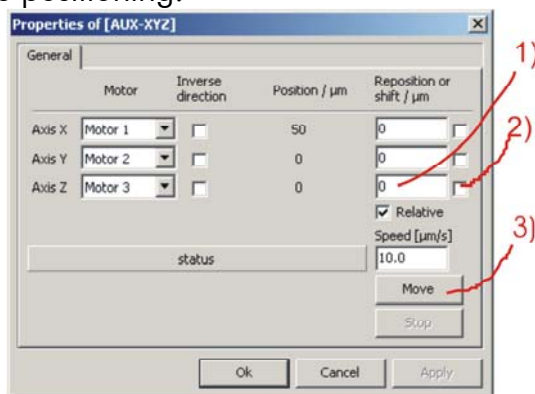


During the first start of the software, you need to tell SECMx at which COM-Port the Märzhäuser positioning system is attached. Select from the menu **Hardware/Setup Port connectivities**. If you have connected the Corvus controll box to COM1 select in the drop down list for COM1 "Märzhäuser". This information is stored in the devices.ini file. It means that this setting must be made for each device\_\*\*.ini file one time.

- 6) Record a cyclic voltammogram in order to test the connections and the quality of the microelectrode. You should choose in IviumSoft the register **Method** and set

the parameters for CV there. You save the result of the measurement as an Ivium data file (\*.idf). [You can also run a CV from the SECMx software, but due to the communication overhead, possibilities are more limited]

- 7) Go back to the SECMx control. Select in the menu **Hardware/Setup devices**. Select Ivium and press properties. In the setup window of the Ivium device, set the potential of the microelectrode to a potential where a diffusion-controlled reaction occurs at the microelectrode. Press **Apply**, **Ok** and **Close** the device selection window.
- 8) Position the tip coarsely with the **Hardware/Move motors**. Pay attention to absolute and relative positioning.

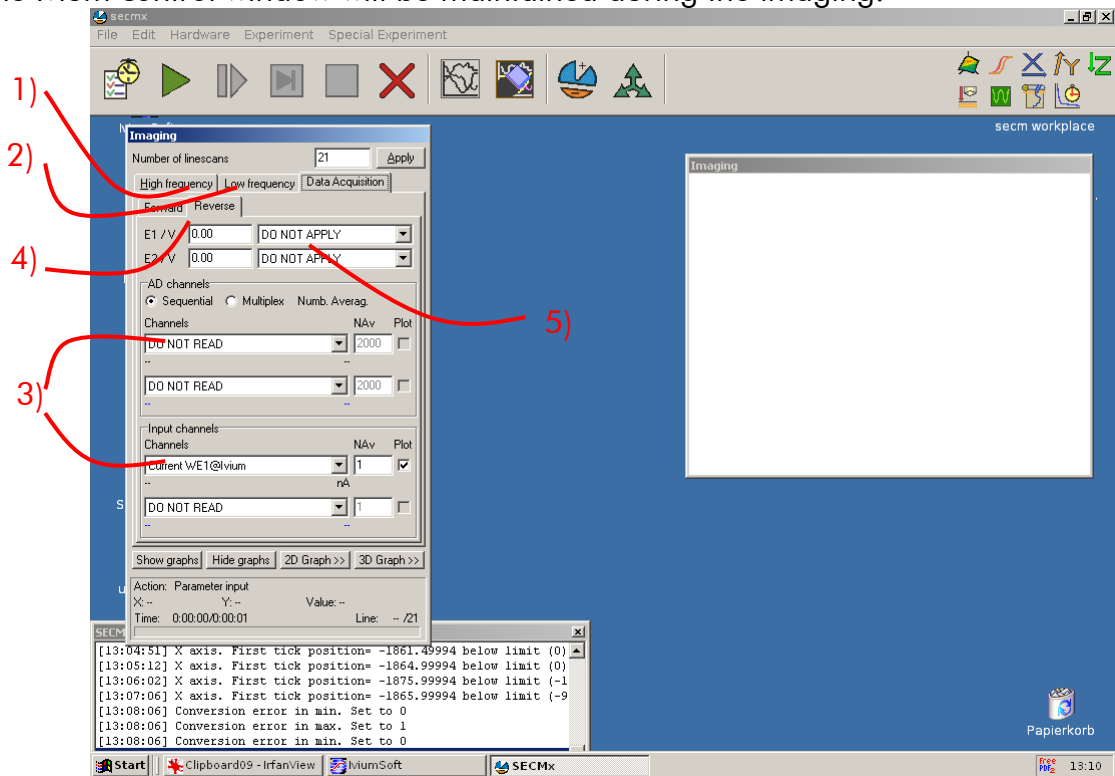


- 9) Select **Experiment/Z Line Scan** and approach the microelectrode to the surface, Interrupt the scan, if the microelectrode touches the surface and retract to the desired distance. Note, that approaching the electrode is the most difficult part of SECM experiments. Depending on the sample, different ways have to be chosen. The detailed explanation of all options is behind the scope of this manual. You must select one motor and at least one data channel. Typically this will be **Current WE1@Ivium**. The value for **Number of averaging** should be set to **1** (when reading IviumSoft!!!!). If you only read AD channels you may send it to a calibrated value (typically ca. 2000). [Alternatively you may use the routine Fast Approach. It moves the electrode until a preset ratio between the initial current and the present current is reached. If you approach an insulator this ratio could be 0.5, for approaching a conductor it could be 2. The routine is faster than the way described above but requires more understanding of the sample. See Section 2.6]

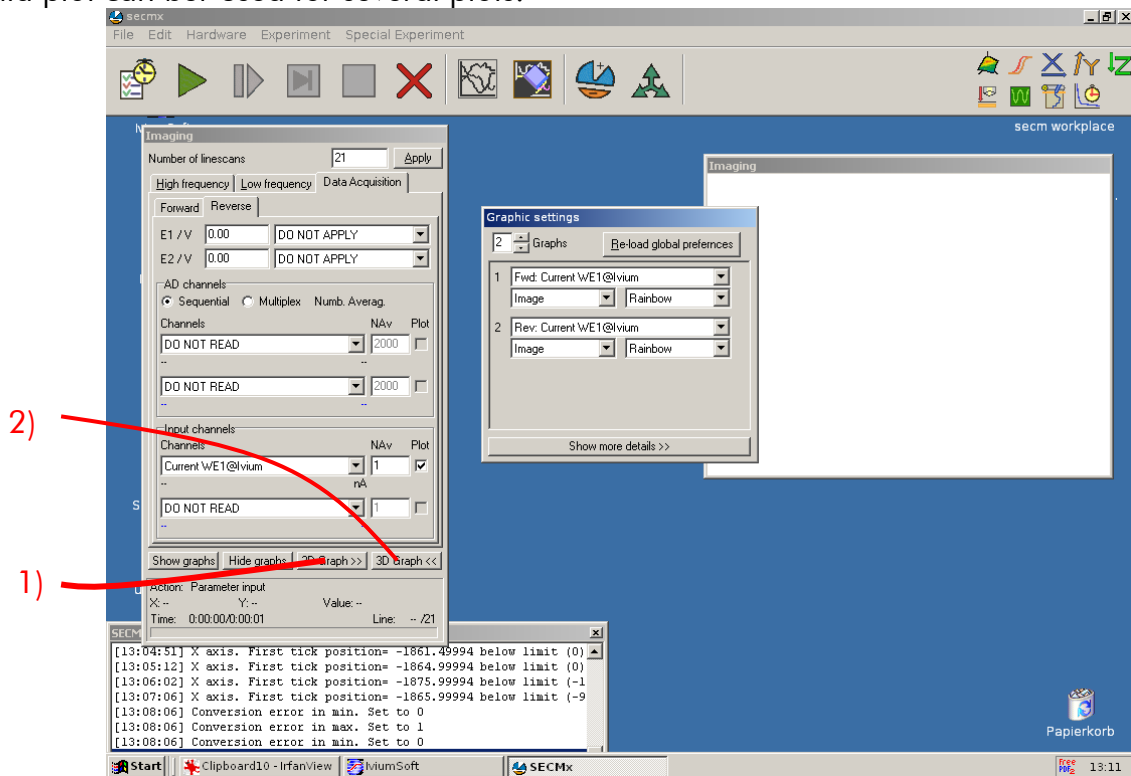
- 10) Test with a horizontal line scan **Experiment/X Line Scan** or **Experiment/Y Line Scan** whether you see the portion of the sample you are interested in.

- 11) Select imaging. Set the parameters for the forward and back ward scans (1). Set the parameters for the steps in the low frequency axis (2). The channels that can read are controlled by the channel selection drop down (3) boxes separately for forward and reverse scan direction (4). You can apply different potentials during the forward and backward scans via the output option (5). You can also use the output for triggering events like switching on light etc. If you do not want that output of any kind is done during imaging, set the selection box to **DO NOT**

**APPLY.** In this case all the settings, that were made before the start of the image in the Ivium control window will be maintained during the imaging.



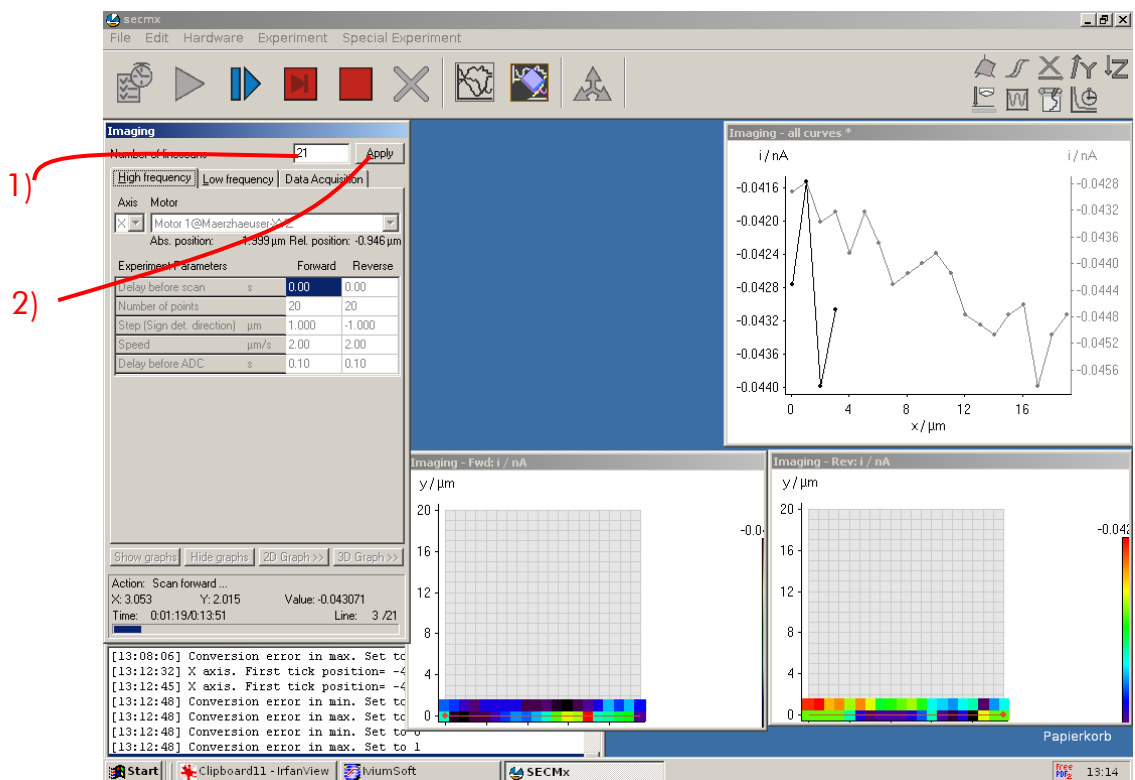
The settings for the graphics are accessible via the buttons **2D Graph>>** (1) and **3D Graph>>** (2). You can select how many 3D plots you want to generate. One data plot can be used for several plots.



## 2.3 Editing parameters during an imaging experiment

Most parameters cannot be edited while an experiment is running. An important exception is the number of line scans during Imaging. This is convenient because only during imaging it becomes obvious that more line scans are needed to capture an entire feature on the sample. When the image is running, the size of the low frequency axis window can be changed (reduced or increased). After editing the number of line scans (1) press **Apply** (2). Graphs and time calculation will be updated after the current line scan.

The number of scans can always be increased and it can also be decreased to the number of the currently running line scan.



## 2.4 Some hardware considerations

In order to make most out of the instrument it is now important to understand a bit more about the hardware and its communication with the computer. The software distinguishes between channels and devices. Devices are typically identical with a hardware device, typically a box filled with electronic compartments. Each device has one or more channel. Channels are data lines over which the PC transfers data to and from an experiment or causes an action. There are several types of channels: motors, channels from which the PC receives information (read channels) and channels over which the PC influences the experiments, e.g. by setting a potential (write channels). There are two fundamentally different ways for the operation of read and write channels. Either the signal to the external device (e.g. a potentiostat) is converted to an analog voltage by a digital-analog (DA) conversion board (DAS 1602) and the potentiostat is then applying that voltage. A current measured at the analog potentiostat can be converted to an analog voltage and this voltage is then read by

analog-digital (AD) converted board (DAS 1602). The software handles this way after selecting the corresponding AD and DA channels and setting the connections between AD and DA channels and external analog devices via **Hardware/Setup AD/DA connectivity**.

Many modern potentiostats communicate with the computer via USB, RS232 or other digital data connections. Typically these devices contain an own microprocessor. The Program on the PC loads methods into this microprocessor. The microprocessor carries out the measurement. The PC only handles data storage and interface to the user. The Ivium potentiostat is such an device. In SECMx the read channels of such devices are called In channels, the write channels are called Out channels. (There might be also devices that contain digital and analog channels and may be interfaced in either way.)

The distinction between the two types of communication is important for a good noise reduction. AD and In channels require a different treatment in this respect. Therefore you will find separate selection boxes for AD and In channels at all places where signals are to be read. Where data must be written from the PC to external devices you may find alternatively selection tools for DA and Out channels (CV and CA) or all possible write channels are listed in one box (Imaging).

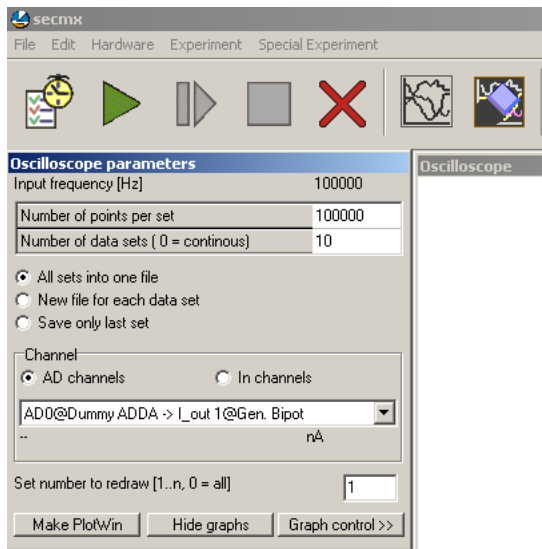
Noise reduction:

The main noise component is typically the line frequency (50 Hz in Europe). One period of this frequency is 20 ms. If the current is integrated over one period of the noise frequency, it almost completely cancelled. For AD channels it means that one has to know the number of AD conversion a AD channel can make at maximum speed within 20 ms. For an AD card with 100 000 kHz frequency, this value would be **NAv** = 2000. Unfortunately, these numbers are not so exact and may depend on the particular PC or version of SECMx. Therefore it is strongly recommended to calibrate the number (see Section 2.5). The obtained number should be used throughout SECMx for **NAv** of the AD channels. The data should be read by the option **Sequential**, i.e. first all averaging is done from one channel, then from the second and so forth. **Multiplexing** means that reading cycles between all AD channels to read. This reduces the time offset between data points if more channels are read. Because the multiplexer used in the DAS 1602 is much slower than the AD conversion rate, a suitable **NAv** must be determined separately. It is not even similar to the value for **Sequential!!!!**

Devices with own microprocessors (such as IVIUM) perform these operation independently and typically each data value delivered is already a result of a signal integration. Therefore, further signal averaging does not make sense and the **NAv** parameter should be left at 1.

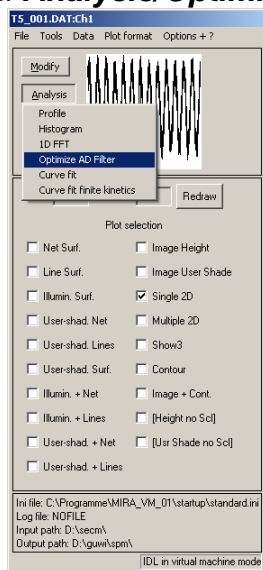
## 2.5 Calibration of **NAv** (only for systems with AD/DA board)

- 1) Start the oscilloscope. Collect 10 data sets each with 100.000 data points. Select a AD channel connected to the instrument you are interested in.

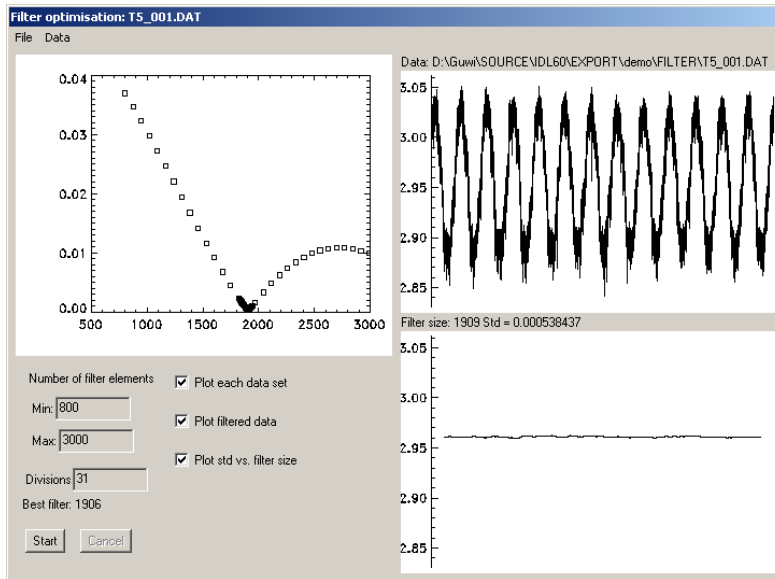


Hint you should save the data as binary. Otherwise saving may take very long!! Settings can be made under **Edit/Preferences/Experimental**.

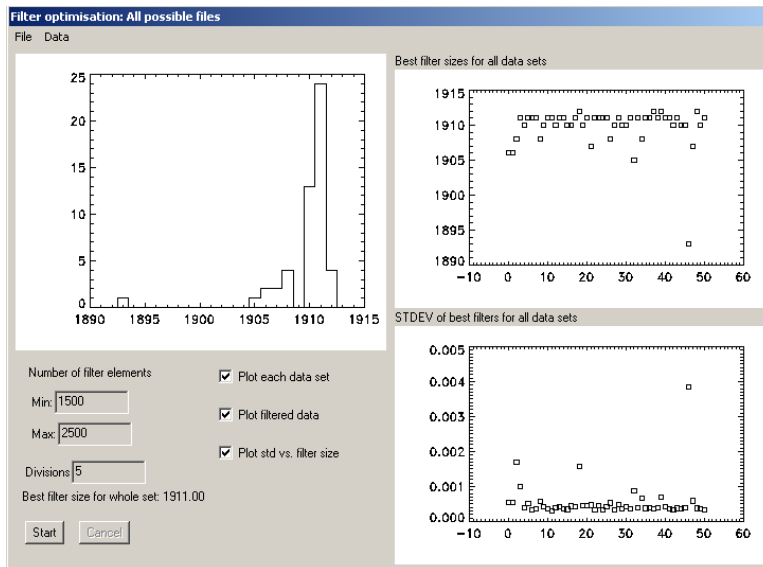
- 2) Start MIRA.
- 3) Load the oscilloscope data set into MIRA (Multiplot should open, click on one data set).
- 4) Select **Analysis/Optimize AD filter**.



- 5) Make the following settings and press start. As the smoothing is calculated, you should see how the smoothing passes through a minimum. The setup is optimized until the best size of the filter is determined. In this particular case it is 1906.

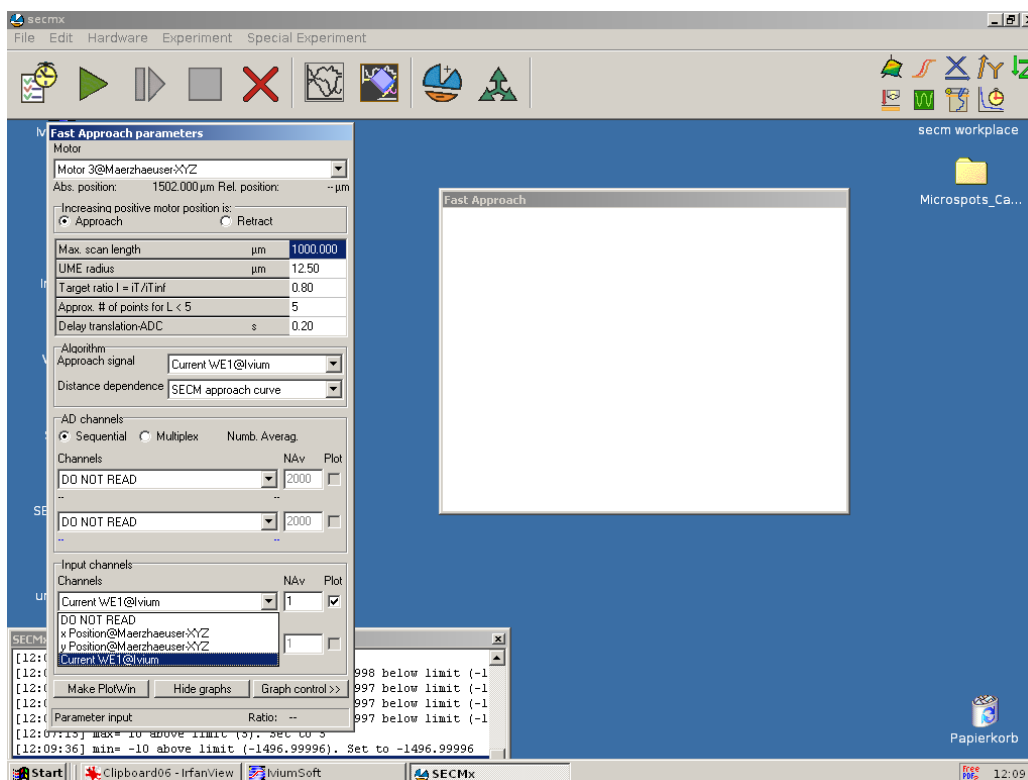


You may want to repeat the procedure with other data sets and make an average of them. This can be done by loading all data sets into the Multiplot window of MIRA. (If you have saved all data sets from step 1 in one binary file, this will automatically be the case.) Then start **Analysis/Optimize AD filter** from the Multiplot window. In this case all loaded data sets will be treated and a summary will be generated.



## 2.6 Operation of Fast Approach as an example of a 2D experiment

The Fast approach is explained as an example of 2D experiment. It serves for fast positioning of the probe close to the surface. The movement is slowed down the closer the probe comes to the target position. It is NOT suitable for recording SECM approach curves for kinetic analysis of the sample.



The picture provides an overview for parameters for approaching an impermeable insulator (e.g. a microscope slide). Depending on the mounting of the z motor and increasing z coordinate may mean approach or retract of the probe (here approach).

The next field set the maximum scan length allowed if no surface is detected.

The UME radius is required to predict the next data point and to slow down the movement appropriately close to the target.

The target ratio is the measured current relative to the current in the bulk solution. In order to measure the current in the bulk the probe retracts and then moves forward. The target ratio must be selected according to the sample type (for conductor  $> 1$ ) for insulator  $< 1$ ). It is recommended to use this routine above sample with either completing inert insulating behavior or with very fast kinetics (bare noble metal).

Approximate number of steps for  $L < 5$ , determines how strong the movement is slowed down close to the surface.

Delay before ADC occurs in each method. In order to allow currents through the motors to decay before a current value is measured it is advisable to have a delay. The



longer the delay, the longer takes the experiment (particular important in imaging). Therefore, exploring the effect of this parameter is important.

The you select the signal for which the target ratio shall be measured.

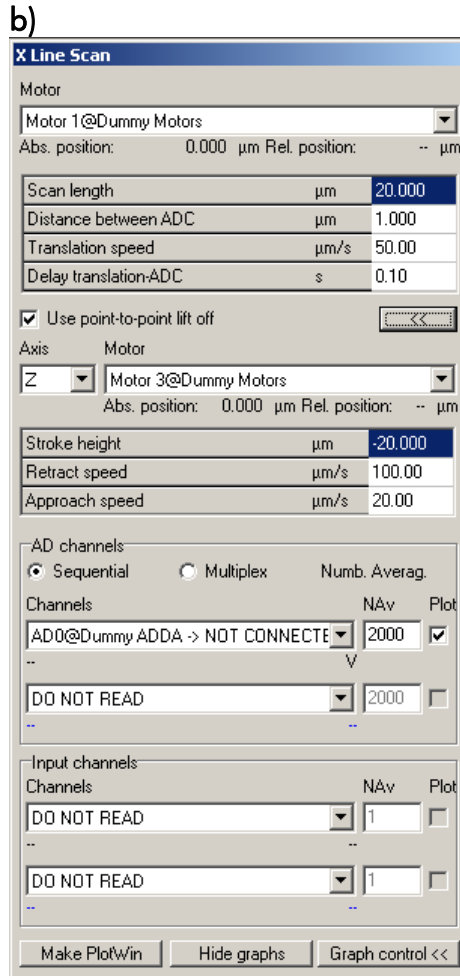
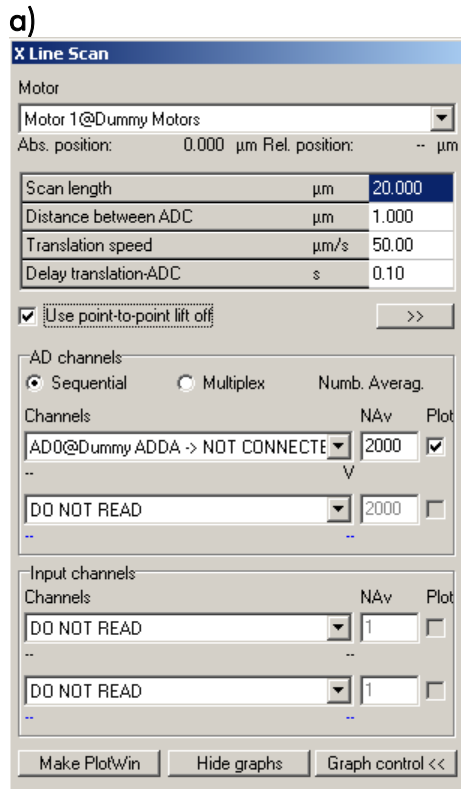
Distance dependence currently contains only the SECM approach curves. For the future potentially different distance dependences could be used to predict the probe movement.

Then you select the AD channels and the In channels to be measured. All measured channels become available for selection as approach channel. You must have selected at least one channel to be measured and you have to have a signal channel for the approach signal.

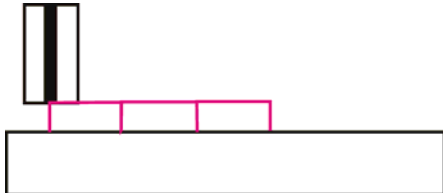
After start the probe is first retracted to measure the current in the bulk. It then moves forward with steps equal to the electrode radius. If the surface is sensed by a change of the current, the step size is decreased. Usually the probe shoots behind the target and is than slowly retracted and kept on the target value.

## 2.7 *Lift-off mode for line scans and imaging*

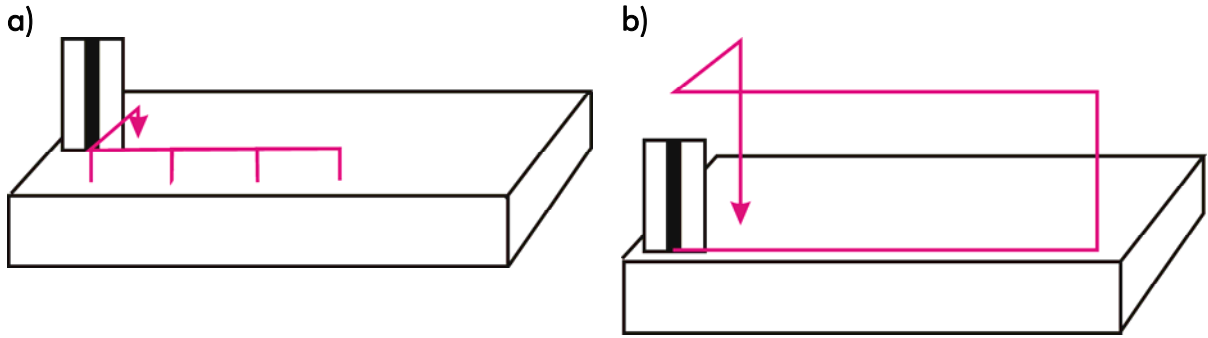
The lift-off mode provides a way to retract the probe between two measurement points. This can be good for using probes that mechanically touch the sample. In the line scans experiments and images you can check the lift of option and than expand a table to specify the **retract motor** to set the **lift of distance**, the **retract speed** and **approach speed**.



The line lift-off makes a retract and re-approach for each measured point



For images there are two options for the lift off. Technically both can be combined, but at the moment that does not seem to make much sense. The point-to-point lift-off mode (a) approaches the surface between each point. The line lift-off (b) does not change the height during the line scan within one images, but increases the working distances during the backward scan. In both modes the step in the low frequency direction is always done at elevated distance.



## 2.8 Four-dimensional measurements (4D, Volume scans)

In 4D experiments the probes takes the same way as during in images (including the options of lif-off). At each point of the grid a complete 2D experiment (CV, chronoamperometry) is performed instead of reading a value of the input channels. The parameters of the dependent experiments can specified in a separate parameters window. The background color of this window is gray in the figure below and can be customized under **Edit/Preferences**.

Parameter for 2D scans

Parameter for dependent experiment

SECMx Application Error Log

```
[20:55:36] Conversion error in max. Set to 1
[20:55:36] Conversion error in min. Set to 0
```

The same color scheme is used to distinguish the graphic windows that refer to the 2D scanning and the individual 2D experiments at each grid point. The image is

reconstructed from a specified parameters of the 2D experiment (average, min, max, ...). This mode can be used to perform redox competition mode or surface modifications.

### 3 Operation with the shear force distance control

The operation of the shear force mode follows closely a paper by Schuhmann et al. which should be cited. We received very detailed information on the Piezo electrode shear force detection. Only the use of the Anfatec controller in connection with the actuators from Physikinstrumente is a new "development" of the Wittstock group. It has the advantage, that the SECM control computer is freed from the task of making the evaluation for the electronic feedback and that the shear-force works completely independent from the SECM main program.

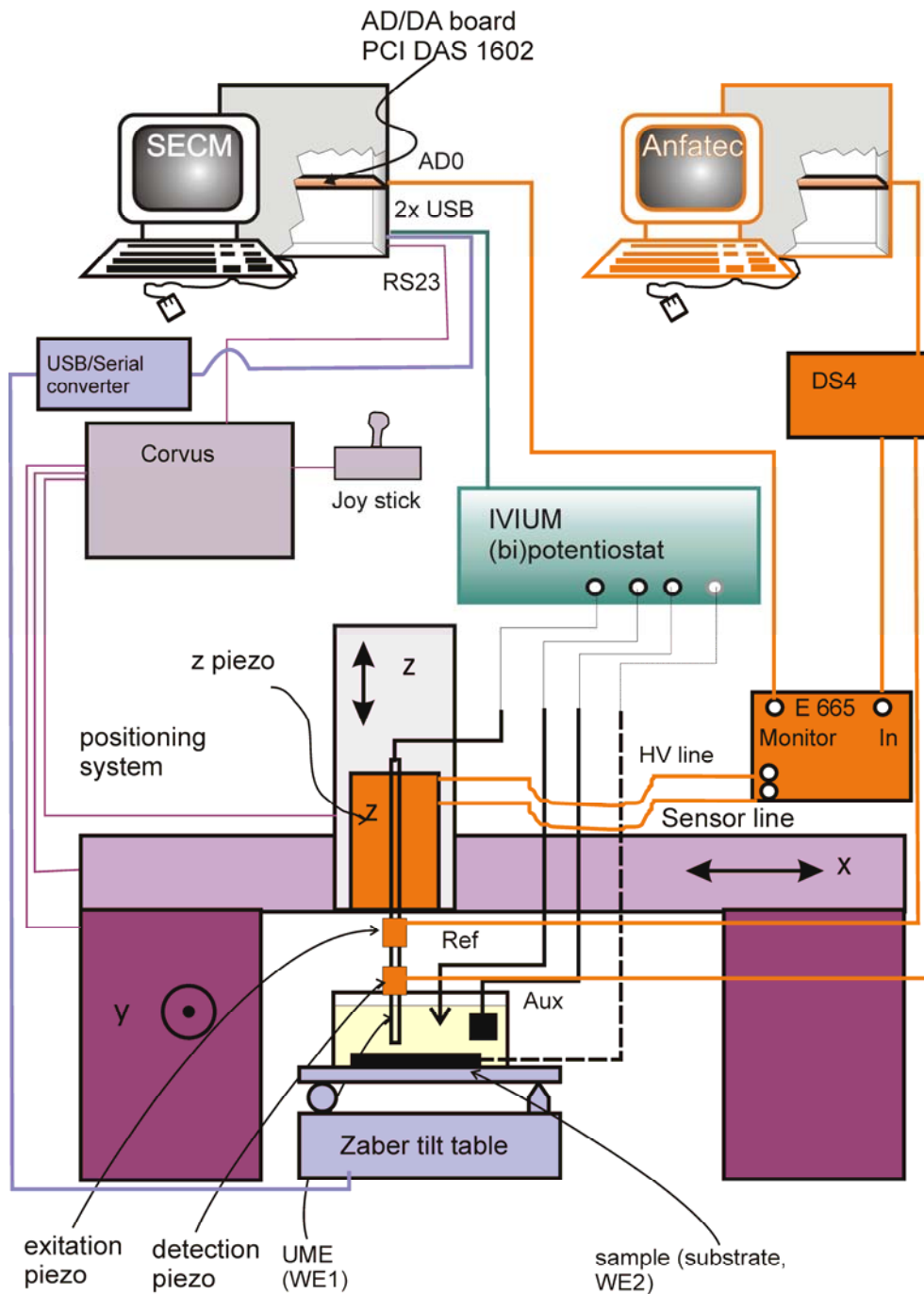
References:

B. Ballesteros Katemann, A. Schulte, W. Schuhmann; Constant-distance mode scanning electrochemical microscopy. Part II: High-resolution SECM imaging employing Pt nanoelectrodes as miniaturized scanning probes. *Electroanalysis* **2004**, *16*, 60-65.

B. Ballesteros Katemann, A. Schulte, W. Schuhmann; Constant-distance mode scanning electrochemical microscopy (SECM)-part I: Adaptation of a non-optical shear-force-based positioning mode for SECM tips. *Chem. Eur. J.* **2003**, *9*, 2025-2033.

For the operation in the shear force mode connect the instruments in the following way.

- a) Perform steps (1) to (8) from section 2. In addition select that **Position@PI-E665** is connected to **AD0@DAS1602/16** (in **Hardware/Setup AD/DA connections**).
- b) Record a vibration spectrum of the pulled microelectrode about 1 mm above the sample.
- c) Record an approach curve (Experiment/Z Line Scan) and read the current Current WE1 (not connected):  $I_{vium}$
- d) Record another vibration spectrum with the tip within 1 micrometer of the surface. Overlay the two vibration spectra and select the excitation frequency at which the highest difference in amplitude or phase is observed.
- e) Retract the microelectrode about 100  $\mu\text{m}$  from the surface.
- f) Give a setpoint. This is the ratio of the amplitude far away from the surface and close to the surface. The change in the signal may be very small (only 2 % giving a setpoint of 98 % for instance). After setting the setpoint, the piezo should expand towards the surface up to the maximum position. Since the sample is not reached it will stay at far most extension.



- g) Now perform a **Experiment/Z Line Scan**. Once the microelectrode comes close to the surface, you should see how the piezo retracts while the motor of the Märzhäuser system drives the microelectrode towards the surface. This is displayed on the screen of the Anfatec PID controller. If the piezo position is about in the middle of the piezo movement range, stop the movement of the Märzhäuser z motor. Now perform horizontal line scans with the spacing and speed you would use for imaging and optimize speed and PID settings. This requires experience and no clear rule can be given.
- h) You can perform imaging and read **Current WE1@Ivium** (= reactivity) and **AD0@DAS1602/16** (= topography).