

Manual SECMx, version 14

Part II: Operational procedures

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1 Standard setup (without using the shear-force distance control)

The hardware and software should first be installed as described in the instruction. 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.

1.1 Using one UME as probe

1.1.1 Setup

The setup is illustrated with a Märzhäuser positioning system, an Ivium Compactstat, and a Zaber tilt table. For the use of other positioning systems and potentiostats proceed in a similar way.



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

1.1.2 Step by Step to an Image

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

😹 IviumStat Corcrol	
File Options Tools Help About	
Connect Not connecte Eovi Iovi Ext 1m4	Basic SigView
Direct Method	Result graph Result data E scan
DC AC IRcorr HiSens Zstat	2D 3D Scale - View -
E = -0.001V I = -0.001uA	2)
Current range Connect	0.10

- 2) Start the SECMx software, select the appropriate user profile.
- 3) If during the loading process the window of the lvium 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 lviumSoft should be WE1 (in most cases this will be the microelectrode). For more details see the manual of the lvium CompactStat.



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

	🐺 Properties of [lvium]
	Connect 🔽 Potstat 🔲 Methods 📄 External 🔲 Cancel
	Start IviumSoft before any other action
1)	Make sure ONE instance of IviumSoft is running. Press in IviumSoft [Connect] button (top, left of window). Frees in SECMs: Ivium driver [Connect to IviumSoft and IviumStat]. 4) Cick [Cell On] / [Cell Off] until IviumSoft and SECMx are in same status. 5) Select the cell type, press [Apply] in SECMx: Ivium driver.
	Connect to IviumSoft and IviumStat Serial number:
	Cell Estat 4: potentiostat with 4 electrode 🔽 Standard 💌
	Cell On Cell Off
	WE1 Potential / V 0.000
	Range 100 µA 💌
2)	Carrent / A
-,	IStat Current / A U.UUUUE+U Press [Apply] to make effective.

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 lviumSoft somehow visible on the screen. SECMx main window will occupy the entire upper range of the screen.

eermx File Edit Hardware Experiment Special Experiment	X
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MumSoft	secm workplace
MIRA	ViumStat Control
	Connect not connecte Ecv/Tov/ Ext 1r
Instacal	Direct Method
	DC AC IRcorr HiSens Zstat
	E = -0.001V = -0.001uA
Winpos	Current range Connect
4	C 1A
SECMx	C 100mA C 10mA standard stability
	C 1mA C 100uA
	C 10uA Apply 0.000 V
SECMx_11	C 10.4 Set MUX channel
RT 1	InA Section endines 12
	C 100pA C 10pA
	C 1pA
SECMX Application Error Log X	
[17:17:45] CHI-701 loaded, index = 5, channels = 3 [17:17:45] Maerzhaeuser-XTZ: initialise() called with indexComHW=1	
[17:17:50] Maerzhaeuser-XYZ: successful initialized.	
[17:17:50] Please check configuration ini files, device c [17:17:51] Ivium: Device not enabled.	Papierkorb
Start SitumSoft	Free 17:18

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 devices_xxx.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 lvium 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 lvium and press properties. In the setup window of the lvium 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. 1724). [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 1.6]
- 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 lvium control window will be maintained during the imaging.

Siectmx File Edit Hardware Experiment Special Experiment	<u>- @ × </u>
	<i>魚」</i> ▲ ♪ ↓2 ピ Ⅲ 賃 煌
2) Imaging Number of Inescans 21 Apply High frequency Law frequency Data Acquisiton Enverta Reverse E1 / y 0.00 DO NOT APPLY E2 / 0.00 DO NOT APP	secm workplace
S DO NOT READ Show graphs Hide graphs 2D Graph>>> 3D Graph>>> Acton. Parameter input X Y:- Value:- Time 00:000/00:00:01 Line: -/21 [13:04:51] X axis. First tick position= -1861.49994 below limit (0) [13:05:12] X axis. First tick position= -1864.99994 below limit (0) [13:05:02] X axis. First tick position= -1864.99994 below limit (-1) [13:05:02] X axis. First tick position= -1875.99994 below limit (-1) [13:06:02] X axis. First tick position= -1875.99994 below limit (-1) [13:06:06] Conversion error in max. Set to 0 [13:08:06] Conversion error in max. Set to 1 [13:08:06] Conversion error in max. Se	Papierkorb 13:10

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.



1.1.3 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.



The movement follows a comb-like movement. The reverse scan retraces the forward scan. In this way two images can be recorded that should be directly comparable. Often there is a small offset between forward and reverse scans depending on imaging mode, scan rate and working distance.



The use of Meander scans is explained in connection with 4D experiments.

The meander scan should not be used for normal imaging experiments, because there is usually a small offset between forward and reverse scans.

1.2 Using a bundle of UMEs

1.2.1 Setup

The routines are bdescribed for a setup with a Märzhäuser positioning system and an Ivium CompactStat with an WE32 extension.



1.2.2 Step by Step to an Image

- 1) 2) See 2.1.2.
- 3) If during the loading process the window of the lvium driver pops up, press *Connect*. (1). Select the cell type you need (2).

	🍀 Properties of [Ivium multipot. WE32]											
	Line Potential offset X offset Y offset i offset Scale factor											
	✓ Connect ✓ Potstat Methods <u>Ok</u> <u>Cancel</u>	Select Current	effective Offset potential potential	New Display offset [V] in IVSc	v xoffset yoffset ift	ioffset Scale corr. [1.0 = no corr]						
		□ 0 … A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Start MumSoft before any other action	□ 1 …A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	1) Make sure ONE instance of lviumSoft is running. 2) Press in luir mSoft (Connect) button (top, left of window)	□ 2 ···A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	 Ress in twansor, Connect, Datan (op), etcal window). Slect in IviumSoft: Tab Direct, Option Histers In twinsort and Environment Environment Interview. (2019) 	□ 3 ··· A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	 a) In Multisof the options/option, parely Evidential Context, and William States and S	□ 4 ··· A		0.000	0.0000 0.0000	0.0000 1.0000						
1)	 Click [Leii On] / [Leii Ori] undi Mumsor and SELMX are in same status. Select the cell type, press [Apply] in SECMX::IviumWe32 driver. 		···· V ···· V									
	Connect to lyiumSoft and lyiumStat Serial number: R09006		VV		0.0000 0.0000							
2)			VV									
	Cell Estat 4: potentiostat with 4 electrode Standard	□ 9 ···A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Cell Estat 4: potentiostat with 4 electrodes	10 A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	WE1	🗖 11 A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Potential / V 0.000	🗖 12 A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Range 1100 pA	🗖 13 A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Current / µA	🗖 14 A	VV	0.000	0.0000 0.0000	0.0000 1.0000						
	Press [Apply] to make effective.	🗖 15 A	VV	0.000 C	0.0000 0.0000	0.0000 1.0000						
	Measured E 7 V Apply			Set	Set	Set						

- 4) If you use an array of microelectrodes you have to check in column Select line which lvium channels/lines you have connected to the channels of the microelectrode array (1). Please note that the channel numbering of SECMx is from 0 to 31 in contrast to lvium MultiWE32 (from 1 to 32!). Example: Channel/Line 0 in SECMx means channel 1 in lvium MultiWE32 and channel/line 23 in SECMx means channel 24 in lvium MultiWE32. The tips of the array may have positional offsets on the sample and differences in electrochemical response (for instance due to slight variations in their size or working distance):
 - x position offset (2) (x offset, x offset[i] = 0 means the *i*-th electrode has the same x coordinate as electrode[0]),
 - y position offset (3) (y offset, y offset[i] = 0 means that electrode i has the same y coordinate as electrode[0]),
 - current offset (4) (*i* offset, *i* offset[*i*] = 0 means that no offset is applied to the values coming from sensor *i*),
 - correction factor of the sensitivity (scale factor) (5) (Scale corr., Scale corr.[i] = 1.0 means no correction is applied for electrode *i*).

Only the original measured data are shown in SECMx and are saved in the files! The correction values are written additionally in the saved data files. The saved data files are treated in MIRA afterwards. In MIRA the original measured values are corrected then with the offsets and scale factors. It is easily possible and intended to change the offsets and scale factors in SECMx via *Hardware/Setup Devices* and afterwards do fine tuning of the correction values in MIRA. Please read also the MIRA manual. After entering the offsets and scale corrections click the corresponding **Set** buttons (6). Now switch on the electrochemical cell (7). Check that the corresponding option control in IviumSoft and the red LED at the CompactStat will also switch on. Then select the current range (8). Enter the potential (9) and select the filter (10). Press *Apply* and then *Ok*.

1)				2)	3)	4)	5)	
💐 Properties of [Ivium multipot. WE32]				1					
Line Potential offset X offset Y offset i offset Scale factor				- 1					
✓ Connect ✓ Pot-stat ✓ Methods □k □ancel □	Select Current	effective Offset potential potential	New offset [V]	Display in IVSof	x offset	y offset	i offset	Scale co [1.0 = no	orr. o corr]
	🔽 0 25.552 μΑ	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	1
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1) Make sure ONE instance of IviumSoft is running.	🔽 2 25.864 μA	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
[2] Press in IviumSoft [Connect] button (top, left of window). [3] Slect in IviumSoft: Tab Direct, Option HiSens	🔽 3 25.708 μA	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
4) In IviumSoft meu Options/Option, panel Environment: check "MultiWE32" 5) Press in SECMy: IviumWa32 driver (Connect to IviumSoft and IviumStat).	🔽 4 25.864 μΑ	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
6) Click [Cell On] / [Cell Off] until IviumSoft and SECMx are in same status.	🔽 5 25.864 μA	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
[7] Select the cell type, press [Apply] in SELMX: I viumWe32 driver.	🔽 6 25.708 μA	0.500 V 0.000 V	0.000	С	0.000	0.000	0.000	1.000	
Connect to IviumSoft and IviumStat Serial number: B09006	🔽 7 25.708 μΑ	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
	🗖 8 25.708 μA	0.500 V 0.000 V	0.000	C	0.000	0.000	0.000	1.000	
Cell Estar 4: porentiostat with 4 electroot	🖵 9 25.552 μA	0.500 V 0.000 V	0.000	С	0.000	0.000	0.000	1.000	
Cell On Cell Off 1 kHz tilter	🗖 10 25.708 μA	0.500 V 0.000 V	0.000	С	0.000	0.000	0.000	1.000	
WE1	🗂 11 25.864 μA	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	
Potential / V	T 12 25.552 μA	0.500 V 0.000 V	0.000	C	0.000	0.000	0.000	1.000	
Range 10 µA	🗂 13 25.864 μA	0.500 V 0.000 V	0.000	С	0.000	0.000	0.000	1.000	
Current / µA 2.5552E+1	T 14 25.864 μA	0.500 V 0.000 V	0.000	С	0.000	0.000	0.000	1.000	
iStat Curren / A	15 25.708 μΑ	0.500 V 0.000 V	0.000	0	0.000	0.000	0.000	1.000	-
Measured /V Apply			Set		S	et		Set	
7) 8) 9)	10)					6			

- 5) 8) See 2.1.2.
- 9) See 2.1.2. Note that you have to select Bundle Experiment/Z Scan Bundle and the correct data channel. For bundle experiments with lvium MultiWE32 two different measuring modes can be used. Sequential means that all active channels are measured one after the other each in 20 ms (noise reducing but time consuming). Multiplex means that all (always all 32!) channels are measured simultaneously in 100 ms (fast but a bit more noisy), but only the measured data of the channels which are selected in SECMx are stored and saved.
- 10) Test with a horizontal line scan Bundle Experiment/X Scan Bundle or Bundle Experiment/Y Scan Bundle whether you see the portion of the sample you are interested in.
- 11) See 2.1.2. (2D image bundle). You have to pay attention using arrays of microelectrodes with respect to LF axis! If the LF scan length is larger then the electrode to electrode distance you will scan some areas of the sample double. This means that the first channel of the array will measure areas which the second channel of the electrode has already scanned within its first scans. This doesn't make sense and you should avoid this situation. The following illustration will help you to understand the meaning of Number of linescans (NOFS) (1) and Low frequency Step (LFS) (2). The first linescan (HF forward scan) of the image is done at the start position. Before each following linescan the Low frequency Step is done. The LF scan length (LFSL) is then calculated by LFSL = (NOLS 1) * LFS and has to be shorter than the electrode to electrode distance (ETED, y Offset) of the array:

(NOLS - 1) * LFS = LFSL < ETED

Example 1:

Electrode to electrode distance of the array, $ETED = 500 \ \mu m$. Low Frequency Step, $LFS = 25 \ \mu m$. Number of linescans, NOLS = 20.

$$=>$$
 (20 – 1) * 25 µm = 475 µm < 500 µm

This is ok!



Example 2: Electrode to electrode distance of the array, $ETED = 200 \ \mu m$. Low Frequency Step, $LFS = 30 \ \mu m$. Number of linescans, NOLS = 8.

 $= > (8 - 1) * 30 \ \mu m = 210 \ \mu m > 200 \ \mu m$

This doesn't make sense! The last linescan of the first channel scans the area which the second channel already has scanned!



Start position 1st electrode channel

In example 2 you should reduce the number of linescans to 7 because then $(7 - 1) * 30 \ \mu m = 180 \ \mu m$ is scanned with each electrode which is less than the electrode to electrode distance of 200 $\ \mu m$.

12)If you want to scan areas which are in LF axis larger than the number of array electrodes with electrode to electrode distances provides then you can select **Bundle Experiment/2D image bundle with large increment step.** You can enter a number of images (1) and a LF large step (2). These images are then made one directly after the other during this experiment. In MIRA these images are merged together to one image. For each single image HF parameters and LF parameters (here Standard step, (3)) are equal to the ones in the 2D image experiment. It is possible to select different motors for standard and large step (explanation will follow in next SECMx manual version). If you use only one motor for LF axis select for standard and large step the same motor (4).



A detailed description of the parameters for standard step and large step are shown in the following figures:



b) Image with explanation:



1.3 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 o the sample.

Seconx File Edit Hardware Experiment Special Experiment	_ @ ×
	☆ ♪ ≿ î γ ! z ⊵ ⊠ ॏ @
Motor Motor Motor 3@Maerzhaeuser:YYZ Abs. position: 1502.000 µm Rel. position:	secm workplace
Increasing positive motor position is:	Microspots_Ca
Max. scan length μm 1000.000 UNE radius μm 12.50	
Target ratio I = ii/ATimi 0.80 Approx. # of points for L < 5	
Lelay translation-ADC s U.20 Algorithm Approach signal Current WE1@Ivium Distance dependence SECM approach curve	
AD channels © Sequential © Multiplex Numb. Averag. Channels NAv Plot	
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Current WE108/num 1 1 V DO NOT FEAD x Position@Mastrbacuser%/2 T T X	
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Description Description Description [12:1] Parameter input Ratio:	Papierkorb
Start Clipboard06 - IrfanView StumSoft	Free 12:09

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 top 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.

1.4 Lift-off mode for line scans and imaging

The lift-off mode provides a way to retract the probe between two measurements 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**.

(Line Scan		
Motor		
Motor 1@Dummy Motors		•
Abs. position: 0.000 μm Rel	. position:	μm
Scan length	μm	20.000
Distance between ADC	μm	1.000
Translation speed	µm∕s	50.00
Delay translation-ADC	s	0.10
Use point-to-point lift off		>>
AD channels © Sequential O Multiplex	Numb.	Averag.
JADU@Dummy ADDA -> NUT CUNN 	ECTE V	2000
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-	- '	
Input channels		
Channels	1	NAV Plot
DO NOT READ	•	1
DO NOT READ	-	1
-		
	1	
Make PlotWin Hide graphs	Graph	n control <<

X Line Scan Motor Motor 1@Dummy Motors Abs. position: 0.000 µm Rel. position: µm Scan length µm 20.000 Distance between ADC µm 1.000 Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off Axis Motor Z ✓ Motor 3@Dummy Motors ✓ Abs. position: 0.000 µm Rel. position: µm Stroke height µm 20.000 Retract speed µm/s 100.00 Approach speed µm/s 20.00 AD channels ⓒ Sequential ⓒ Multiplex Numb. Averag. Channels ⓒ Sequential ⓒ Multiplex Numb. Averag. Channels Channels Channels Channels Channels D0 NOT READ I 1 D0 NOT REA	o)		
Motor Motor 1@Dummy Motors Abs. position: 0.000 µm Rel. position: µm Scan length µm 20.000 Distance between ADC µm 1.000 Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off Axis Motor Z Motor 3@Dummy Motors v Abs. position: 0.000 µm Rel. position: µm Stroke height µm 20.000 Retract speed µm/s 100.00 Approach speed µm/s 100.00 Approach speed µm/s 20.00 AD channels ⓒ Sequential ⓒ Multiplex Numb. Averag. Channels NAv Plot AD0@Dummy ADDA -> NOT CONNECTE 2000 ♥ V DO NOT READ 2000 ♥ Input channels Channels NAv Plot DO NOT READ 1 1	X Line Scan		
Motor 1@Dummy Motors ✓ Abs. position: 0.000 µm Rel. position: µm Scan length µm 20.000 Distance between ADC µm 1.000 Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off	Motor		
Abs. position: 0.000 µm Rel. position: µm Scan length µm 20.000 Distance between ADC µm 1.000 Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off Axis Motor Z Motor 3@Dummy Motors Abs. position: 0.000 µm Rel. position: µm Stroke height µm 20.000 Retract speed µm/s 100.00 Approach speed µm/s 20.00 AD channels Channels Channels Channels Channels Channels Channels NAv Plot D0 NOT READ 1 D0 NOT READ 1 D0 NOT READ 1	Motor 1@Dummy Motors		•
Scan length μm 20.000 Distance between ADC μm 1.000 Translation speed μm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off	Abs. position: 0.000 µm Rel.	position:	μm
Distance between ADC µm 1.000 Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off	Scan length	μm	20.000
Translation speed µm/s 50.00 Delay translation-ADC s 0.10 ✓ Use point-to-point lift off □ Axis Motor 3@Dummy Motors ▼ Abs. position: 0.000 µm Rel. position: - µm Stroke height µm 20.000 Retract speed µm/s 100.00 Approach speed µm/s 20.00 AD channels O Multiplex Numb. Averag. Channels NAv Plot AD0@Dummy ADDA -> NOT CONNECTE 2000 ✓ V 2000 ✓ V 2000 ✓ DO NOT READ 1 □ DO NOT	Distance between ADC	μm	1.000
Delay translation-ADC s 0.10 ✓ Use point-to-point lift off	Translation speed	µm∕s	50.00
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Make BlotWin Hide graphs Graph control //	Make PlotWin Hide graphs	Grap	h control <<

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.



1.5 Some hardware considerations

1.5.1 Noise reduction by signal averaging

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 lvium potentiostat is such a 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 were 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 conversions 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.

1.5.2 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 an AD channel connected to the instrument you are interested in.

실 secmx						
File Edit Hardware	Experiment	Special B	Experiment			
			×	Þ	T	1
Oscilloscope param	eters				Oscillo	oscope
Input frequency [Hz]			100000			
Number of points per s	set		100000			
Number of data sets (0 = continous]		10			
 All sets into one file New file for each d Save only last set 	ata set					
Channel	O Ir) channels				
AD0@Dummy ADDA	-> I_out 1@G	en. Bipot		-		
-		r	ιA			
Set number to redraw [1n, 0 = all]		1			
Make PlotWin	Hide graphs	Gra	ph control :	»		

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 be 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.



1.6 Generic and hardware-specific experiments

1.6.1 Generic Experiments

Generic experiments are designed to work with any hardware. Hardware-specific experiments require the availability of particular hardware. For instance, a CV can be performed by incrementing the potential of the working electrode in regular intervals through a command from SECMx. This is a generic way of performing the experiment. However, due to the time delay in passing information through an USB connection, the timing accuracy is limited and rather large potential steps may be required even at moderate scan rates. At analog potentiostat driven by a voltage from an DA board (with much faster communication with the PC), this procedure may yield acceptable results at moderate scan rates. Use of such a routine is fine as long as a steady state response is expected (like an ultramicroelectrode cyclic voltammogram).

Many commercial potentiostats offer the possibility of programming the entire CV before the start. The timing and realisation of the signal is performed by an internal microprocessor of the potentiostats and the resulting data are transferred to the PC on which SECMx is running during or after the potential cycle. That is, SECMx is programming the CV on an microprocessor inside the digital potentiostats and picks up the results if the experiment is done. The definition of the CV depends on how a CV is specified by the commercial potentiostats and therefore varies from instrument to instrument.

Here only the definition of the potential program is given for generic experiments. The CV is defined by the start potential, the first vertex potential, the second vertex potential, the final potential, the number of half cycles, the potential step and the scan rate. HALF cycles refer to complete sweep between the two vertex potentials. Before this, a sweep towards the first vertex potential can be added as well as a segment after reaching the vertex potential for the last time. With those parameters, wave forms can be defined very flexibly. Some examples are give below for typical situations.



1.6.2 Special Experiment

Special Experiment routine can be used with a digital (Bi)Potentiostat which can be controlled with its own software, e.g. lvium CompactStat with lviumSoft. An experiment like cyclic voltammetry can be opened and started via SECMx user interface in lviumSoft. Therefore the experiment is completely controlled by lvium. This has several advantages, such as the usage of all device specific parameters, e.g. high scan rates up to kV/s, and additional experiments like impedance spectroscopy. All parameters and measured data can be saved in SECMx format. This offers interesting opportunities for Volume scans (see 2.8).

List of integrated lvium CompactStat experiments (changed 22.10.2010):

- Transients ChronoAmperometry
- CyclicVoltammetry Standard
- Impedance Constant E
- Impedance Constant I
- Impedance PotentialScan
- Impedance CurrentScan

For the Gamry potentiostats the following special Experiments are available

- Cyclic Voltammetry
- Chronoamperometry

1.6.3 Operation with lvium potentiostats

Start IviumSoft before using SECMx! It is strongly recommended to change nothing in Iviumsoft while SECMx is running! Save a method file in IviumSoft in a folder of your choice.

1	Ivium								
File	Options Too	ols Help	About						
l	Load data Save data		Eovil	ovi Ext 1m4	Ad	vanced 💌	SigVie	w BatchMode	
,	Add data				Result	graph Result data	a 🛛 E scan		
l	Load dataset Save dataset			•	Scale	e 🔹 🗌 Analysis	▼ Edit	▼ ZLPhi Rs, Cs Z', Z"	- Y.
	Save Visible Dat	aSet		-	2D				
l	Load method				3D				
	5ave method				3Di			Res	ult
E	Export data as A	SCII					0.10		
E	Export DataSet	asAscii			Zm				
1	Import data as A	ASCII		Unit	Cor		-		
E	Exit								
Т	itle	Scan	1		Aire		1		
E	start		0.000	o V	Ain		-		
+D	ynamicVertexes		Off		ocp				
V	ertex 1		1.000	o V	pre		-		
					Q		0.05		

You should save the method file with "cell after meas: ON". Otherwise the cell will be switched off after one experiment and you have to switch it on again in SECMx via *Hardware/Setup devices* if you want to make SECMx experiments.

Then start SECMx. Special Experiment will only be available if you have loaded and connected the lvium Bipotentiostat correctly in SECMx. Select the menu **Special Experiment/Load Ivium method**. Then load the lvium method by clicking button

Load Ivium method and selecting the *.imf file. A help pdf file will be opened by clicking the button **Open help**. The needed Ivium Special Experiment channels are selected automatically. They are different for different kinds of experiments.

Section									
File Edit Hardwa	are Experiment Special	Experiment							
		X	1	2	A 5	1			
Special Experime For help pleas help button (pr required)	ent Ivium e click df reader Load Iviu	help n method	D D Di	anaiysis Y Edit		Special Experiment Iviur	n		
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Ivium Techniqu Ivium Output Che C DA Channel SpecExp OutChe Ivium Input Chan Channels SpecExp InChan Load Ivium method	ue: © Dut Dhanny annel@tvium Bipot inels inel2@tvium Bipot unel2@tvium Bipot d	els NAV Pic 1 1 17	K In P P P	Recent Desktop Desktop Eigene Dateien	Eigene Datei Arbeitsplatz Netzwerkum; Impedance T Programming SECMxBacku SECMxBacku CVImf guw IBIT Printser	en gebung astMessungen Lsg I pi65July2010 p16August2010 ver			
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Pretreatment	<u>ju</u>	levels			o olonyp.	Times (.mm)		100	

Then click *start*. You can see the plot during the experiment in lviumSoft, not in SECMx. After the experiment has finished you can save it in SECMx and/or in lviumSoft. In the file saved in SECMx all information like the used parameters and so on from the lvium method file are saved as well as the measured values. Loading the experiment in SECMx is not possible!

1.6.4 Operation of Gamry Special experiments

The paramters are set within an Window of SECMx

(Example to be filled)

1.7 Four-dimensional measurements (4D, Volume scans)

1.7.1 Area scan and dependent experiments

In 4D experiments the probes takes the same way as during in images (including the options of lift-off). At each point of the grid a complete 2D experiment (CV, chronoamperometry, z-linescan) is performed instead of reading a value of the input channels. The parameters of the dependent experiments can be 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 experime	nt
Secmx File Edit Hardware Poperiment Special Experiment		_ <u>8</u> ×
	🛯 🗙 🔯 🌇 😫 🛦	
Volume Scan	Yolume Scan Fwd: Company Incomperometry	Volume Scan all curves
Number of linescans 21 Apply	Levels # E/V Time/s Tbase/s Tbase ex	
Use lift off for entire HF rev. line + LF axis >>		
High frequency Low frequency		
Axis Motor		
Motor 1@Dummy Motors	Delay before start s 3.00	Graph for 4D experiment
Abs. position: 0.000 μm Rel. position: μm	Number of cycles 1	
Experiment Parameters Forward Reverse	Time between cycles 0.00	
Delay before scan s 0.00 0.00	Potential program Out Channel Out Channels	
Step (Sign det. direction) µm 1.0000 1.0000	DA0@Dummy ADDA -> NOT CONNECTED	
Speed μm/s 50.00 50.00	-10.000 V>	
Delay before exp. s 0.10 0.10	AD channels	
Use point to point lift-off high freq. forward	© Sequential C Multiplex Numb. Averag.	
Use point to point lift-off high freq. reverse >>>	Channels NAV Plot	Nolumo Scon Fuel Chronoomnevenativu all sumues
Forward Reverse		Volume Scarri wa, chronoamperometry an curves
E1 /V 0.00 DO NOT APPLY		
E2/V 0.00 DO NOT APPLY		
Evo: Eucli Change and a state of the	Input channels	
rwu. chloridamperonietty	Channels NAV Plot	
Show graphs Hide graphs 2D Graph >> 3D Graph >>		Graph for the dependent experiment
Action: Parameter input		
X: Y: Value: Time: 0:00:00/0:00:01 Line: /21		
	Make PlotWin Hide graphs Graph control 33	
π	Parameter insut	
	Farameter inplut Lycle:/	
SELMX Application Error Log		
[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.

1.7.2 Meander scan

4D experiments can take very long. Therefore, it can be a good compromise to avoiding the retracing and record dependent experiments also in the reverse scans (especially for hopping mode, see next section). The meander scan is caused by setting the check mark on the Tab *Low frequency*. Please not that the background color of the

input field on the tab *High frequency* is changing to indicate that the software is in the meander mode.



In the Meander Scan Mode, the data acquisition and scan parameters for forward and reverse scans are identical. Input data for reverse scan are ignored. The parameters of the dependent experiment for the reverse experiment are copied from the dependent experiment of the forward experiment at the moment when the experiment is started. In order to force an intermediate copying of the parameter for the reverse experiment during setup of the experiment use the button for pre-calculate the duration of the experiment in the SECMx menu bar.

The movement of the electrode is shown below.



As a result, two data files are stored. One datafile contains the data of the forward and reverse scans as separate data blocks. This file can be loaded into SECMx. A second data file with the appendix "_MERGED" contains the data in one data block. It can be read by MIRA for data processing. It cannot be loaded by SECMx.

1.7.3 Hopping mode experiments

Hopping mode experiments can be realized when selecting 4D experiments with meander mode and z-scan as the dependent experiment. Within the z-scan parameter the options Automatic stop upon threshold detection and Automatic retract are selected. Within the expandable Retract control, Retract by Fixed distance is selected. The regular scan length is then the maximum scan length and must be larger than the fixed estimate distance is a selected and the selected and

fixed retract distance. In oder to avoid collisions of microelectrode and sample during the reverse scan, there are two possibilities: i) use the line liftoff or ii) use the same dependent experiment (z scan with threshold detection and retraction by a fixed distance for the reverse scan).

🔮 secmx										
File Edit Hardware Experiment ?										
Volume Scan	Volume Scan Fwd: Z Line Scan	Volume Scan Rev: Z Line Scan								
Number of linescans 21 Apply	Motor	Motor								
Lise litt off for entire HE rev. line + I E avis	Motor 3@Dummy Motors 🔹	Motor 3@Dummy Motors 🔹								
	Abs. position: 0.00 μm Rel. position: -μm	Abs. position: 0.00 μm Rel. position: – μm								
High frequency Low frequency Data Acquisition	Delay before scan s 0.00	Delay before scan s 0.00								
Axis Motor	Scan length µm 150.00	Scan length µm 150.00								
X ▼ Motor 1@Dummy Motors ▼	Distance between ADC µm 1.00	Distance between ADC µm 1.00								
Abs. position: 0.00 μm Rel. position: – μm	Translation speed µm/s 50.00	Translation speed µm/s 50.00								
Experiment Parameters Forward Reverse	Delay translation-ADC s 0.10	Delay translation-ADC s_0.10								
Delay before scan s 0.00 0.00	Use point-to-point lift off	Use point-to-point lift off								
Number of points 21 21	Automatic stop upon threshold	Automatic stop upon threshold								
Step (Sign det direction) µm 1.00 -1.00	Automatic retract	Automatic retract								
<u>Speed μm/s</u> 50.00 50.00	C To start Fixed distance	Output signal during exp. >> 1								
Delay before exp. s 0.10 0.10	Retract speed after exp. µm/s 10.00	-AD channels								
Reverse scan parameter set automatically	Fixed retract distance µm -20.00	C Multiplex								
Use point to point lift-off high freq. forward	Output signal during exp.	Channels NAv Plot								
Use point to point lift-off high freq. reverse	AD channels	AD1@Dummy ADDA->U=f(i) UME@Schram 🗾 2000 🛛								
	Sequential C Multiplex	Α								
Show graphs Show graphs Show graph >> Show	Channels NAV Plot	DO NOT READ								
Action: Parameter input	AD1@Dummy ADDA->U=f(i) UME@Schram ▼ 2000									
X:- Y:- Value:-		Input channels								
Time: 0:00:00/0:00:01 Line: - /21	JDO NOT READ									
CtrlSelectChannel.cpj GrdParam-		ponornovo								
CtrlSelectTwinChanne GrdParam-	Input channels NAv. Plot									
CtrlSelectMultipleLine GrdParam-										
GrdParam-										
GrdParam-		Make PlotWin Hide graphs Graph control >>								
SECMx Application Error Log		×								
SECMx Application Started										
[17:26:06] Digital communication ports lo	Make Plotwin Hide graphs Graph control >>									
[17:26:06] Dummy ADDA loaded, index = 1, crammers - 44										
[17:20:06] Schram pBirg Loaded, index = 2, channels = 29										
[17:26:06] Schramm µBiP2: Warning: requested digital output to port that is not connected										
[17:26:06] Schramm µBiP2: Warning: reque	sted digital output to port that is not co	nnected								
Tributes Approaches and active reader										

Please note that SECMx cannot accurately predict the time for such experiments because the length of the forward experiment cannot be predicted for corrugated samples. The tip movement is given below for one line scan within a 4D experiment.



2 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 controler 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. *Electronalysis* 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.

U. M. Tefashe, G. Wittstock; Quantitative characterization of shear force regulation for scanning electrochemical microscopy. C.R. Chimie 2013, 16, 7-14

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 *PI sensor 0@PI* P6xx family is connected to *AD0@DAS1602/16* (in *Hardware/Setup AD/DA connections*). (the number of the PI ensor may vary depending on the setup)
- 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): Ivium
- d) Record another vibration spectrum with the tip within 1 micrometer off 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 μ m from the surface.
- f) Give a setpoint. The setpoint 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 mircoelectrode 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).

3 Procedure Checklist

In order to operate the SECM efficiently, you should know what the following terms mean within the SECMx program

- □ What is a 'channel'
- □ What is a 'device'
- □ What is a 'bundle'
- □ What is a 'mixed bundle'
- □ Which channels or devices require signal averaging? Which parameter controls signal averaging? How is signal averaging optimized?
- □ What are 'generic experiments'?
- What are 'special experiments'? What are their advantages?
- □ What is a generic cyclic voltammogram. How do I define the potential program?
- □ What is a line scan?
- □ What is the difference between a 'z-scan' and a 'fast approach"? Which of them should I use when I want to compare the approach curve to the theory for steady state response?
- How are the parameter defined for Imaging experiment?
- □ What is the Meander mode?
- □ What is a 'Volume scan'?