SpectroInlets

Enabling real-time analysis

EC-MS analysis system

Manual version 1.16

Version	Date	Author	Changelog
0.1	June 2018	BSE, TWJ	Document created
1.0	July 2018	BSE, DBT, TWJ	First public version
1.1	October 2018	BSE	Updated Fig. 1
1.2	November 2018	FCC	General revamp, added and updated figures, added paragraphs on PTFE spacer, added footer, converted optionals to standards
1.3	February 2019	FCC	Updated figures and text with the new design and sample mounting procedure after Søren's visit
1.4	March 2019	FCC	Added gas exchange section, framed warnings and added warning symbols to them
1.5	March 2019	FCC, DBT	Transformed to full user manual. Merged all documents in one.
1.6	March 2019	FCC	Proof-read calibration section, edited full text, updated figures and tables
1.9	December 2019	FCC	Added pulse section, renewed figures, revised gas exchange
1.9	December 2019	KNI	Updated software screenshots and software description to include PC
1.10	March 2020	KNI	Minor correction to chip exchange section and added "First time setup of PC for Zilien" section
1.11	April 2020	FCC	Added latest QMS configuration settings
1.12	June 2020	FCC	Corrected equation in quantification section
1.13	August 2020	FCC	Added troubleshooting section
1.14	June 2021	FCC, BSE	Updated introduction. Added specs in system overview. Updated first time PC setup section. Added comments for improvements and edits
1.14	December 2021	KNI	Added information on mains supply, system properties and acceptable operating conditions. Added section on safety with information on handling and chemical and gas safety.
1.15	Februar-March 2022	KNI	Added information on attaching rack earthing wire to electronics box earthing pin. Added information on decommissioning. Added update to the RS485 converter setup after electronics box change. Declaration of conformity added.
1.16	October 2022	ANW, JNH	Updated recommended QMS configuration settings and corrected procedure. Updated recommended torque for fastening cell.

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1 Introduction

The Spectro Inlets system is a unique instrument for high-sensitivity time-resolved detection of volatile electrochemistry products directly from a liquid electrolyte. This instrument is optimized for half-cell investigations, i.e., it allows the user to decouple the evolution of volatile products and consumption of reactants at the working and counter electrodes during electrochemical reactions. Due to its extraordinary sensitivity, the system can measure all the individual volatile molecules desorbing from an electrode surface during a single electrochemical turnover. Product formation can be measured from total Faradaic currents of 1 mA all the way down to 200 nA, corresponding to approximately 0.2% of a monolayer (ML) desorbing from the electrode surface in 1s. These features enable time-resolved, fully quantitative measurements of transient phenomena during electrochemistry, providing fundamental insight in the electrochemical reaction mechanisms. Furthermore, an accurately calibrated on-chip gas system allows rapid gas switching between different gases, both inert and reactive. Due to the near-instantaneous equilibration between gas and electrolyte, the transient response of electrodes to rapid gas exposure changes can be measured.

This document provides an overview of the hardware, software, installation instructions, a guide to use the system, and troubleshooting information.

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2 Declaration of conformity

CE

DECLARATION OF CONFORMITY

According to

2014/30/EU EMC directive

2014/35/EU Low voltage directive

2011/65/EU RoHS

We: Spectro Inlets ApS
Ole Maaløes Vej 3
DK-2200 København
Denmark

do hereby declare on our own responsibility that the below product:

Designation: ECMS

Type: ECMS v1.5

Which are covered by this declaration, all conform to the following standards:

EMC 2014/30/EU:

- EN 61326-1:2013 - Electrical equipment for measurement, control and laboratory use - EMC requirements - Part 1: General requirements

Safety 2014/35/EU:

- EN 61010-1:2010+EN 61010-1:2010/A1:2019+EN 61010-1:2010/A1/AC:2019 - Safety requirements for electrical equipment for measurement, control, and laboratory use - Part 1: General requirements

RoHS 2011/65/EU:

- EN 50581: 2012 Technical documentation for the assessment of electrical and electronic products with respect to the restriction of hazardous substances

Spectro Inlets ApS

Date 28-02-2022

Place Copenhagen

Name Daniel B. Trimarco

Signature Daniel B. Trimarco

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3 Safety

3.1 Lifting and carrying

 **WARNING**: Take care when handling. **Heavy system.**

The main system weighs 46 kg and has no built-in handling points for moving. Therefore, when the system is to be moved, it should be handled by at least two people, who should:

1) Clear a path up front where the system is to be carried and make room for the system up front at its new position
2) Use a good lifting posture with a straight back and use the legs for lifting
3) Use thick workers gloves to prevent discomfort from the edges of the side plates and, as far as it is possible, handle the system by the corners, but take care not to have fingers squeezed under the feet.

Both electronics boxes in the rack weight 24 kg. If the electronics is to be moved, use the handles on the side of the rack and use a good lifting posture. Furthermore, make sure the weight is appropriate for the person doing the moving, otherwise get assistance.

3.2 Operating safety and training requirements

 **ATTENTION**: The system contains potentially dangerous substances and must only be operated by appropriately trained personnel

3.2.1 Electrolyte safety and training requirements

Depending on the electrolyte selected for use in the electrochemical cell, the chemical may be **corrosive**, **poisonous**, **flammable** or **dangerous in some other way**. Furthermore, the

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electrolyte may be pressurized in the cell, yielding an additional **pressurized harmful liquids danger.**

No one may operate the system with electrolyte present, without having received the appropriate local training in the handling, use and disposal of the chemicals in question and in the mitigation of dangers associated with pressurized harmful liquids.

3.2.2 Gas safety and training requirements

Depending on the gasses connected to the system, they may be **corrosive**, **poisonous, flammable/explosive** or **dangerous in some other way**. Additionally, certain gasses, while less dangerous themselves, may form more dangerous (e.g., explosive) mixtures if allowed to mix on the system or in the tubing. Furthermore, the presence of pressurized gas of any kind forms a danger, due to the contained potential energy due to the pressure.

No one may operate the system with gasses connected, without having received the appropriate local training in the handling, use and disposal (ventilation) of the gases in question and in mitigation of the dangers associated with compressed gasses.

3.3 Electrical safety and earthing

Ensuring proper electrical earthing is important for electrical safety of the system. Therefore:

1. Ensure that the systems mains cable and the mains socket it is attached to match, so a proper earthing connection is made
2. That the electronics rack is appropriately earth connected to the electronics box, see section 7.1

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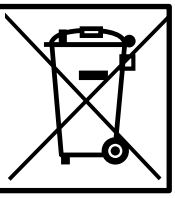
3.4 Systems safety; preventing harm to system components

Several performance critical and costly components of the system, such as the turbo molecular pump and the mass spectrometer can be damaged by misuse.

To prevent damage, no one should operate the system without user training from Spectro Inlets.

4 Decommissioning of the ECMS

ATTENTION: The ECMS equipment must not be disposed of as regular waste upon decommissioning



The ECMS equipment contains electronics and therefore must be appropriate disposed of, in the event of decommissioning.

Upon decommissioning the entire ECMS system (main system, cables and electronics boxes) must be disposed of as electronic waste, according to local regulations for the disposal of such OR sent back to Spectro Inlets for appropriate disposal and recycling.

5 Hardware description

5.1 Mains supply requirements

Voltage	184-253 VAC
Frequency	50 Hz
Nom./Max Power	60/125 W
Nom./Max Current (at 184V)	0.4/0.7 A

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5.2 System specifics and operating conditions

Electronics weight	24 kg
Main systems weight	46 kg
IP rating	IP20
Acceptable operating temperature	5-40ºC
Acceptable operating humidity	≤93% at operating temperature, non-condensing

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5.3 System overview

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Item	Description	Quantity
EC-MS system	Main instrument, including cables	1
Electronics box	Electronic control of all the components in the EC-MS system	1
Vibration mat	Vibration mat covering the electronics box, used to support the backing pump	1
Backing pump	Scroll pump used to back the EC-MS turbo pump	1
Backing line	KF25 corrugated hose to connect scroll pump and instrument, with KF25 centering rings and clamps	1
Potentiostat	Bio-Logic SP-200 potentiostat	1
Interface block	Stainless steel fixture for interfacing the membrane chip to the EC-MS system	1
Shim plates	Shim plates defining distance between the clamping ring and the interface block	3
PTFE spacer	PTFE foil defining the distance between the EC cell and the chip	1
Clamping ring	Stainless steel ring for fixing the membrane chip to the interface block	1
EC-cell	PCTFE stagnant thin-layer cell for electrochemistry	1
EC-cell O-ring	Kalrez O-ring for sealing EC-cell onto membrane chip. 10 mm inner diameter, 1 mm thickness, Kalrez 6375.	1
Membrane chip	Silicon membrane chip, pre-mounted in the interface block. Dimensions 1.5 cm x 1.5 cm.	1
Membrane chips	Spare silicon membrane chips	4
Fluidic adaptors	Idex P-624 male UNF 1/4”-28 to female luer	4
Fluidic adaptors	Idex P-625 male UNF 1/4”-28 to male luer	4
Chip O-rings	Viton O-rings for sealing membrane chip against interface block. 2 mm inner diameter, 1 mm thickness, FPM 75.	16
U-cups	Pine Instruments spare PTFE U-cups	3
U-cup assembly	Pine instruments assembly for mounting electrodes in U-cups	1
Mounting block	PCTFE block for mounting cylindrical electrodes in the U-cup assembly	1
Tubing	EFTE tubing, 100 mm length, 1/16’’ outer diameter, 1 mm inner diameter, with female luer terminations	2
Glass adaptors	Glass pipes with ground joint standard taper NS 14.5 and male luer fitting, with PP female luer caps	2
Fasteners	M1.6x5 for fixing shim plates to interface block. 4 pre-mounted in interface block and 4 extras. Stainless steel A4.	8

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Fasteners	M3x8 for fixing Clamping ring to interface block. 4 pre-mounted in interface block and 4 extras. Stainless steel A4.	8
Fasteners	M3x20 and M3 washers for fixing EC-cell to clamping ring. 4 pre-mounted in interface block and 4 extras. Stainless steel A4.	8
Software	Zilien, EC-Lab, PV Mass Spec	1
Cables	Male-male USB cable Ethernet cable Ion Gauge to QMS interlock cable Festo Valve Control cable Turbo Power cable Pirani 1 cable Pirani 2 cable Pirani 3 cable MFC 1 cable MFC 2 cable PC cable Ion Gauge cable	12

5.4 EC-MS

The system is shown in Figures Figure 1, Figure 2, and Figure 3.

The colored plates are made in anodized aluminium, whereas the frontal top plate is in stainless steel for maximum chemical resistance.

Connections to the instrument are shown in Figures Figure 1 and Figure 2, whereas the physical occupancy of the instrument is shown in Figure Figure 3. To function, the instrument must be coupled to an external pressurized air supply (not supplied), an external scroll pump (supplied, not shown in figure), to a pressurized He supply (not supplied), and to the electronic box (supplied, not shown in figure).

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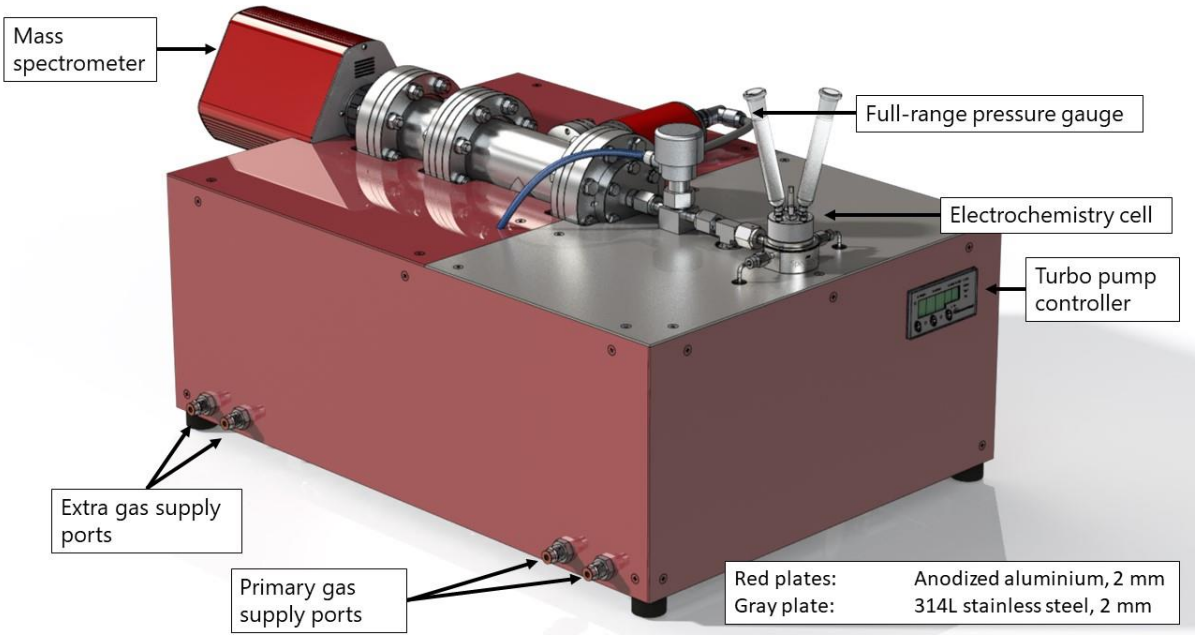

Figure 1. Front view of the instrument

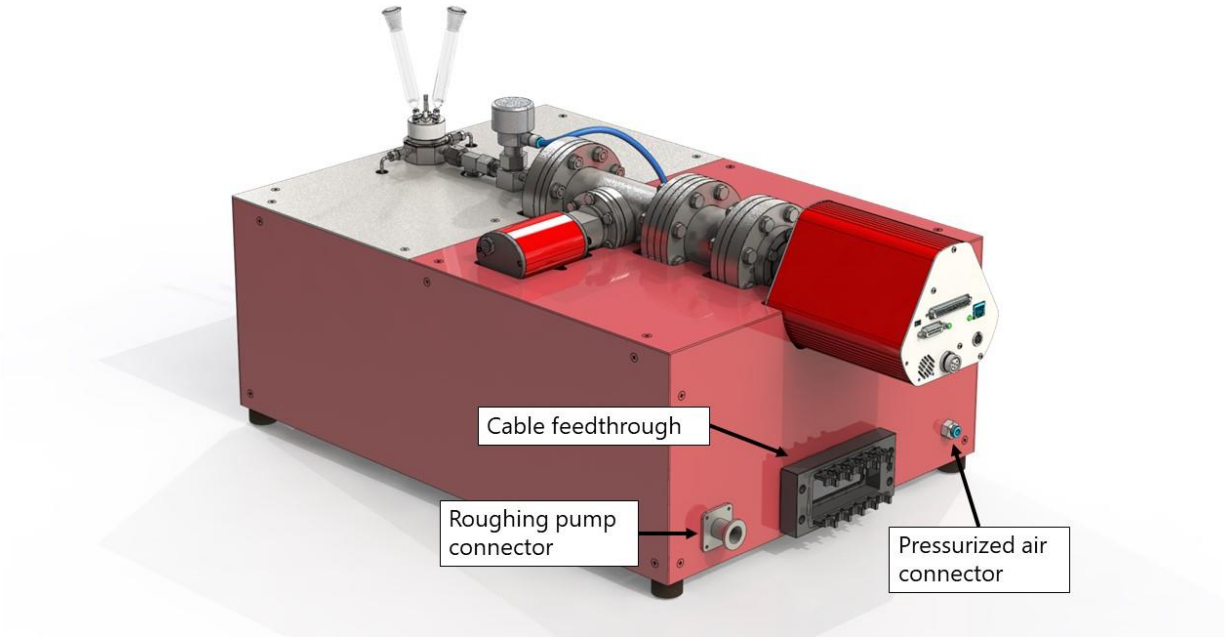

Figure 2. Rear view of the instrument

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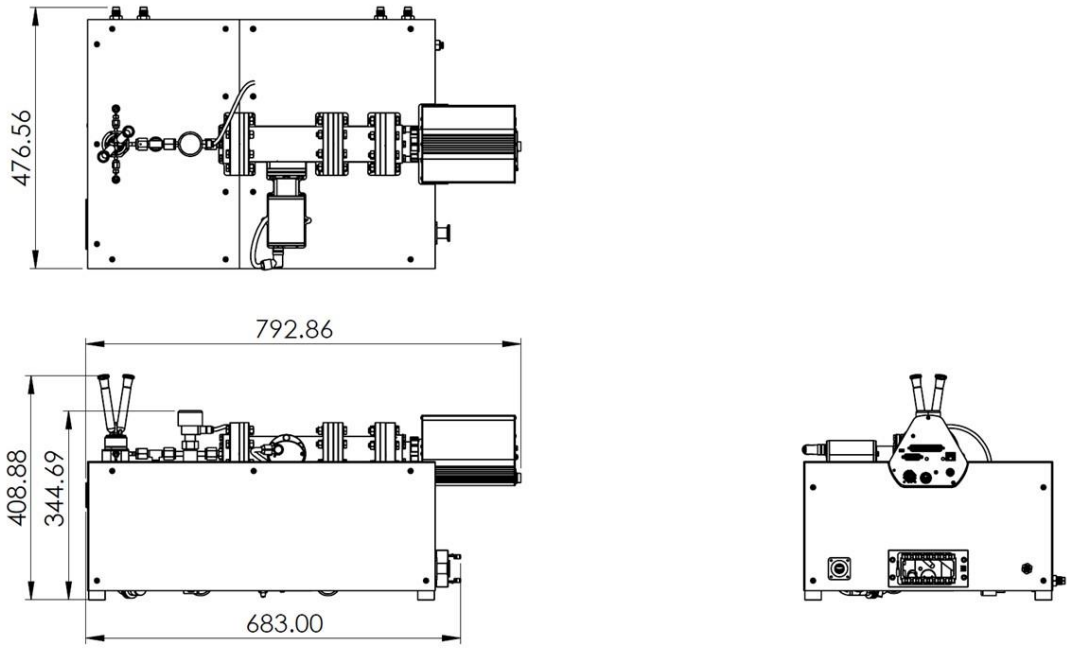

Figure 3. Dimensional drawing with physical occupancy. Dimensions are shown in mm.

5.5 Inlet system description

5.5.1 Working principle of the membrane chip

A key part of the systems functionality comes from the patented membrane chip developed by Spectro Inlets. Here, its working principle is explained. The membrane chip creates a direct coupling between the electrolyte and the high vacuum of a mass spectrometer *without* the use of differential pumping (Figure 4).

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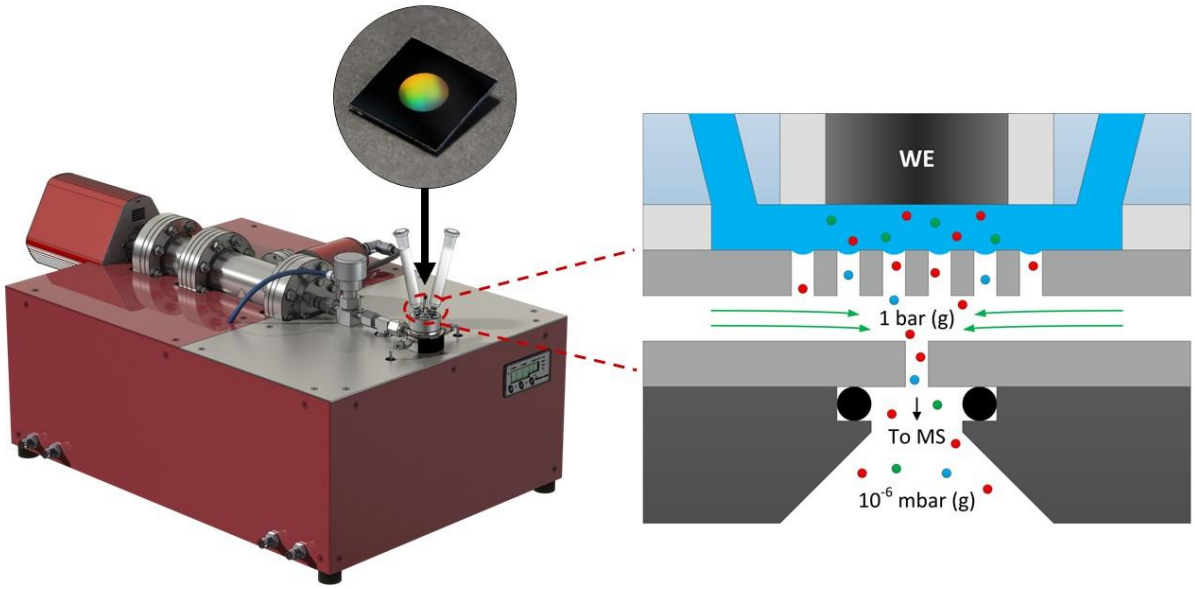

Figure 4. Working principle of the membrane chip. The chip is placed inside the interface block, on top of which the EC-cell is coupled. In the cartoon, the equilibration of volatile analytes between electrolyte and sampling volume is shown.[1]

The membrane chip creates a well-defined liquid-gas-vacuum interface and controls the volatile substance transfer from the electrolyte to the mass spectrometer. Inside the chip, a buried sampling volume equilibrates to the outer environment without letting liquid in. The pressure in the sampling volume is precisely controlled by our embedded gas handling system. To pressurize the sampling volume, any type of make-up gas can be used (see Section 13 for further details on the embedded gas handling system). Owing to the small size of the sampling volume and of the electrolyte layer, equilibration between the gas and the liquid is nearly instantaneous. During equilibration, all volatile species in the liquid fill the sampling volume according to their vapour pressure. The sampling volume is connected to the MS by a capillary which is designed to limit the flow of molecules to a precisely defined rate of 10^{15} molecules/sec. No differential pumping stage is thus necessary, and the fact that all the molecules are collected to the MS allows the direct conversion of mass spectrometry signal to mol/sec. This is what makes the Spectro Inlets the only existing truly quantitative EC-MS system. Finally, the pressurization of the sampling volume allows EC experiments at elevated pressures and temperatures.

The membrane chip (Figure 6) consists of a microfabricated membrane, coated with a hydrophobic polymer layer. A small sampling volume is located below the membrane, which is connected to the vacuum connection on the backside of the chip by a capillary. This capillary induces a pressure drop from atmospheric pressure to high vacuum in the vacuum chamber.

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The chip requires a make-up gas to work, which counteracts the pressure of a liquid placed on top of the chip. For the make-up gas, there are two connections on the backside: one inlet and an outlet. The pressure in the sampling volume, controlled by the pressure of the make-up gas, must be equal to the liquid pressure at the membrane. For further details, please see [2].

Chips have to be installed with the membrane facing upwards (towards test environment) and the vacuum connector on the backside of the chip facing downwards, aligned with the vacuum connector on the interface (Figure 5).

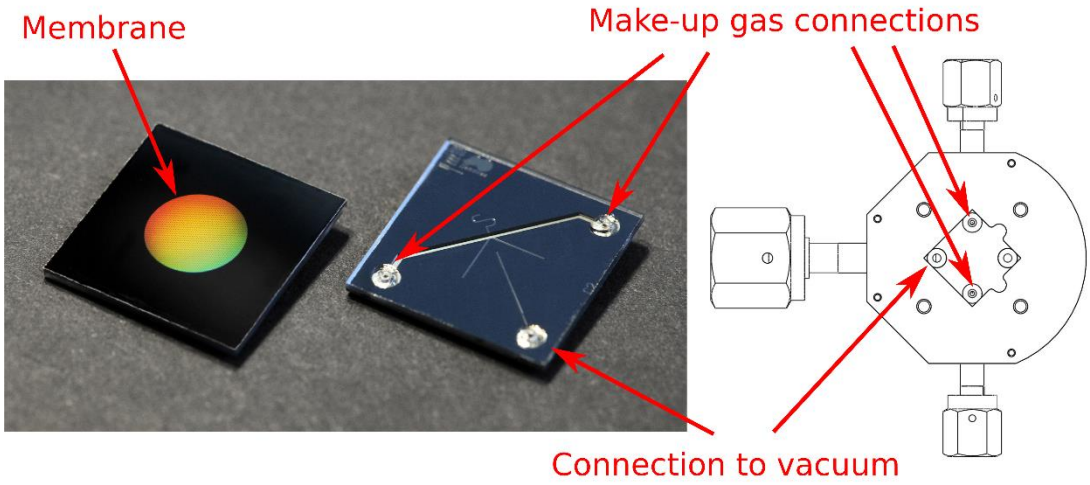

Figure 5: Image of the membrane chip and its correct alignment. When mounted onto the interface assembly the membrane should be facing upwards and the vacuum connector on the chip should be aligned with the vacuum connector on the interface block.

NOTE: When the inlet is used for gas analysis (chip exposed to gas, no liquid in contact with the chip), no make-up gas is needed.

NOTE: The direction of the make-up gas flow does not affect the workings of the interface.

5.5.2 Parts of the inlet system

An exploded view of the full EC-MS inlet system equipped with EC cell is shown in **Figure 6**.

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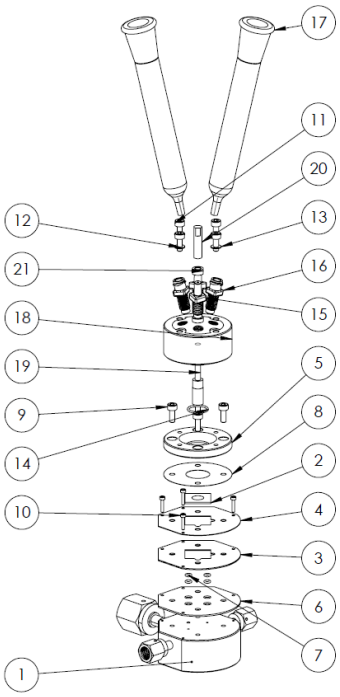

ITEM NO.	PART NUMBER	DESCRIPTION	QTY.
1	Interface block		1
2	Membrane chip		1
3	Microchip plate - thick		1
4	Microchip plate - thin		1
5	Clamping ring		1
6	O-ring plate		1
7	OR 2.00 - 1.00, FPM 75		4
8	0.1 mm PTFE spacer 40-14		1
9	DIN 912 M3 x 8 --- 8C		4
10	DIN 912 M1.6 x 8 --- 8N		4
11	DIN 912 M3 x 8 --- 8N		4
12	Washer DIN 433 - 3.2		1
13	plain washer small grade a_din		3
14	OR 10.00 - 1.00, KZ 6375		1
15	P-625		2
16	P-624		2
17	Glass pipes		2
18	Stagnant thin layer EC cell		1
19	Disk contact core assembly		1
20	Disk core nut		1
21	Disk core spacer		1
24	Working electrode	Not provided	1

Figure 6: Exploded view of the EC-MS inlet system.

5.5.3 Details of the interface block assembly

To connect the chip to the instrument, an interface block is available. The interface assembly is equipped with connectors to vacuum and make-up gas (#1 in Figure 6), a plate with openings for the four 2.00 – 1.00 FPM O-rings (#5 and #10 in Figure 6), two plates with different thickness with openings for the microchip (#3 and #4 in Figure 6) and 4 M1.6x5 screws (#12 in Figure 6) to keep the different parts together. The metal parts of the assembly are manufactured from acid-resistant stainless steel. The top surface of the interface block is polished, in order to provide a smooth sealing surface to the O-rings.

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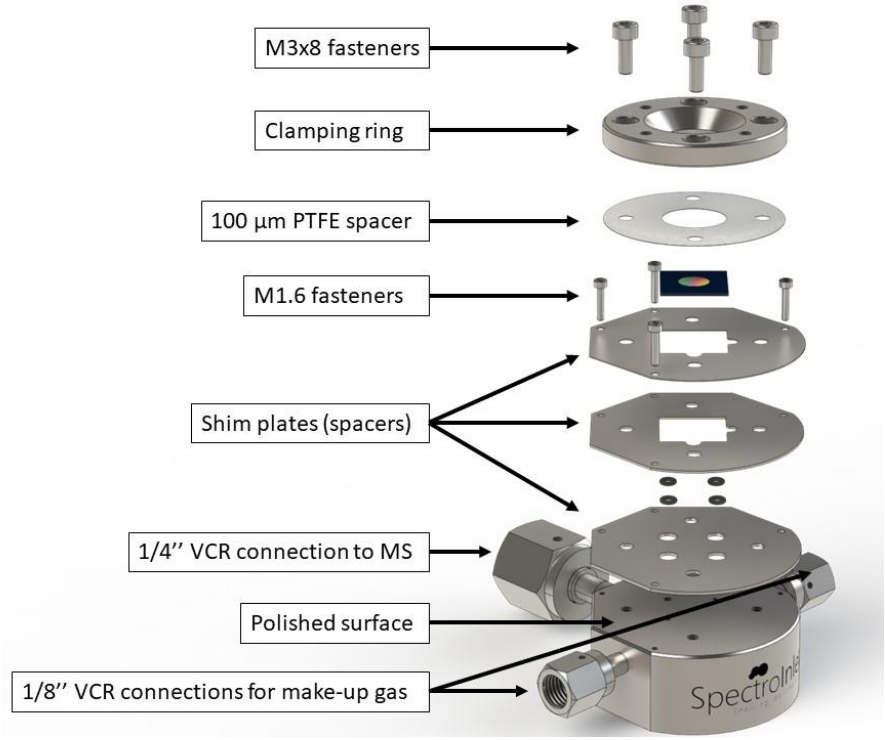

Figure 7: Parts of the interface block.

WARNING: The supplied fasteners are made of stainless steel, thus softer than normal steel fasteners. Do not overtighten the M1.6 screws as they may break into the screw holes. These screws are not supporting forces. The tightening torque should not exceed 0.15 Nm.

WARNING: Do not scratch the polished stainless-steel surface of the interface block. This can lead to insufficient sealing with the O-ring and air leaking to the vacuum chamber. If this happens, disassemble the interface block and repolish its surface (see Chapter 12).

The membrane chip is attached to the interface block with a precisely machined stainless-steel clamping ring (#6 in Figure 6 and Figure 8) with 4 clearance holes for M3 screws. This ring serves as the base for the EC cell or any user-designed attachment to the membrane inlet system. Attachment of add-ons is possible using the four threaded M3, 4 mm deep holes, distributed on a Ø 15 mm circle (Figure 8). The clamping ring has a Ø 7 mm opening for contact with the chip and a thickness of 5 mm. The dimensional drawing is available upon request.

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WARNING: Forcing M3 screws into the threaded holes on the clamping ring (Figure 8) might cause the bottom face of the clamping ring to become uneven around the threaded holes. If this happens the clamping ring must be replaced. Do not force M3 screws into the threaded holes without the EC cell. Do not use screws longer than M3x20 with the EC cell.

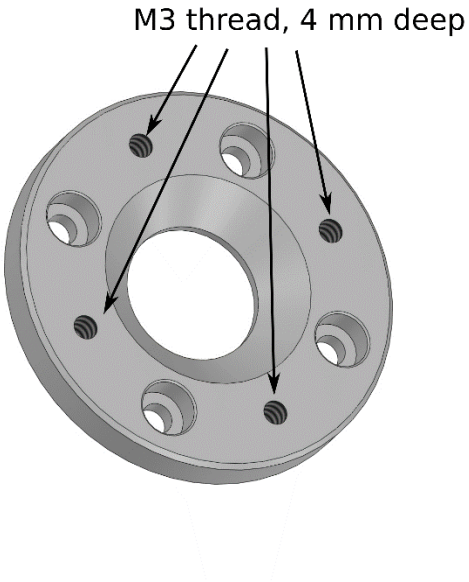

Figure 8: Details of the clamping ring.

5.5.4 Details of the stagnant thin-layer EC cell

Figure 9 shows a cross section of the stagnant thin-layer electrochemical cell. The cell has four M3 clearance holes on its perimeter to attach it to the interface assembly. Four flat-bottom holes with 1/4”-28 UNF thread allow the attachment of microfluidic fittings to connect reference and counter electrode as well as to fill the cell with electrolyte. A clearance hole for the disk contact core assembly and a groove for the 10.00 – 1.00 Kalrez O-ring are featured in the center of the cell.

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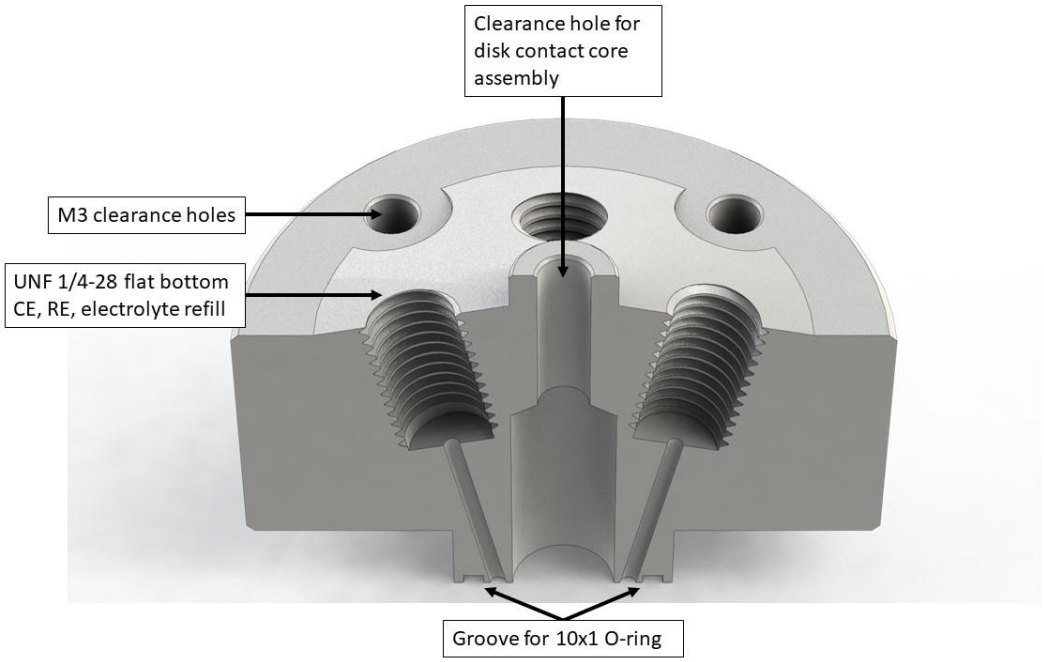

Figure 9: Overview of the stagnant thin-layer EC cell.

5.5.5 Technical data

The table below summarizes the properties of the EC inlet system. For further technical details please contact Spectro Inlets at info@spectroinlets.com.

Membrane chip		
Parameter	**Value**	**Comments**
Materials:	SiO_2, Si, Pyrex, FDTS	
Size:	15 mm x 15 mm x 0.87 mm (L x W x H)	
Weight:		
Flow rate through capillary:	Approx. 2.1 nmol/s ($1.3 \cdot 10^{15}$ molecules/s) for air and 2.6 nmol/s ($1.6 \cdot 10^{15}$ molecules/s) for He	Expected pressure with a standard CF63 turbomolecular pump (80 l/s N_2 pumping speed) is approx. $4 \cdot 10^{-7}$ - 10^{-6} mbar
Resistance of the microchip to chemicals:	The microchip is usable with aqueous solutions at pH 1-7.	For operation in higher pH, please contact us.
Size of the membrane on the chip (diameter):	Ø 7 mm	

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Interface assembly		
Parameter	**Value**	**Comments**
Materials:	Stainless steel (interface block 316L, plates 301, fasteners 316), FPM	
Process connections:	1/4” female VCR face-seal for high vacuum 1/8” female VCR face-seal make-up gas inlet 1/8” female VCR face-seal make-up gas outlet	The direction of the make-up gas flow does not affect the workings of the interface.
Bounding box size:	Approx. 87 mm x 82 mm x 23.8 mm (L x W x H)	

EC cell	
Materials:	PCTFE, Kalrez (O-ring)
Bounding box without working electrode mounted:	Approx. 40 mm x 40 mm x 27.5 mm (L x W x H)
Materials:	Stainless steel (interface block 316L, plates 301, fasteners 316), PCTFE, PTFE, FPM, SiO_2, Si, Pyrex, FDTS

Complete EC-MS inlet system with working electrode attached:	
Bounding box size:	Approx. 87 mm x 82 mm x 71.5 mm (L x W x H)
Height of the electrochemical reaction chamber	Approx. 100 µm
Electrolyte volume required to fill up the EC cell	Approx. 0.15 ml

All weldings are He leak-tested as part of the quality control procedure. The quality control is passed if no leak is detected, corresponding to a leak rate lower than 10^{-9} mbar·l·s^{-1} under the experimental conditions. All chips are individually tested prior to delivery by placing a Milli-Q water droplet on the surface and recording the QMS signals.

The electrochemical cell can be cleaned using strong acids such as piranha solution.

ATTENTION: The EC cell is not cleaned prior to delivery.

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ATTENTION: The stainless-steel parts are manufactured from either 316L or 301 stainless steel. These materials are acid-resistant, however some discolouring might occur depending on the used electrolyte.

5.6 Mass spectrometer description

Add figure and elaborate on MS description

5.7 Potentiostat

Brief introduction to potentiostats.

Works only with Bio-Logic (SP-200-optimized but compatible with others)

Potentiostat is included

Cannot operate potentiostat via software but trigger measurements (see Section Software)

5.8 Electronics box and cables

WARNING: Do not connect or disconnect the circular M23 connectors on the back of the rack units under power.

WARNING: Do not open up the rack units while under power. Both mains voltage and 24V DC voltage can be found in the units when they are powered on and mains voltage is present even when Q1 switch is switched off in Unit 1 until mains power cord is disconnected.

WARNING: On power cycling the box controlling the DC voltage (switch Q2/bottom box) the pressure setpoint of the pressure controller resets to zero. This might close the chip to breach immediately and increases the backing pressure in the system significantly. Before turning back on the power to the pressure controller, always make sure it is safe to do so!

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 **ATTENTION**: After turning on Box II, the mass spectrometer is not powered for about 15s. After this time-delay it is powered on automatically.

 **ATTENTION**: Unit I contains a USB-to-ethernet converter which shows up as a new network card. This has to be configured to an **IP address** of **192.168.100.5** and a **subnet mask** of **255.255.0.0** in order for the communication with the QMS to work.

 **ATTENTION**: If one of the power indicator LEDs appear to be less bright than the others, that can be sign of a blown fuse. If one of the components are not powered and the corresponding LED appears to be less bright, inspect the fuse in the corresponding unit.

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Figure 10: Overview of the electronics control unit.

The system is controlled by two standard 3U high 19 rack units placed in a 6U high desktop rack as shown in Figure 10. Unit I contains the valve control electronics, 24V DC power supply and communications electronics. Unit II contains the wiring necessary to supply and communicate with the gauges, mass flow controllers and pressure controller on the system. It also supplies power to the mass spectrometer.

Additional information about the wiring can be found in the attached wiring schematics.

5.8.1 Overview of the connectors and switches found on the rack units

Figure 11: Overview of the front of Unit I.

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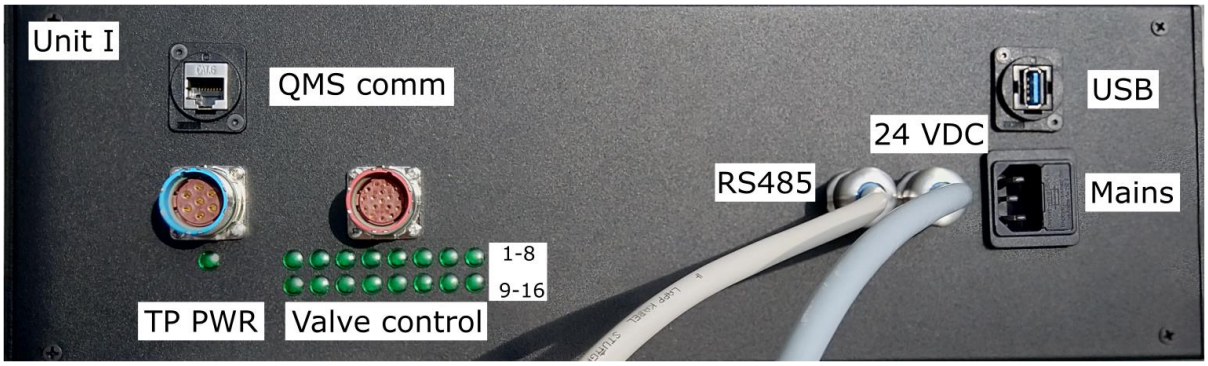

Figure 12: Overview of the back of Unit I

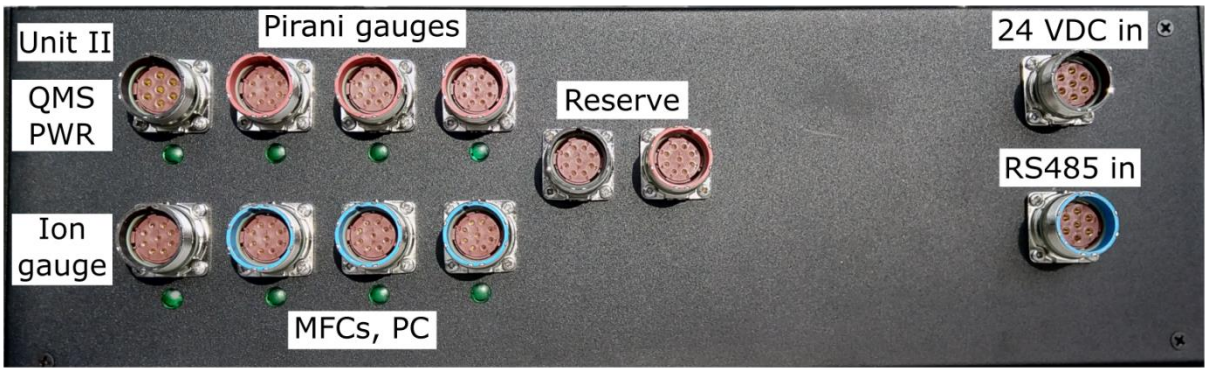

Figure 13: Overview of the back of Unit II.

Component	Description	Pinout	Misc.
	Unit I		
Q1	Mains pushbutton switch	-	When turned off, nothing is powered on the system. In case of power fallout, the latching is released (no automatic turn on when power is reestablished)
Q2	Power switch for Unit II Turned left: ON (green LED) Turned right: OFF (red LED)	-	Power supply for Unit II, thus to gauges, MFCs, PC and QMS on the system.

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<table>
<tr><td>QMS comm</td><td>RJ45 socket for ethernet cable to QMS unit.</td><td>-</td><td>Cable is required for connecting to the mass spectrometer.</td></tr>
<tr><td>TP PWR</td><td>7pin, p coded, M23 circular connector and indicator LED for powering the turbomolecular pump on the system.</td><td><table><tr><th>Pin</th><th></th></tr><tr><td>1</td><td>DC+ (24 V)</td></tr><tr><td>2</td><td>DC+ (24 V)</td></tr><tr><td>3</td><td>DC- (0 V/GND)</td></tr><tr><td>4</td><td>DC- (0 V/GND)</td></tr><tr><td colspan="2">Rest: NC</td></tr></table></td><td>Fused with 10A, 10x38 mm DC rated cartridge fuse (e.g. Littelfuse 0KLK010.T)
LED ON: power available</td></tr>
<tr><td>Valve control</td><td>17pin, p coded, M23 circular connector and indicator LEDs for powering the turbomolecular pump on the system.</td><td>Pin 1…16: corresponding valve number on NI data card (see details in wiring schematics)
Pin 17: DC- (0V/GND)</td><td>The unit is capable of controlling 16 valves, out of which only 14 are connected. LED is on, when the corresponding valve is open, except for valve 14, where LED on means the valve is closed.
First row: Valve 1-8
Second row: Valve 9-16</td></tr>
<tr><td>RS485</td><td>7 pin, e coded, blue M23 circular plug. It has to be attached to RS485 in on Unit II.</td><td><table><tr><th>Pin</th><th></th><th>Wire</th></tr><tr><td>1</td><td>RS485+</td><td>Pink</td></tr><tr><td>2</td><td>RS485-</td><td>Grey</td></tr><tr><td colspan="3">Rest: NC</td></tr></table></td><td>If not attached there is no communication between the components on the system and the computer.</td></tr>
<tr><td>24 VDC</td><td>7 pin, e coded, black M23 plug. It has to be attached to 24 VDC in on Unit II.</td><td><table><tr><th>Pin</th><th></th><th>Wire</th></tr><tr><td>1</td><td>DC+ (24 V)</td><td>1</td></tr><tr><td>2</td><td>DC- (0 V/GND)</td><td>2</td></tr><tr><td>3</td><td>GND</td><td>green-yellow</td></tr><tr><td colspan="3">Rest: NC</td></tr></table></td><td>This cable supplies power to the gauges, MFCs, PC and QMS on the system. Q2 switches power on and off through this cable.
Fused with 10A, 10x38 mm DC rated cartridge fuse (e.g. Littelfuse 0KLK010.T)</td></tr>
</table>

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			LED ON: power available
USB	USB A female port. It has to be connected to a free USB port on the controlling computer.	-	Communication with the components on the system and the QMS as well as the control signals to the valves go through this USB port.
		Unit II	
QMS PWR	7pin, p coded, black M23 circular connector and indicator LED for powering the QMS	Pin 1 DC+ (24 V) 2 DC+ (24 V) 3 DC- (0 V/GND) 4 DC- (0 V/GND) Rest: NC	QMS power turns on with an approx. 15s delay. Fused with 4A, 5x20 mm DC rated cartridge fuse (e.g. Littelfuse 0477004.MXP) LED ON: power available
Pirani gauges	3x 9pin, p coded, M23 circular connector and indicator LED for providing power and communication to the pirani gauges.	Pin 1 DC+ (24 V) 2 DC- (0 V/GND) 3 RS485+ 4 RS485- Rest: NC	The connectors are identical and the attachment order of gauges does not matter. Fused with 1A, 5x20 mm DC rated cartridge fuse (e.g. Littelfuse 0477001.MXP) LED ON: power available
Ion gauge	9pin, p coded, M23 circular connector and indicator LED for providing power and communication to the ion gauge on the system.	Pin 1 DC+ (24 V) 2 DC- (0 V/GND) 3 RS485+ 4 RS485- Rest: NC	Fused with 1A, 5x20 mm DC rated cartridge fuse (e.g. Littelfuse 0477001.MXP) LED ON: power available
MFCs, PC	3x 9pin, p coded, M23 circular connector and	Pin 1 DC+ (24 V)	The connectors are identical and the attachment order of the

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	indicator LED for providing power and communication to the MFCs and PC on the system.	2 DC- (0 V/GND) 3 RS485+ 4 GND 5 RS485- Rest: NC	MFCs and PC does not matter. Fused with 1A, 5x20 mm DC rated cartridge fuse (e.g. Littelfuse 0477001.MXP) LED ON: power available
Reserve	2x 9pin, p coded, M23 circular connectors	NOT CONNECTED	For future expansion/development
24 VDC in	24 VDC power input, 7pin, p coded, M23 circular connector.	Pin 1 DC+ (24 V) 2 DC- (0 V/GND) 3 GND Rest: NC	24 VDC cable from Unit I has to be attached here.
RS485 in	RS485 communication wire input, 7pin, p coded, M23 circular connector.	Pin 1 RS485+ 2 RS485- Rest: NC	RS485 cable from Unit I has to be attached here.

5.8.2 Overview of cables supplied

5.8.2.1 Pirani gauge power and communication

Pin-out connector #1 LAPP EPIC M23 circular, 9 pin, e coded, male	**Pin-out connector #2** D-sub 9pin, female		**Wire marking/color in the cable**
1	3	DC+ (24 VDC)	Brown
2	4	DC- (0 V/GND)	White
3	9	RS485+	Pink

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4	7	RS485-	Grey

Rest: NC

5.8.2.2 Ion gauge

Pin-out connector #1 LAPP EPIC M23 circular, 9 pin, e coded, male	**Pin-out connector #2** M12, 5 pin male		**Wire marking/color in the cable**
1	2	DC+ (24 VDC)	Brown
2	3	DC- (0 V/GND)	White
3	1	RS485+	Pink
4	4	RS485-	Grey

Rest: NC

5.8.2.3 Ion gauge to QMS

Pin-out connector #1 DIN 6 pin, male (Amphenol T 3424 005)	**Pin-out connector #2** M12, male 8 pin		**Wire marking/color in the cable**
1	3	ID	Green
2	4	GND	Yellow
3	9	Input (analogue signal +)	Brown
4	7	Analogue GND (signal -)	White

Rest: NC

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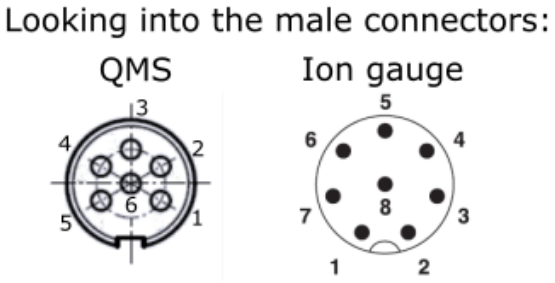

5.8.2.4 MFC/PC

Pin-out connector #1 LAPP EPIC M23 circular, 9 pin, e coded, male	**Pin-out connector #2** D-sub 9pin, female		**Wire marking/color in the cable**
1	2	DC+ (24 VDC)	Brown
2	1	DC- (0 V/GND)	White
3	5	RS485+	Pink
4	7	PE	Green
5	9	RS485-	Grey

Rest: NC

5.8.2.5 Turbomolecular pump power

Pin-out connector #1 LAPP EPIC M23 circular, 9 pin, e coded, male	**Pin-out connector #2** 4 pin male (Kycon KPPX-4P)		**Wire marking/color in the cable**
1	1	DC+ (24 VDC)	1
2	2	DC+ (24 VDC)	2

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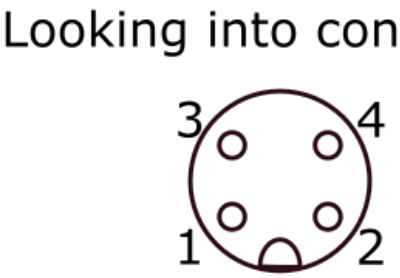
3	3	DC- (0 V/GND)	3
4	4	DC- (0 V/GND)	4

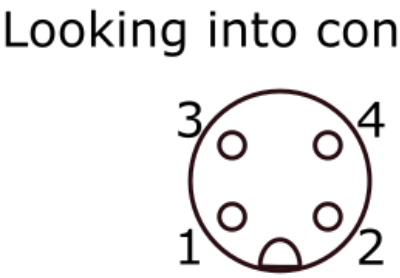
Rest: NC



5.8.2.6 QMS power

Pin-out connector #1 LAPP EPIC M23 circular, 9 pin, e coded, male	**Pin-out connector #2** 4-pin male (Kycon KPPX-4P)		**Wire marking/color in the cable**
1	3	DC+ (24 VDC)	1
2	4	DC+ (24 VDC)	2
3	1	DC- (0 V/GND)	3
4	2	DC- (0 V/GND)	4

Rest: NC



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5.8.2.7 Valve control cable

Pin-out connector #1 LAPP EPIC M23 circular, 17 pin, e coded, male	**Pin-out connector #2** D-sub 25 pin, female		**Wire marking/color in the cable***
1	1	Valve 1 control	White
2	2	Valve 2 control	Brown
3	3	.	Green
4	4	.	Yellow
5	5	.	Grey
6	6		Pink
7	7		Blue
8	8		Red
9	9		Black
10	10		Violet
11	11		Grey/Pink
12	12		Red/Blue
13	13		White/Green
14	14		Brown/Green
15	15		White/Yellow
16	16	Valve 16 control	Yellow/Brown
17	25	Return/DC-(0 V)/GND	White/Grey

*: First color is the color of the wire, second one is printed as rings (colors according to DIN 47100)

Rest: NC

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6 Software and GUI introduction

This section contains an introduction and map of the Graphical User Interface (GUI), followed by a description of a few selected topics concerning how the software operates.

6.1 General description

Zilien is the name of the main software for the EC-MS system. The software enables:

- Manual operation of gas system components such as 2- and 3-way valves, mass flow controllers (MFCs), pressure controller (PC), and readout of pressures from gauges
- Chip pumpdown automation, which enables an easy transition of the system to measurement mode
- The ability to setup and run combined mass spec and electrochemistry experiments and save the data to easily parseable files
    - Continuous monitoring of specific masses (MID) throughout the full extent of an experiment, including chip exchange, mounting of EC-cell and gas exchange
    - Explorative EC-MS features that enable triggering newly configured EC measurements and full mass spectra at relevant points during the experiment
- System and software logging, both in GUI and to file. This allows tracking of past events

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6.2 General GUI and Valve Control tab

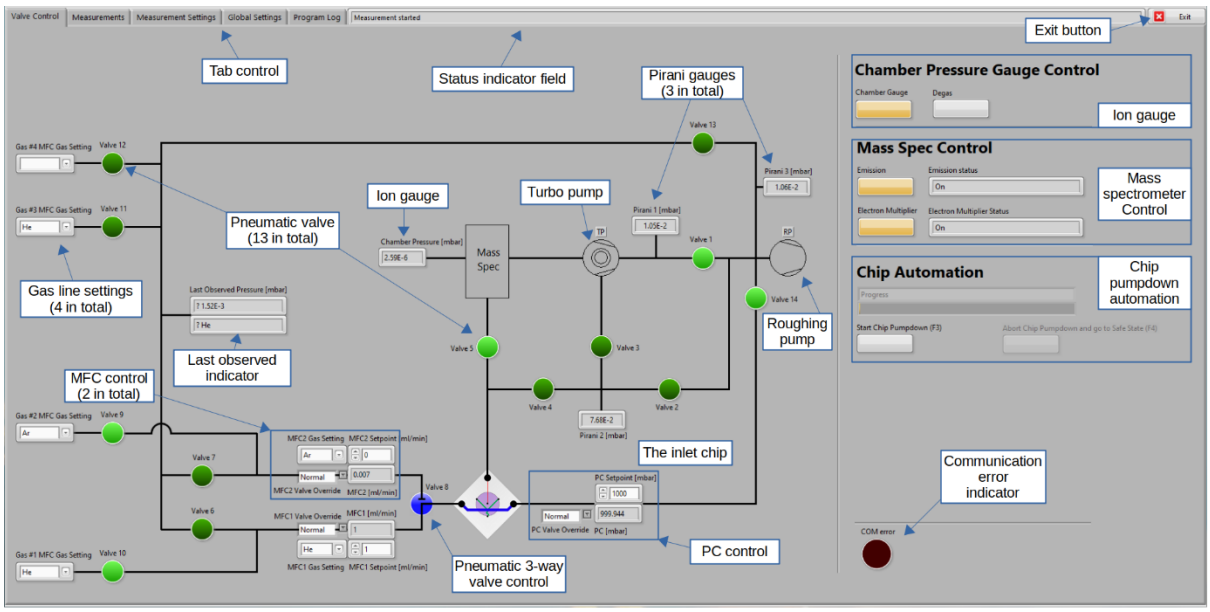

Figure 14. Main Zilien tab

In the screenshot in Figure 14 a few general items are illustrated:

- The **tab control** is used to navigate between different sections of the software in a similar fashion to e.g. internet browsers.
- The **status indicator field** is used to display messages from the software to the user about what is currently going on. This will be used to keep the user updated on status changes, progress in procedures etc. Important messages will also be displayed in a dialog so that they are not missed.
- The **exit button** is used to shut down the software nicely. It is important to use this to shut the software down (even if running the software in Labview from source code, where the big Labview stop-button is also available). The reason for this is that when shutting the software down nicely, all the links to equipment will be shut down and the current software state will be saved (e.g. settings).

Valve control is also shown in Figure 14. It consists of:

- **Pneumatic 2-way (open/close) valves (with labels like "Valve #")** are represented by green circular buttons. Bright green means open and dark green means closed. Be aware that these color indicators apply independently of the normally open/closed configuration of the valves.
- The **pneumatic 3-way valve** is used to switch between the two inlet gas lines to the chip, represented by a blue circular button. The illustration of the piping inside the circle, shows which MFC line is connected to the chip inlet and which is valved off.

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This is an ordinary 3-way valve, which means that it is not possible to connect both lines at the same time or to close both off at the same time.

- **Pirani gauges (with labels like "Pirani # [mbar]"** show the pressure at a point in the gas and pumping system. The working pressure range of these Pirani gauges is 1000 mbar to 10^{-5} mbar.
- **Ion gauge** is a full range gauge that shows the pressure in the vacuum chamber where the mass spectrometer is connected. The working pressure range of the ion gauge is 1000 mbar to 10^{-10} mbar.
- **Roughing pump** and **turbo pump** are the two pumps for low and high vacuum, respectively. In the diagram, the connection of the left of the pump indicates the primary pumping point, the connection on the right (if any) indicates the exhaust and the connection at the bottom (if any) indicates an intermediate pumping stage.
- **The inlet chip** is the main interface between the test environment and the vacuum of the mass spectrometer
- The **last observed indicator** is an indication of the last observed pressure and gas type in the gas manifold. The gas type is updated when there is a connection between one of the supply lines and the gas manifold and the pressure is updated with real values only when valve 13 is open and there is active pumping on the manifold. When Zilien has been shut down, the values from last run are re-established, but prefixed with a question mark, to indicate that Zilien cannot be sure that the conditions of the gas manifold did not change since last run.

WARNING: Although the last observed indicator looks like a gauge, it is very important to realize that it is not. There is no real-time monitoring of the pressure in the gas manifold, except when valve 13 is open.

- **COM Error** is short for communications error and indicates that the communication with one or more pieces of equipment in the setup is not working

WARNING: If the COM error light is on or blinking, the software control of the setup may not work correctly, and it is strongly discouraged to run experiments or automation steps until the problem has been solved

- **Gas line settings** is used to select which gas is available in the gas line

Each MFC has a total of 4 widgets associated with it, shown in Figure 15 and described in detail below.

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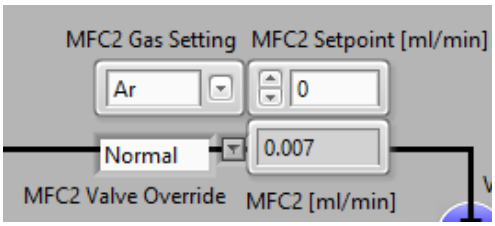

Figure 15. Screenshot detail of the MFC controls

- The **MFC# Gas Setting** control is used to select gas on the MFC (more specifically it sets the gas constant used when converting the MFC's real measurement into a flow).

> **ATTENTION**: If the gas setting is not set according to the gas flowing through the MFC, the measurement and hence the flow control will be wrong.
>
> **ATTENTION**: After changing the gas setting, it takes a little while (~10s) for the values of the MFC to stabilize to the new gas constant. Watch the flow readout to see when the value has stabilized.

- The **MFC# Setpoint [ml/min]** control is used to set the desired setpoint of the MFC.
- The **MFC# Valve Override** is used to change how the MFC regulates the flow. It has 3 possible values "Normal", "Flow Off" and "Purge". "Normal" means that the MFC will follow the entered setpoint. "Flow Off" means that it will close fully, independently of the setpoint. "Purge" means that it will fully open, independently of the setpoint. In both cases of setting the mode to "Flow Off" and "Purge", the MFC will remember the setpoint in the meantime, which makes it a convenient way to toggle between a specific flow and 0.

> **WARNING:** There is **no** confirmation step when switching the valve override mode, which means that it is possible to e.g. let the full pressure in the MFC supply line into the chip causing damage, if it is accidentally set to "Purge" at the wrong time. Please exercise caution.

- The **MFC# [ml/min]** indicator shows the current flow measured by the MFC. This is a readout, not an input field (notice the slightly grey background).

The PC has a total of 3 widgets associated with it, illustrated in Figure 16 and explained in detail below:

- The PC Setpoint [mbar] control is used to set the desired setpoint of the PC.
- The PC# Valve Override is used to change how the PC regulates the pressure. It has 3 possible values "Normal", "Flow Off" and "Purge". "Normal" means that the PC will

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follow the entered setpoint. “Flow Off” means that it will close fully, independently of the setpoint. “Purge” means that it will fully open, independently of the setpoint. In both cases of setting the mode to “Flow Off” and “Purge”, the PC will remember the setpoint it was on before and return to that value when the valve override is set to “Normal”.

WARNING: There is **no** confirmation step when switching the valve override mode. Please exercise caution.

- The PC [mbar] indicator shows the current flow measured by the MFC. This is a readout, not an input field (notice the slightly grey background).

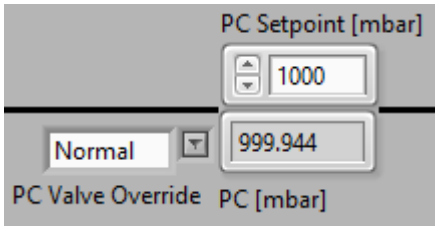

Figure 16. PC controls

6.3 The Measurements tab

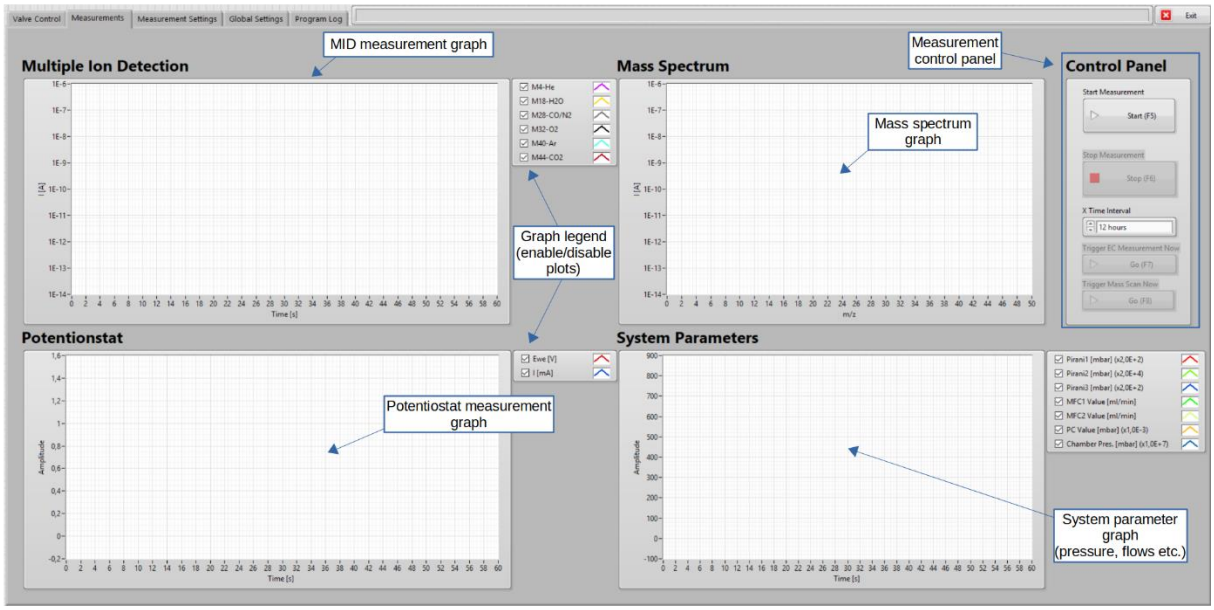

Figure 17. Screenshot of the Measurements tab in Zilien

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The measurement tab (Figure 17) is used to control the measurement and display values in graphs. It consists of:

- 4 graphs:
  - The **Multiple Ion Detection** graph which displays the values for the specific m/z channels defined in the **Multiple Ion Detection** sub-tab in the **Measurement Settings** tab. Values displayed are current I [A] as a function of time [s] for each m/z channel.
  - The **Mass Spectrum** graph is used to display complete mass spectra, acquired with the settings defined in the **Mass Spectra** sub-tab in the **Measurement Settings** tab. Values are current I[A] as a function of m/z.
  - The **Potentiostat** graph which displays working electrode voltage and current values from the potentiostat, both as function of time.
  - The **System Parameters** graph which display values from the gas and pumping system on the EC-MS system such as pressures and flows. The plotted channels are those enabled in the **System Parameters** sub-tab of the **Measurement Settings** tab.
- **Graph legends** allow to change the color of the displayed traces and to toggle the display of individual traces on/off while the measurement is running.
- The **Control Panel** (shown in detail in Figure 18), contains the following controls:

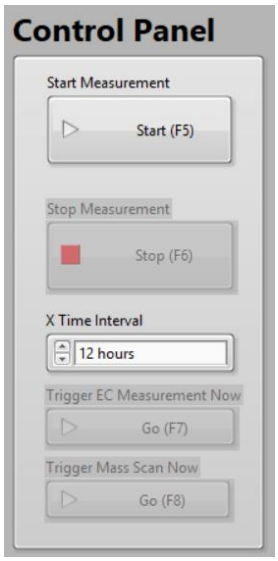

Figure 18. The measurement control panel

  - **Start** and **Stop** buttons, used to start and stop a measurement with the settings set at start time (see the next section for details)
  - **X Time Interval** control, used to set the time scale that the values in the plot are shown over

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- **Trigger EC Measurement Now** button (only available during measurement if the **Enable Electrochemistry Measurement** button has been selected on the **Electrochemistry** sub-tab of the **Measurement Settings** tab. This button will start the measurement currently set in EC-Lab® **provided that, in EC-Lab®, a potentiostat is connected, a channel is selected, a measurement is setup and ready to run, and that the measurement could be started in EC-Lab® without any other dialogs than the save file dialog showing up.**
- **Trigger Mass Scan Now** button, used to request to pause the **Multiple Ion Detection** whilst obtaining a full mass scan.

6.4 The Measurement Settings tab

The **Measurement Settings** tab has its own sub-tabs, used to configure the different aspects of a measurement. Each of these different sub-tabs are covered below. The screenshots have been cropped to show only the sub-tab of the relevant part of the sub-tab.

6.4.1 General and system settings sub-tab

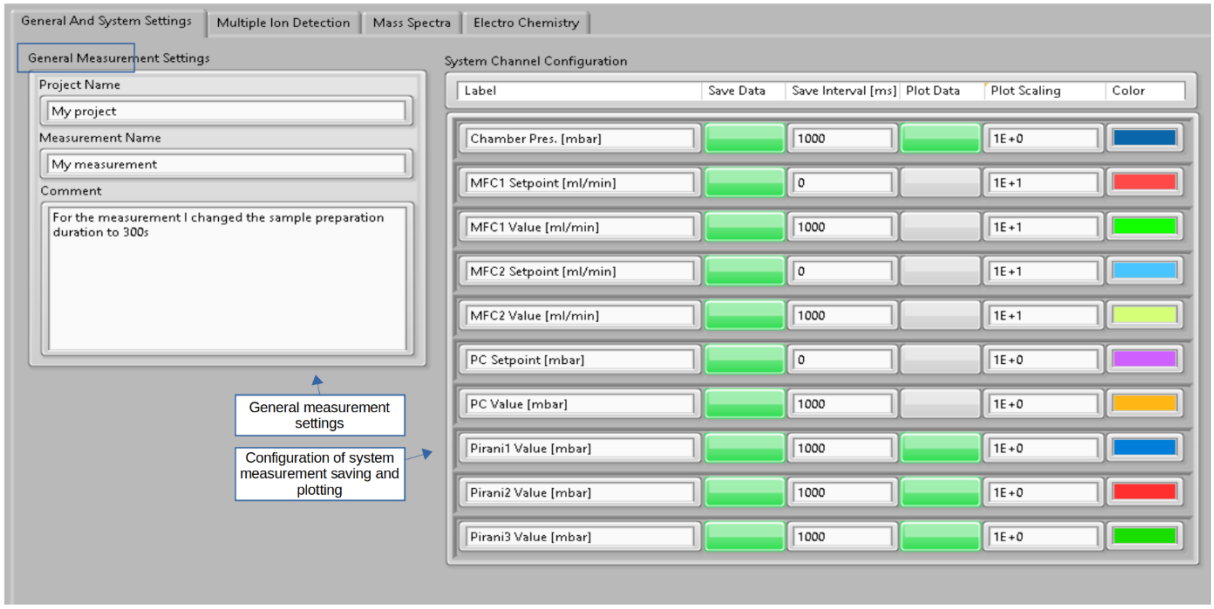

Figure 19. Screenshot of the General and System settings sub-tab within the Measurement Settings tab

In Figure 19 on **the left-hand side are the general measurement settings**. The project name will become the path of the measurement files. The measurement name will be the base of the filename of all files generated within this measurement. Both project and measurement name and comment will be present in the measurements metadata.

In Figure 19 on **the right-hand side are the system channel measurement configuration**. This table is used to configure which system channel will be saved (and how often) and plotted.

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The **Label** column is fixed and cannot be changed. The **Save Data** column indicates whether this system channel will be saved to the measurement file. **Save Interval [ms]** indicates the minimum time interval after which a new point is saved. **Plot Data** indicates whether the channel should be plotted. **Plot Scaling** indicates the factor which values should be multiplied with before being plotted (to allow data with significantly different ranges to be plotted on the same plot). The scaling is not recorded in the datafile, it is merely an internal setting for display within Zilien. **Color** indicates the color used in the plot and clicking this control will make a color selection dialog appear.

6.4.2 The Multiple ion detection sub-tab

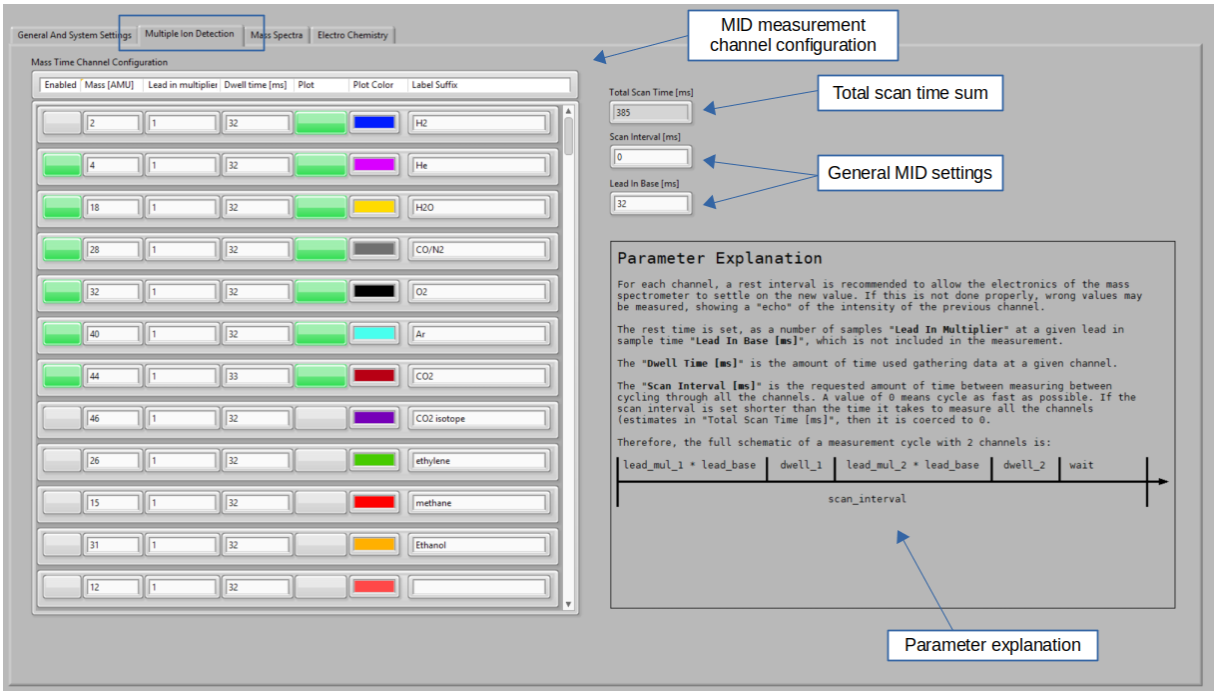

Figure 20. Screenshot of the Multiple Ion Detection sub-tab within the Measurement Settings tab

In Figure 20 on **the left-hand side are the settings for the multiple ion detection measurements**. Each row in the tables corresponds to one out of the 149 usable channels. A description of the columns follows. **Enabled** indicates whether this channel will be measured or not. Disabled channels will not affect the measurement in any way. **Mass [AMU]** is the desired m/z to measure. **Lead In Multiplier** is a multiplier indicating how many times **Lead In Base [ms]** should be multiplied by to give the total Lead In Time. The Lead In Time indicates the amount of time the spectrometer will measure at the given channel before starting the actual measurement. The lead in measurements are not included in the measurement, i.e. they are discarded. This setting is used to allow for spectrometer stabilization upon changing from channel to channel. **Dwell Time [ms]** is the time spent on the actual measurement. **Plot** indicates whether the channel is added to the plot or not. **Plot Color** is the color initially used

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on the plot for this channel and **Label Suffix** is a description added (besides the m/z value) to the label for this channel.

In Figure 20 on **the right-hand side** the **Total Scan Time [ms]** is shown, indicating how much time approximately will be used to measure all the channels with the given settings. **Scan Interval [ms]** is an indication of how often a measurement of **all the channels** should be started. If this value is less than Total Scan Time (plus a little for channel change), then the value will be forced to 0, which means "measure as fast as possible". **Lead In Base [ms]** is the sample time for the lead in measurements, that will not be included in the reported value.

The interplay between dwell times, lead in base and lead in multipliers is explained and illustrated in the **Parameter Explanation** box. The whole point about splitting the time on each channel into the lead in (whose measurements **are discarded**) and the dwell time (whose measurements **are recorded**) is to allow for the electronics to settle in the configuration of the new channel (m/z etc.), and ultimately determines the quality of the Multiple Ion Detection data. If the lead in time is insufficient, the measurements will contain an "echo" of the previous channel. The following test can be performed to establish an appropriate Lead In Time. Set a short dwell time and progressively increase the Lead In Time (given by the product of Lead In Base and Lead In Multiplier). Observe if the changes in Lead In time cause any variation in the measured values. When further increases in Lead In Time cease to affect the measured values, an appropriate Lead In Time has been found.

6.4.3 The mass spectra sub-tab

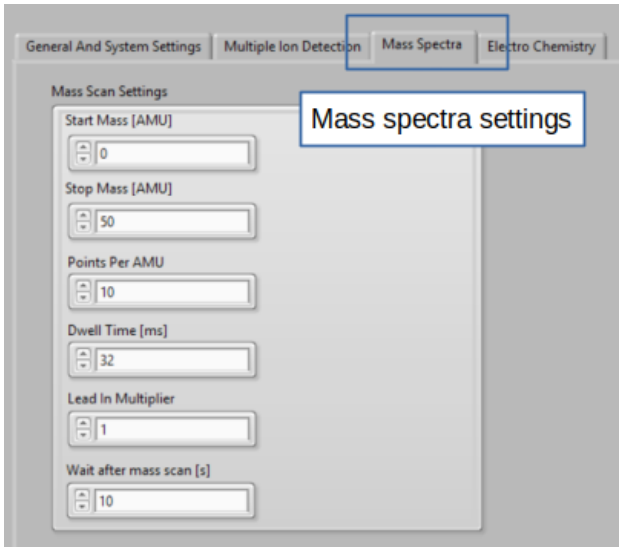

Figure 21. Screenshot of the Mass Spectra sub-tab within the Measurement Settings tab

This sub-tab contains the settings for the complete mass spectra that can be triggered during the measurement. **Start** and **Stop Mass [AMU]** are the start and stop m/z values for the spectrum. **Points Per AMU** is the spectrum resolution, indicating how many points should be measured

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per AMU. **Dwell Time [ms]** and **Lead In Multiplier** are (as in the Multiple Ion Detection sub-tab) the time spent measuring each point and the number of lead in samples spent before the measurements at the Lead In Base given in the Multiple Ion Detection sub-tab.

6.4.4 Electrochemistry sub-tab

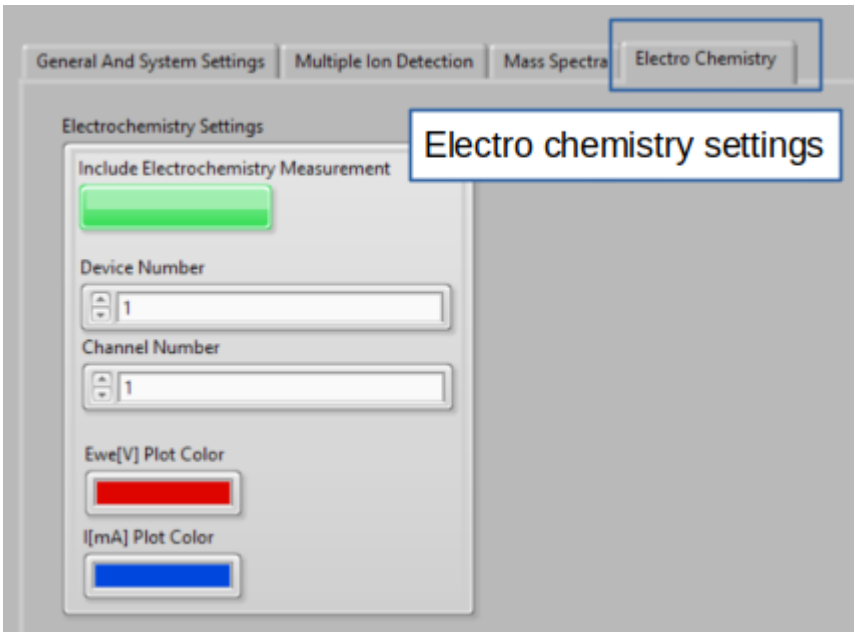

Figure 22. Screenshot of the Electro Chemistry sub-tab within the Measurement Settings tab

The Electro Chemistry settings in Zilien contains only few settings, because the electrochemistry measurement is configured in EC-Lab®. The **Include Electrochemistry Measurement** button is used to enable EC measurements. If the button is not activated, a measurement can be started including Multiple Ion Detection and Mass Scans, but the ability of triggering EC measurements will not be available. **Device Number** is the number of the potentiostat that should be used for the EC measurements. The number can be obtained in the Devices tab in EC-Lab®, starting from 1 as the topmost listed potentiostat. **Channel Number** is the number of the channel on the potentiostat that should be used (in the case of single channel potentiostats, this must be 1). It is important to note, that it is a requirement in order for the overall measurement to start (not the triggered EC measurement) that the configured device is connected, and a channel is chosen. This is checked at measurement start, to ensure that everything is in order for later, so that it is not possible to be denied an EC measurement in the middle of a long measurement series. The **Ewe[V] Plot Color** and **I[mA] Plot Color** respectively indicates the colors used in the plots of the voltage at the working electrode and the current.

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6.5 The global settings tab

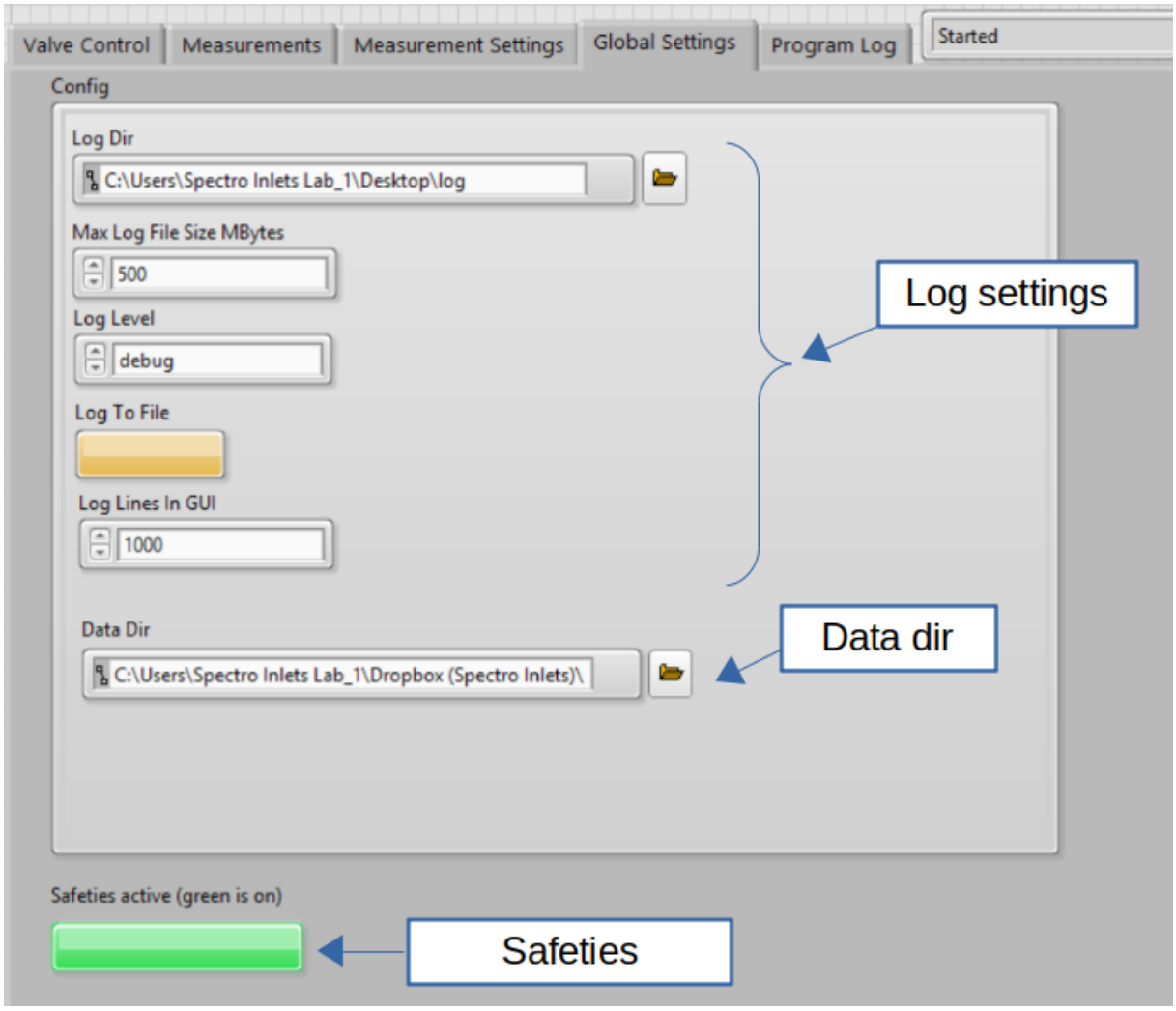

Figure 23 Screenshot of the Global Settings tab in Zilien

The global settings tab contains settings for the program itself. **Log Dir** is the directory to which log files will be written. There are always two log files, the current log file and the old log file. **Max Log File Size MBytes** indicates how large the current log file is allowed to get before it is saved as an old log file and a new one started. **Log Level** indicates the level of log detail that should be shown in the **Program Log** tab, the lower the level the more log messages are shown. The levels (from high to low) are:

Critical (highest)	Only show events that are about to stop the program
Error	Also show recoverable errors and unexpected behaviour
Info	Also show general information events

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Debug (lowest)	Also show (large amounts) of debugging information

The **Log To File** control indicates whether the log also should be written to a file (highly recommended) and finally **Log Lines In GUI** indicates how many lines of the log should be saved on the **Program Log** tab.

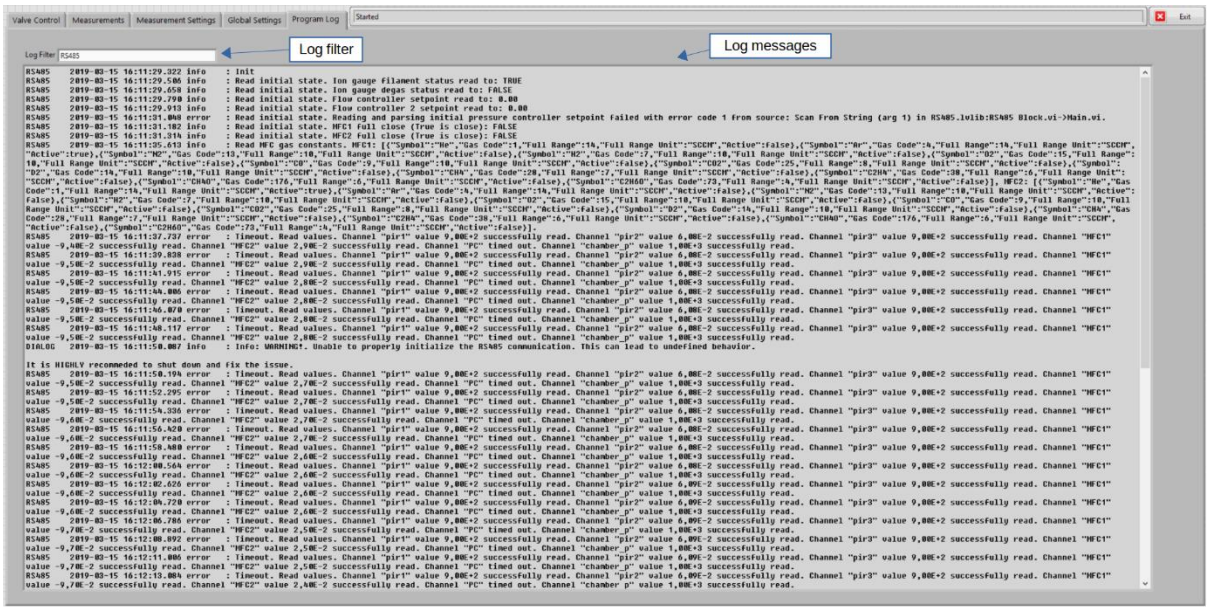
Below the log settings is the **Data Dir**. This is the base directory for all saved data files.

The **Safeties active (…)** control indicates whether the program safeties are active or not. The safeties consist of the following:

- Checks before certain actions like e.g. opening a valve. The check will determine whether it is allowed or should be denied out of concern for the equipment.
- Continuous monitoring of equipment safety critical parameters and taking measures to make the system safe if dangerous values are observed

ATTENTION: It is **HIGHLY** recommended to always run the system with the safeties on during normal operation. However, the safeties should be switched off during complete system shutdown and complete system start-up.

6.6 Log tab



The log tab shows the program log (think of it like a laboratory log book, but for the program) where Zilien writes everything happening within the software. This is useful if, as a user, you are in doubt about what the program is doing, and it is extremely useful if it becomes necessary

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to debug the program. The **Log Filter** is a text input field for a filter term. This gives the option to filter the log messages and only show new messages that contain the filter term.

6.7 Special topics

This section contains in-depth explanation of certain software concepts and procedures.

6.7.1 Save file folder structure

The saved files are organized in the following manner. All saved files are placed under the global data directory in order to simplify backup etc. Under that, a directory is created for each project. If the project name turns out to be ambiguous, consider attaching a user name to the project name. Under the project directory, a directory is created for each measurement. The whole structure therefore is:

[Global data directory] \ [project directory] \ [measurement directory] \ measurement files

The measurement files consist of:

- [measurement name].tsv which is the main Zilien measurement data file
- mass scans\ mass scan started at measurement time [measurement time].tsv which are the triggered mass scan data files
- [measurement name] [EC-Lab suffix].[mpg, mpr, mps] which are the raw EC-Lab® files

6.7.2 Enable Electrochemistry measurements and communications with EC-Lab®

In order to provide the full experimental configurability, the electrochemistry measurements are performed in EC-Lab® and data is pulled into Zilien from EC-Lab®. This requires a data link and care should be taken to use it the right way:

- The Enable Electrochemistry button is used to indicate whether any electrochemistry will be done during the experiment. If it is enabled, the data link to EC-Lab® will be created when the measurement is started. When the data link is created, it is required that EC-Lab® is set up so that it is ready “to press play” on a measurement. I.e., a potentiostat must be connected, a channel selected, and an experiment setup and ready to go. The reason for not forming the data link when Zilien is started is not to require EC-Lab® to be open and configured for experiment if only mass spectrometer measurements are required.
- EC-Lab® should not be closed during an experiment that involves electrochemistry measurements.
- Electrochemistry measurements in EC-Lab® should be **started from Zilien**, using the “Trigger EC measurement now” button.

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- It is not possible to stop a measurement in EC-Lab® from Zilien. Therefore, EC experiments either run to an end, or they must be stopped in EC-Lab®

6.7.3 End of measurement and temporary files

During a measurement all measurement data is continuously written out to temporary files. This means that in case of e.g. software or computer problems or a power outage, everything but the last few seconds of data will be available in these temporary text files (but it will require a little bit of programmatic processing in order to extract the data sets). When the measurement is ended, the temporary files will be processed, and the data will be gathered into the permanent data file. This process takes a few seconds, which is the reason that the **Start Measurement** button is not available immediately after experiment end. The status message "Measurement has ended" will appear in the status field when the data has been processed and the experiment completely ended. If the measurement is very large, spanning days, processing temporary data in permanent data files will take a little while and progress messages will be displayed in the status field.

6.7.4 Program shutdown

The software should always be shut down with the **Exit** button, for all program components and equipment links to be terminated properly. Measurements should be fully ended before the program is stopped.

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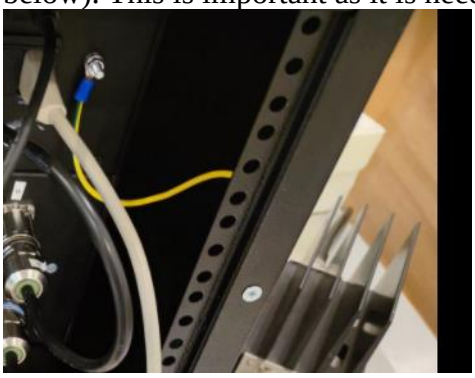
7 How to install and start the full system

7.1 Connections

- Connect power to lab computer, start it and install all necessary drivers
- Connect the electronics box to the computer, but do not power the box yet
- Connect the instrument with the electronics box while the box is not connected to the mains power supply. Ensure that all cables are connected to the electronics box. Cables and connectors are color-coded, with three different colors and three different pin counts: 7-pin, 9-pin, and 17-pin. There is no specific position for each cable, if connector type and color match.
- IMPORTANT. Connect the rack earthing wire to the earthing pin on unit I (see picture below). This is important as it is needed to ensure electrical safety of the setup.



- Connect the instrument to the scroll pump using the supplied KF25 corrugated hose.
- Connect pressurized air using a 6 mm tube on the push-in connector on the back panel of the instrument. Pressurized air supply must be at least 4 bar. Pressure must be supplied before turning on the system.
- Connect potentiostat, electronics box, and scroll pump to the mains power supply.
- Connect He supply to the bulkhead connector. Refer to Section 13.2 before pressurizing the line.
- Optionally, connect other gas supplies.
- Turn the electronics on using the power button on the front panel (step 1 in Figure 24)
- Turn the switch on the front panel (step 2 in Figure 24)
- Wait 15 seconds before starting the Zilien software
- In the main tab in Zilien, make sure the configuration is as shown in Figure 24d
- Turn on roughing pump by pressing the green button on the pump controller (step 3 in Figure 24).
- Set the pressure controller to 1000 mbar.

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ATTENTION: The PC resets to 0 every time the system is powered off. When Zilien is started, the PC reading may not be accurate, so set it to 1000 mbar anyway.

- Turn on turbo pump by pressing the power button on the front panel controller (step 4 in Figure 24)

ATTENTION: The turbo pump is equipped with a venting valve which is open by default if the turbo pump is off. As soon as the turbo pump is started by pressing the power button (step 4 in Figure 23), the venting valve will close.

- Make sure Pirani 1 drops below 1 mbar.
- Wait for the pump to be running at full speed, as shown in Figure 24c
- Check pressures in the main tab in Zilien (see Figure 24d)
- Wait until the pressure in the main chamber falls below 1E-6 mbar
- Turn on the MS filament
- Turn on the MS multiplier
- Wait for the MS to stabilize, ideally for a minimum of 24 hours. The instrument can be used immediately, but stability will be compromised.

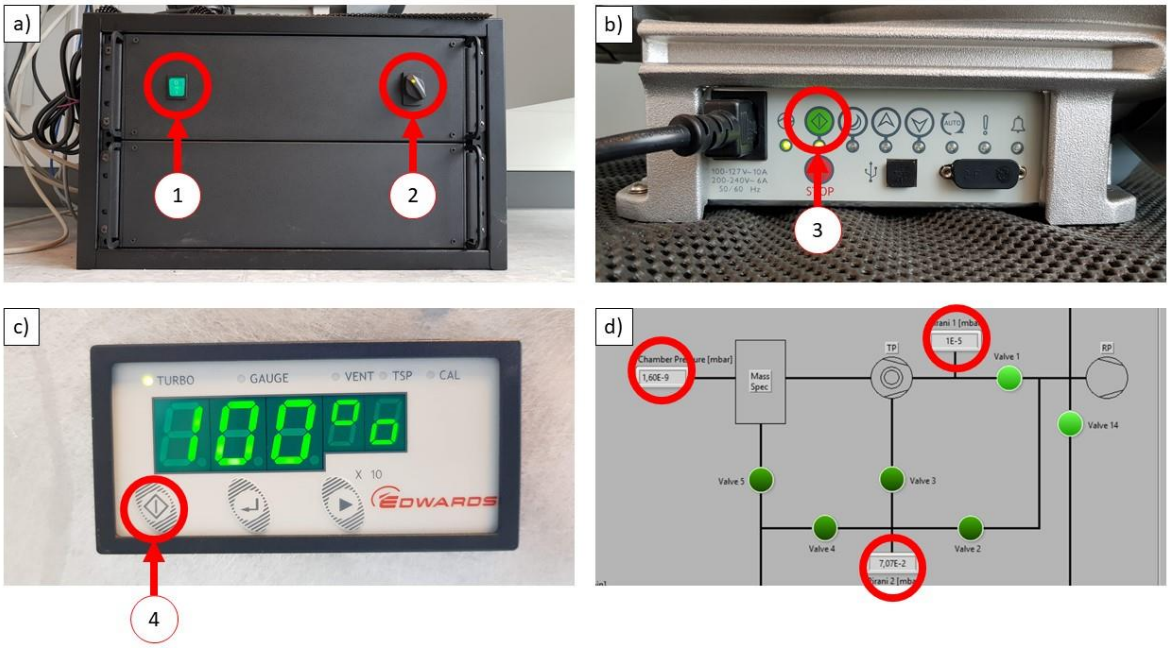

Figure 24. Instrument start-up

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8 How to shut down the system

- Go to main tab in Zilien
- V5 shall be closed and the system shall be in safe state (Figure 27)
- Deactivate mass spectrometer Multiplier
- Deactivate mass spectrometer Emission
- Go to the Global Settings tab in Zilien
- Deactivate System safeties. The button should turn red.
- Go to the main tab in Zilien
- Shut off V1 and V14
- Shut down turbo pump
    - Press button 4 in Figure 24
    - “Stop” will appear on the controller display
    - Press the enter button (in the middle)
    - The controller will display 100 %, where the lowest of the percent sign zeroes blinks, indicating the pump is spinning down
    - The pump speed will slowly decrease until 50%. When 50% speed is reached, a venting valve will open, and the speed will rapidly decrease to 0%.
- Wait until the pump has fully stopped. The chamber is now at atmospheric pressure.
- Stop scroll pump pressing the red Stop button on the pump controller.
- Exit Zilien
- Switch the electronics control box off. First the rotating switch (marked 2 in Figure 24), then the main power button (marked 1 in Figure 24).

9 How to install/exchange a chip

WARNING: Removing the chip (#2 in Figure 6), will vent the lines connected to the interface block. Therefore, it is important that the high-vacuum equipment is protected. Valves 4 and 5 must be closed, or the system must be off (pumps not running, filaments off etc.).

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ATTENTION: The chips are chemically resistant and can last a long time. However, using different electrolytes and electrodes might introduce some cross-contamination. We recommend dedicating different chips to specific working conditions.

ATTENTION: A non-airtight chip connection may be caused by worn O-rings, dust on the O-rings, or a cracked chip. For further details, refer to the troubleshooting section (Chapter 12).

WARNING: Incorrect alignment of the chip might lead to no signal in the mass spectrometer or leak through the gas channels.

Replacement of an installed chip in the interface block can be performed following the steps below. If no chip is installed in the interface block, and it is only needed to install a new chip, skip directly to step 6.

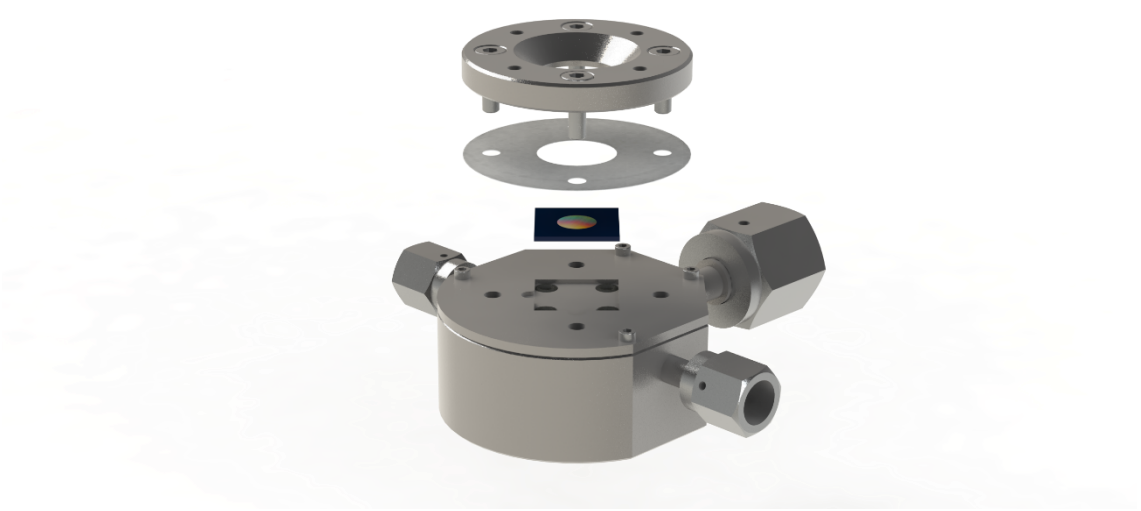

Figure 25: Installation of a membrane chip.

1. Make sure the high-vacuum equipment is either sealed off from the interface block, using e.g. a valve, or that it is turned off/spun down.
2. Bring the system to the state shown in Figure 27 by following these steps
    a. Close V5

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b. Set PC to a pressure greater than 1100 mbar and then set the Valve Override mode to “Flow Off” to fully close it.
c. Stop gas flow through both MFCs by setting the flow to 0.0 and set the Valve Override Mode to “Flow Off”
d. Open V14

3. Detach the clamping ring. Use a 2.5 mm Allen key to unscrew the four M3 screws (#11 in Figure 6) used to fix the clamping ring (#6 in Figure 6) to the interface block.
4. Remove the PTFE spacer
5. Remove the chip (#2 in Figure 6) with tweezers, using the notches in the steel plates (#3 and #4 in Figure 6). Be aware that the chip may stick to the interface block, due to the vacuum on its back side.
6. Make sure the 2-mm O-rings (#10 in Figure 6) are correctly placed in the holes of the steel plate (#5 in Figure 6), and that they are free from dust or defects.
7. In case the O-rings are dirty, extract them with a tweezer and wipe them clean with lens paper and ethanol or isopropanol. Do not use acetone.
8. In case the O-rings are defective, exchange them.
9. Beware not to scratch the polished metal surface under the O-rings. A scratched surface may compromise sealing.
10. Insert a new chip, checking that the holes in the chip are aligned to the holes in the interface block (Figure 25)
11. Place the PTFE spacer onto the interface block, aligning the holes in the spacer with those on the block.
12. Place the clamping ring onto the interface block and tighten the four M3x8 screws in a criss-cross pattern. Maximum tightening torque: 0.1 Nm.
13. Activate the pumpdown procedure in Zilien
14. Alternatively, the pumpdown may be carried out manually as follows:
    a. Start from safe state (Figure 27 and Figure 28 a).
    b. Close V1 and V14.
    c. Open V2.
    d. Open V4 (Figure 28 b).
    e. Wait until Pir 2 falls below 1E-2 mbar.
    f. Open V3.
    g. Close V2 (Figure 28 c).
    h. Open V14. Wait until Pir 3 falls below 1E-2 mbar. V14 connects the pressure controller to the scroll pump. If pressure builds up between V14 and the pressure controller while V14 is closed, it is important that the line gets evacuated before opening to V1 to avoid a pressure burst in the backing line to the turbo pump.
    i. Open V1 (Figure 28 d).
    j. Wait until Pir 2 falls below 4E-3 mbar.
    k. Open V5.
    l. Close V4.
    m. Close V3.

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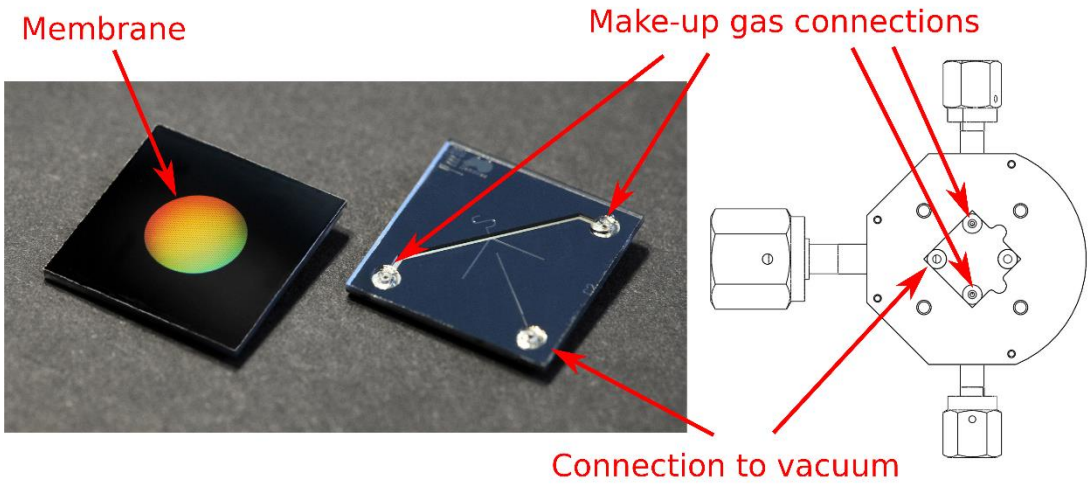

Figure 26: Image of the membrane chip and its correct alignment. When mounted onto the interface assembly the membrane should be facing upwards and the vacuum connector on the chip should be aligned with the vacuum connector on the interface block.

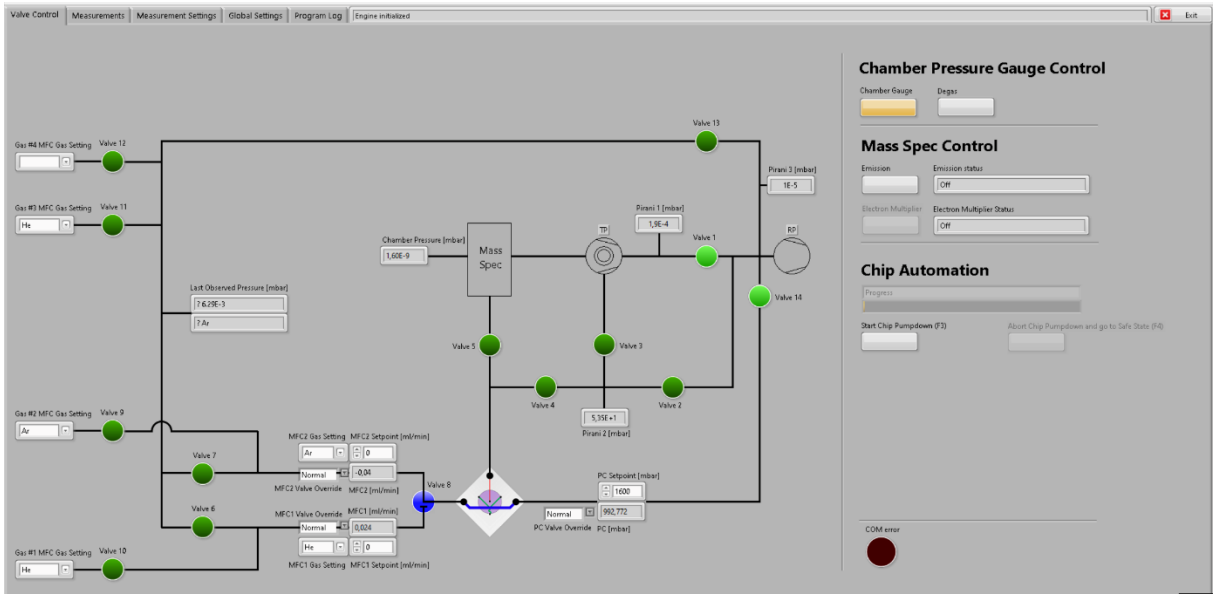

Figure 27. Basic safe state.

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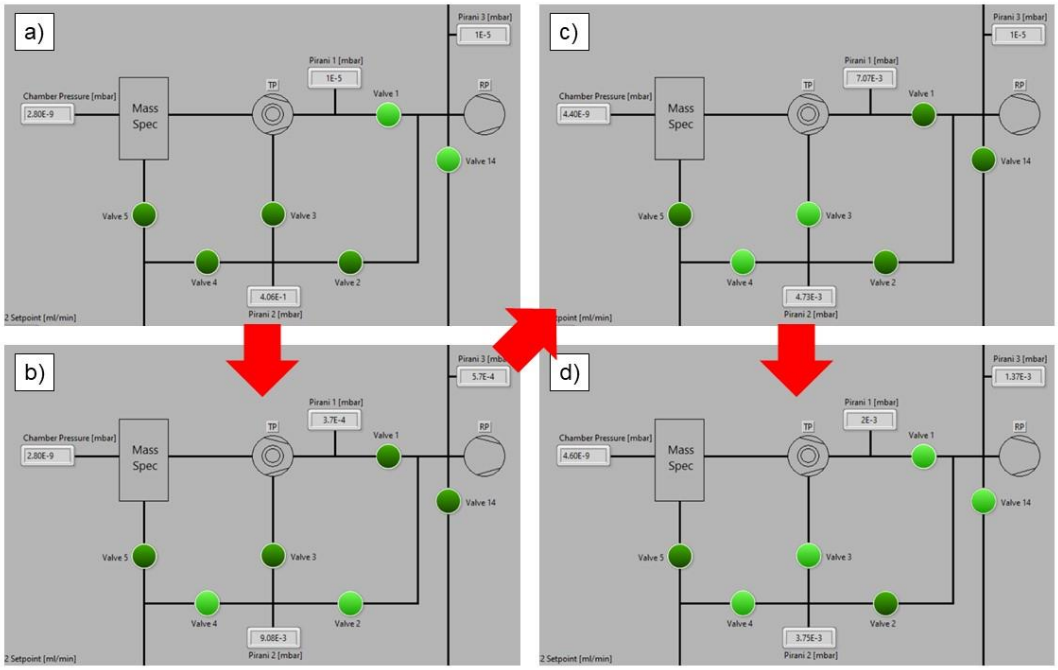

Figure 28. Manual pumpdown procedure

10 How to perform breath and drop tests

The following two tests can rapidly provide information about the state of the inlet system, thus they serve as a handy tool for troubleshooting.

1. The main chamber pressure with a working chip open to air is approximately 2E-6 mbar
2. With a chip open to atmosphere, start a measurement in Zilien and follow the levels of He (4 amu), H_2O (18 amu), N_2 (28 amu), O_2 (32 amu), and CO_2 (44 amu) as a function of time.
3. Set a He flow of 1 sccm/min and a pressure of 1 bar and remove anything covering the surface of the membrane.
4. The mass-time plot should show the expected values in air. If you record a mass spectrum as well, you should see an air spectrum appear.
5. Exhale onto the chip, and rapidly fan with your hand to mix air over the chip. You should see the CO_2 or Ar signal spike and decay relatively fast. When exhaling on the chip, the H_2O signal should increase, whereas the O_2 and N_2 signals should decrease, but less drastically. In case of using Ar, all H_2O, N_2, and O2 signal should decrease.
6. Using a pipette, put a small droplet of clean water on the chip covering the entire membrane. You should see a rapid change in the mass signals. In particular, the He signal should dominate, while the O_2 and N_2 signals should drop significantly. The H_2O signal should also increase if the system is sufficiently water vapour-free.

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7. The main chamber pressure with a working chip covered with water is approximately 5E-7 mbar. If the chip is breached, the main chamber pressure rises higher than 1E-5 mbar and the water signal usually increases greater than that of He.
8. The remaining O_2 and N_2 signal are due to diffusion through the droplet. The difference between the H_2O signal under the droplet and in the air should correspond to 100% minus the relative humidity in the room (given that the vacuum chamber and gas lines are water vapour-free).

This experiment is described in greater detail in[2] and an example dataset is shown in Figure 29.

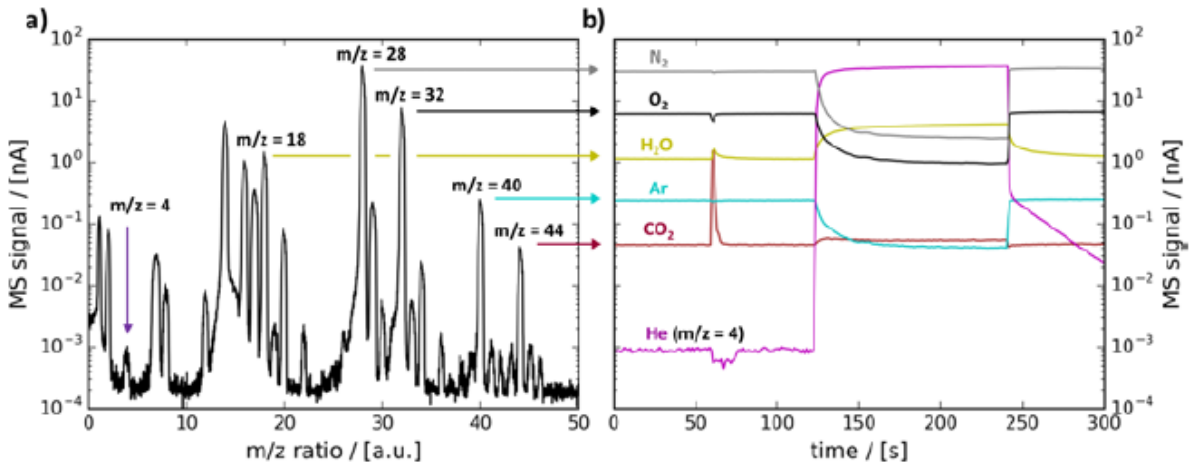

Figure 29: **a)** Air spectrum recorded through a membrane chip before placing a water droplet onto the membrane, **b)** Recording of the signals of He, N_2, O_2, H_2O, Ar and CO_2 as a function of time. At t ≈ 60 s the user exhales on the chip showed by the increase of the H_2O and CO_2 signals and the decrease in the O_2 signal. After placing a droplet of water on top of the membrane, the water equilibrates with the sampling volume under the membrane and the make-up gas (He) fills the pressure up to 1 bar. This experiment also provides indication of the time-response of the system showed by the near instantaneous changes.

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11 How to mount electrodes and prepare EC experiments

11.1 Cleaning the EC cell

If ultraclean EC experiments are required, we recommend following this procedure.

 **WARNING**: This procedure involves very hazardous chemicals and procedures. The operator must be properly trained, protected, and aware of the danger before performing this procedure.

 **WARNING**: Only components made of glass (preferably borosilicate), PTFE and PCTFE can be exposed to piranha solution.

1. Prepare fresh piranha solution (concentrated sulfuric acid and 35% hydrogen peroxide in a 3:1 ratio)
2. Clean all the glassware that will be in contact with the electrolyte and the electrode using the solution by filling the glassware with piranha solution and letting rest for at least 30 min, better overnight.
3. Clean U-cup, fluidic fittings, EC cell, and Teflon tweezers by submerging them with piranha solution and letting rest for at least 30 minutes, better overnight.
4. Rinse all the equipment with abundant Milli-Q water at least 4 times
5. Boil all the equipment in Milli-Q water for 5 minutes and discard the water
6. Keep all the clean equipment submerged in Milli-Q water until they are used
7. Blow-dry equipment thoroughly prior to installation

 **ATTENTION**: The pressurized gas used for blow-drying should be oil- and particle-free to avoid contamination

11.2 Assembling the EC cell

The EC cell consists of the disk core assembly and the cell described in Chapter 5.5.4. The following sections and Figure 30 describe how to assemble the EC cell before a measurement.

For additional information on the disk core assembly we refer to the description from Pine Research Instrumentation[1].

1. Prepare a clean working surface where to rest all the materials. We recommend using a clean piece of aluminium foil.
2. Place a PTFE U-cup and the U-cup nut on the disk contact core and tighten the nut as shown in Figure 30 a.
3. Place the working electrode with the active surface facing down in the small circular groove in the mounting block as shown in Figure 30 b. The mounting block is designed to minimize surface exposure of the electrode during mounting, thereby preserving a clean surface. Alternatively, a clean planar surface can be used (such as an upside-down glass petri dish covered with aluminium foil).
4. Slide the U-cup assembly onto the electrode as shown in Figure 30 c and d. Since the U-cup is larger than the electrode, at this stage the electrode is not retained by the U-cup assembly and is still free to fall off. Leave the U-cup assembly on the mounting block as shown in Figure 30 d.
5. Slide the EC-cell onto the U-cup assembly (Figure 30 e). Push the EC-cell down until it grips the U-cup and the contained electrode. Just push enough that the electrode does not fall off. This will make sure that the U-cup assembly stays in the EC cell when the mounting block is flipped in the following step.
6. Turn the mounting block to expose the larger groove (Figure 30 f).
7. Insert the Cell into the mounting block groove (Figure 30 g).
8. Push the electrode into the U-cup but leave the U-cup out of the cell. In this phase, use a finger to apply pressure on the shaft, and do not apply pressure on the cell (Figure 30 h).
9. Push electrode together with U-cup into the cell (Figure 30 i). The goal is to bring the surfaces of electrode, U-cup, and EC-cell exactly flush.
10. Make sure that the surface of the electrode and the edge of the U-cup is flush with the bottom surface of the stagnant thin-layer EC cell (Figure 31). We recommend no more than ± 10 µm difference in height. If the electrode or U-cup is sticking out, there is a risk of breaking the chip. If the electrode surface is indented with respect to the EC cell surface, the reaction volume is larger, thus lowering the time resolution.
11. Inspect the result with a magnifying glass. If the result is not satisfactory, repeat the insertion until a perfectly flush surface is obtained.

[1] https://www.pineresearch.com/shop/wp-content/uploads/sites/2/2016/07/DRP10047-Electrode-Information-E5TQ-Series-REV005.pdf

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12. Place the U-cup spacer and nut on the threaded end and slightly tighten them to keep the shaft fixed. Tightening the nut moves the U-cup and electrode assembly further into the flow cell. This can also be used to change the alignment.
13. Install the 10 mm O-ring into its groove at the bottom of the flow cell using a pair of tweezers. Place the O-ring on the groove (Figure 32) and press the cell into the mounting block (Figure 30j) Be careful not to touch the active surface of the working electrode.
14. For installation of the cell onto the interface assembly, see Chapter 11.3.

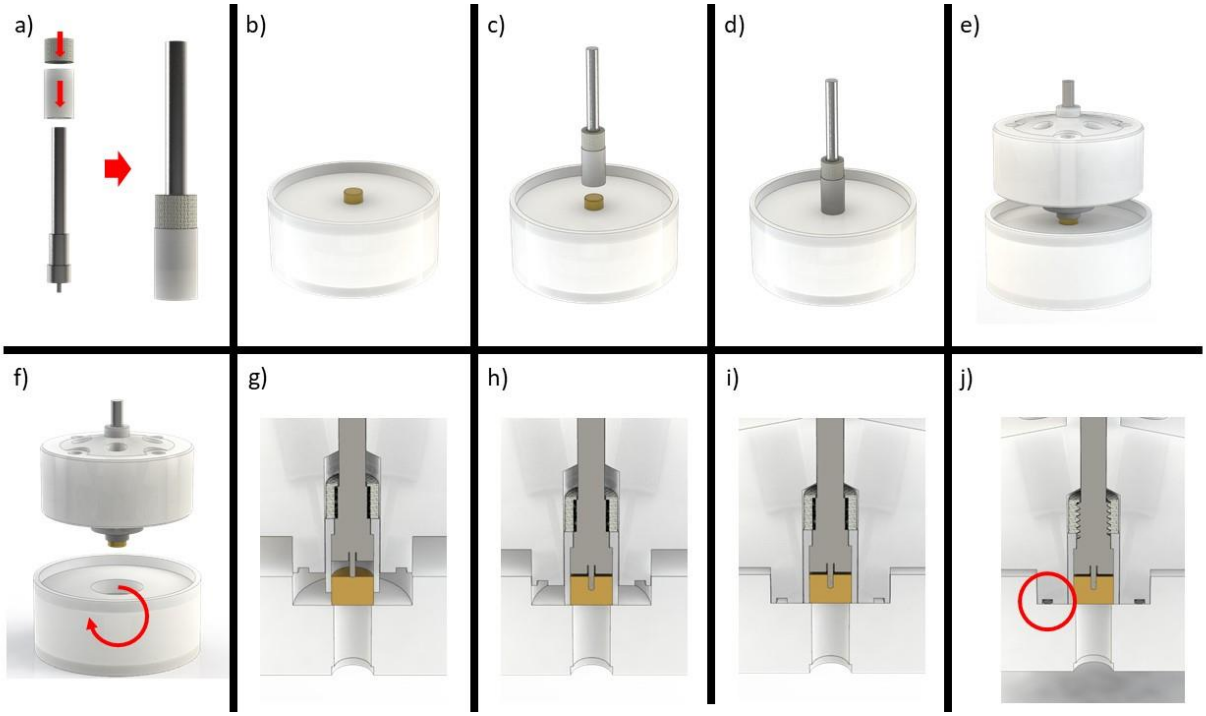

Figure 30: Assembly of the EC cell.

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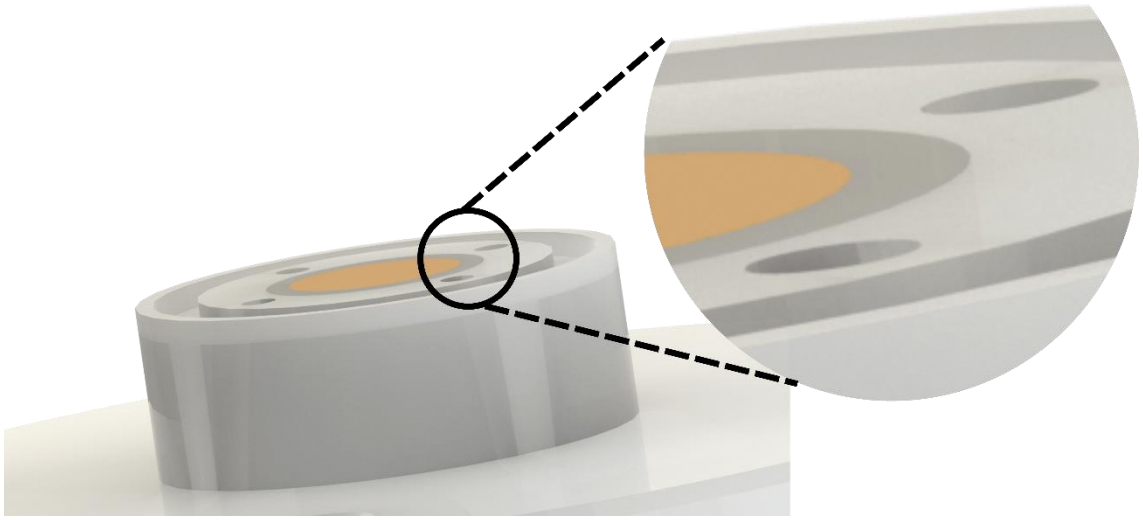

Figure 31: Make sure that the bottom surface of the stagnant thin-layer EC cell, the active surface of the working electrode and the U-cup is aligned and flush.

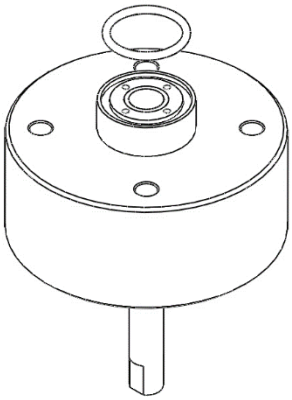

Figure 32: Installation of the O-ring to the EC cell.

ATTENTION: Trying to mount the EC cell with U-cup and/or working electrode protruding out from the bottom face of the cell more than 100 µm can lead to microchip cracking. Due to the tight tolerance, we recommend checking the alignment of the surfaces with a microscope or loupe.

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11.3 Installing the EC cell

Once the working electrode is mounted into the EC cell, the cell can be installed on the interface block using the four M3x20 screws.

1. Place the EC cell concentrically onto the clamping ring with the working electrode facing downwards.
2. Insert four M3x20 screws with washers
3. Tighten the M3x20 screws in a criss-cross pattern. Recommended tightening torque is 10 Ncm.

 **ATTENTION**: Always mount the EC cell when it is dry. Experience shows that filling up a cell with electrolyte without bubbles is challenging if residual water is present on the cell.

11.4 Filling up the EC cell with electrolyte and attaching reference and working electrodes

 **WARNING**: The EC cell is equipped with 4 1/4”-28 UNF threaded connectors, for attaching reference and counter electrodes, and filling it up with electrolyte. One of these must be open to atmosphere all the time, to avoid overpressure build-up in the reaction volume. The chip might breach and become unusable if the pressure of the electrolyte becomes higher than the pressure in the gas lines.

 **ATTENTION**: In case the O-ring is not seated properly into its groove or the screws attaching the flow cell to the clamping ring are not sufficiently tight, electrolyte might seep out of the reaction volume. In case this happens, try tightening the screws or remounting the EC cell. If this does not solve the problem, replace the O-ring.

 **ATTENTION**: Ensuring that air bubbles are not trapped in the flow cell is crucial in order to get good conductivity and reproducible experimental results. Make sure that bubbles are not pushed or transported into the flow cell when filling it up with electrolyte. Finding the best way to fill up the cell with electrolyte requires some experimentation from the user.

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1. Either before or after mounting the EC cell, install the provided fluidic fittings into the flat-bottomed 1/4”-28 UNF threaded holes (see Figure 33 a). Mount two female luer fittings opposite to each other for the reference and counter electrodes, and two other fittings in the remaining threaded holes for electrolyte in- and outlet. The inlet and outlet fittings can be either male or female, depending on the chosen filling method. In Figure 33, two male luer fittings are shown as an example.
2. Through the chosen inlet, fill the EC cell with electrolyte until the fluid oozes out of the three remaining adapters (a liquid meniscus should be visible). Due to the small internal liquid pathways, a certain amount of pressure must be applied for the filling procedure. This can be achieved with a syringe or by gravity using a d. However, the overpressure cannot exceed approx. 200 mbar, as this may cause the electrolyte to breach the membrane. Two different filling methods are shown in Figure 34 and Figure 35. In Figure 34 a burette equipped with a stopcock is used to fill the cell by gravity, and the output port in the EC cell is connected to a beaker to collect excess electrolyte.
3. Fill the glass tubes with electrolyte.
4. Fill the Luer tip cavity of the glass tubes with electrolyte. This can be done using a syringe needle. It is essential that no bubble is left between the ceramic frit and the tip of the tube. A liquid meniscus should be visible at the tip.
5. Insert the glass tubes in the female fittings on the EC cell. Make sure that the liquid menisci on the tubes contact those on the fittings, to avoid trapped air bubbles.
6. Insert counter and reference electrodes inside the glass tubes.
7. Connect the working electrode using a crocodile clip on the nut on top of the EC cell.

NOTE: Using a burette and gravity to fill up the EC cell ensures that the pressure in the liquid lines can be accurately controlled, thus the chip will not breach during fill-up. Using a syringe requires experimentation and some practice.

ATTENTION: The order of connection of working, counter, and reference electrodes (WE, CE, and RE, respectively) is not irrelevant. To avoid potential jumps and current flows, we recommend mounting electrodes in this order: CE→RE→WE.

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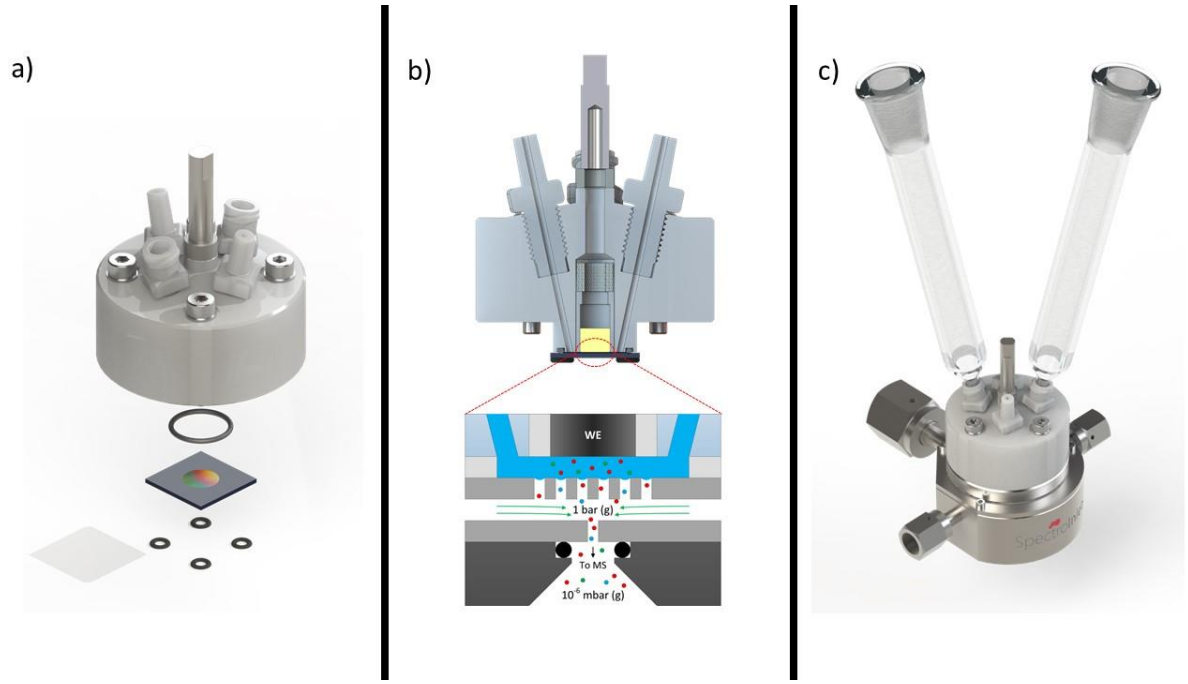

Figure 33: a) mounting of the EC cell onto membrane chip, b) cross-sectional view of the assembled EC cell. c) The electrochemical cell mounted on the interface block and equipped with two glass compartments for reference and counter electrode, respectively.

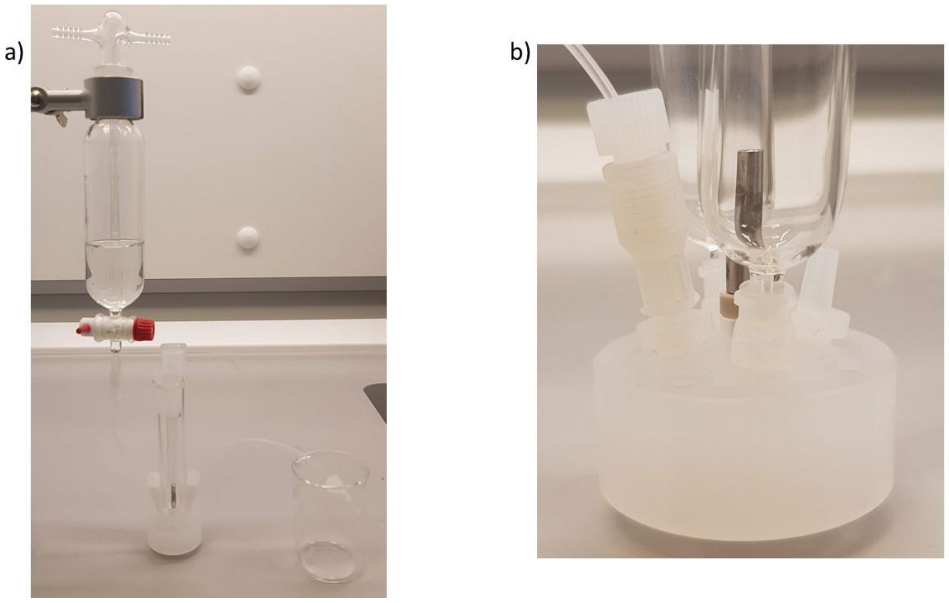

Figure 34: EC cell connected to burette for electrolyte filling. The burette can be used to flow electrolyte if the cell is used in flow mode. In this example, the EC cell is equipped with two female and two male luer connectors. The shown burette is equipped with a bubbler, so electrolyte purging can be carried out.

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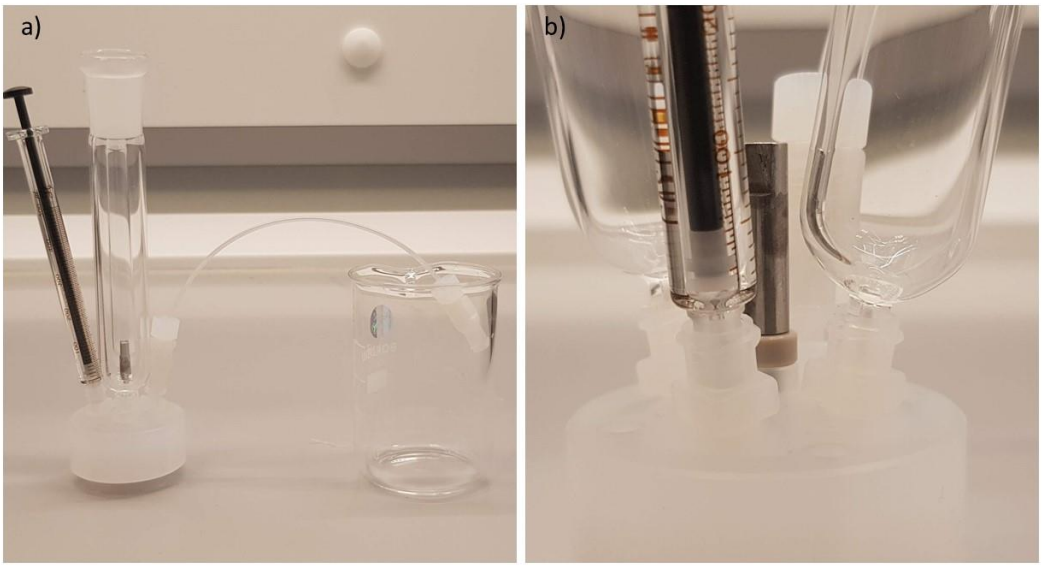

Figure 35: EC cell connected to a gas-tight syringe for filling electrolyte in controlled quantity. In this example, the cell is equipped with three female and one male luer connectors.

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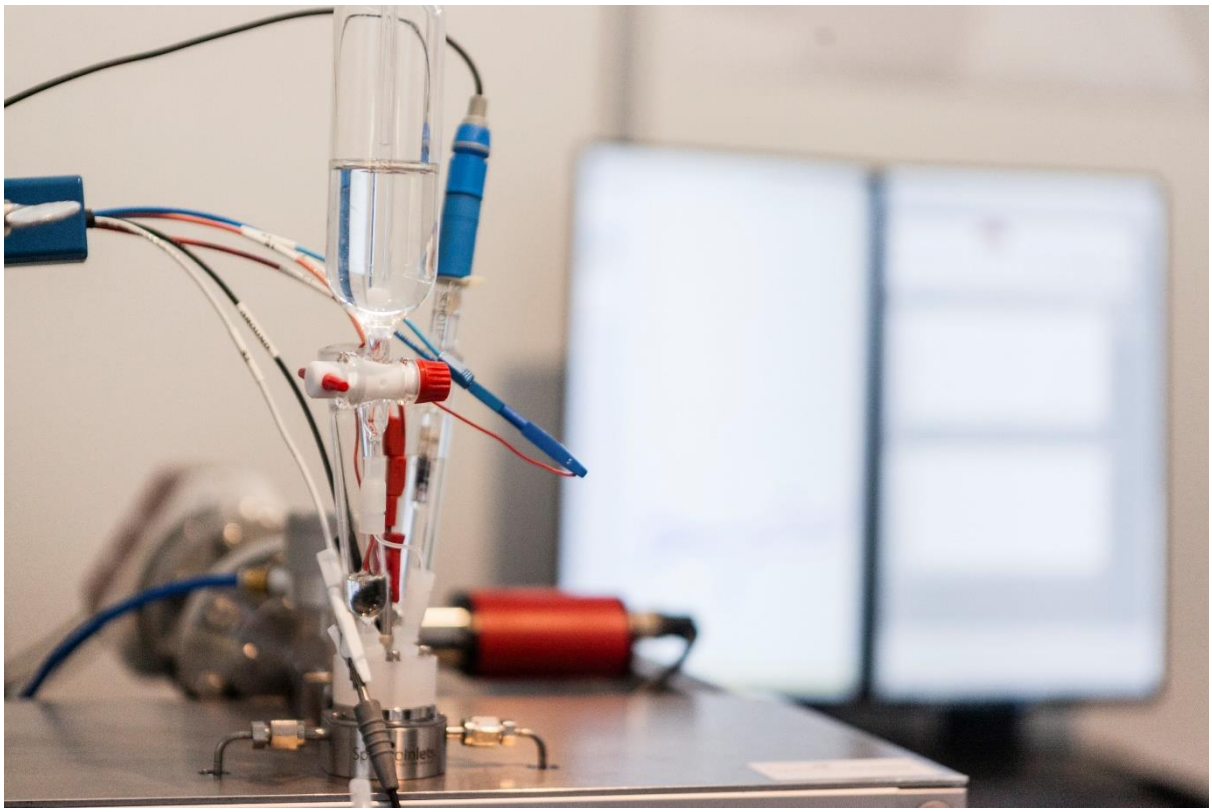

Figure 36. Photograph of the EC cell equipped with a B 3420+ Ag/AgCl electrode, a coiled Pt wire as counter electrode, and an electrolyte reservoir.

11.5 Dismounting the EC cell from the interface assembly

After finishing an experiment, remove the residual electrolyte before detaching the EC cell. There are multiple options to remove the residual electrolyte after an experiment:

- If a syringe was used to fill up the EC cell, it can be used to syphon the electrolyte away. In this method, most of the electrolyte can be removed from the cell and possibly reused. This can be useful when using expensive, isotopically labelled electrolytes.
- The electrolyte can be rinsed off by flowing ultrapure water via the inlet and collecting the excess.

Alternatively, the EC cell can be dismounted by unscrewing the four M3x20 screws attaching it to the clamping ring. After removal, the residual electrolyte or liquid in the cell forms a droplet in the middle of the chip which can be soaked up with a lens tissue.

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After removing the EC cell and drying up the remaining electrolyte, the chip should be rinsed by placing a clean water droplet on the surface and soaking it up multiple times.

 **ATTENTION**: After removing the EC cell, rinse it thoroughly with clean water to get rid of residual electrolyte. Due to the small liquid pathways, electrolyte drying into the EC cell can block these lines completely due to residual salts. The best way to ensure thorough rinsing is to flow a small stream of clean water on the working electrode, while the cell is turned upside down (working electrode facing upwards). This way the water is removed from the surface through the small electrolyte channels, rinsing them thoroughly. We recommend placing the cell into a drying cabinet to ensure it is completely dry at the next experiment.

11.6 Dismounting a working electrode from the EC cell.

In order to dismount the U-cup shaft from the flow cell:

1. Untighten the U-cup nut fixing the shaft, but do not remove it completely.
2. Turn the flow-cell upside down, place the upper cup of the nut on a hard surface, e.g. the experimental table, and slightly push down on the cell. The shaft should come loose.

 **ATTENTION**: When removing the U-cup shaft, the working electrode may be ejected due to the spring-loaded pogo pin in the disk contact core. We recommend restraining the electrode using clean gloves or tweezers.

 **ATTENTION**: The fluidics connectors and lines should be thoroughly rinsed to avoid salt formation and blockage of flow paths. After rinsing, we recommend placing all these components into a drying cabinet for storage.

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12 How to run an experiment using Zilien

In this section, a brief step-by-step guide on how to use Zilien is provided. Please refer to the Software Section for further details.

- Once the cell is mounted as described previously, an electrochemistry experiment can commence.
- Go to measurement tab → Multiple Ion Detection in Zilien (Figure 37)
- Start EC-lab. We recommend having EC-lab and Zilien on two separate screens
- Input the desired parameters for the electrochemical experiment in EC-lab. Do not press play in EC-lab.
- Input the desired measurement parameters in Zilien
- Go to Measurements tab in Zilien (Figure 38)
- Click on Start measurement
- When desired, click on "Trigger EC measurement now" to start the EC-lab recipe. Data will be visualized in the Potentiostat panel within the Measurements tab
- A full mass spectrum acquisition can be triggered at any time by clicking on "Trigger mass scan now"
- Follow the experiment. When the experiment is over, click Stop measurement.

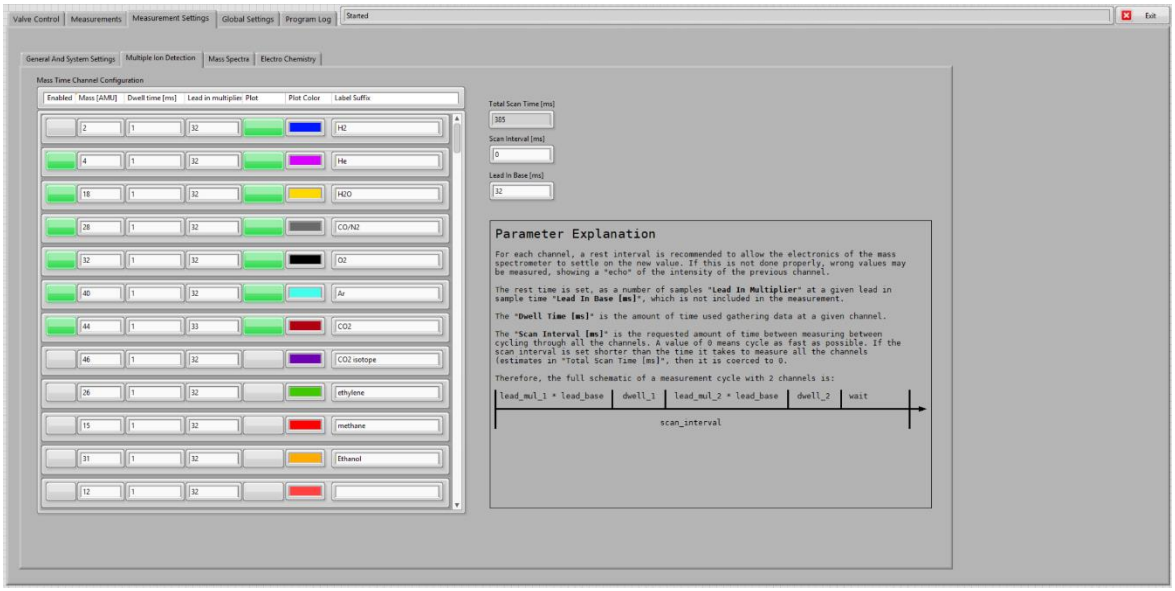

Figure 37: Measurement Settings → Multiple Ion Detection tab in Zilien. Here the user can select the desired m/z values to be measured and displayed, choose the lead in and dwell times for each of them, assign trace colors, and labels.

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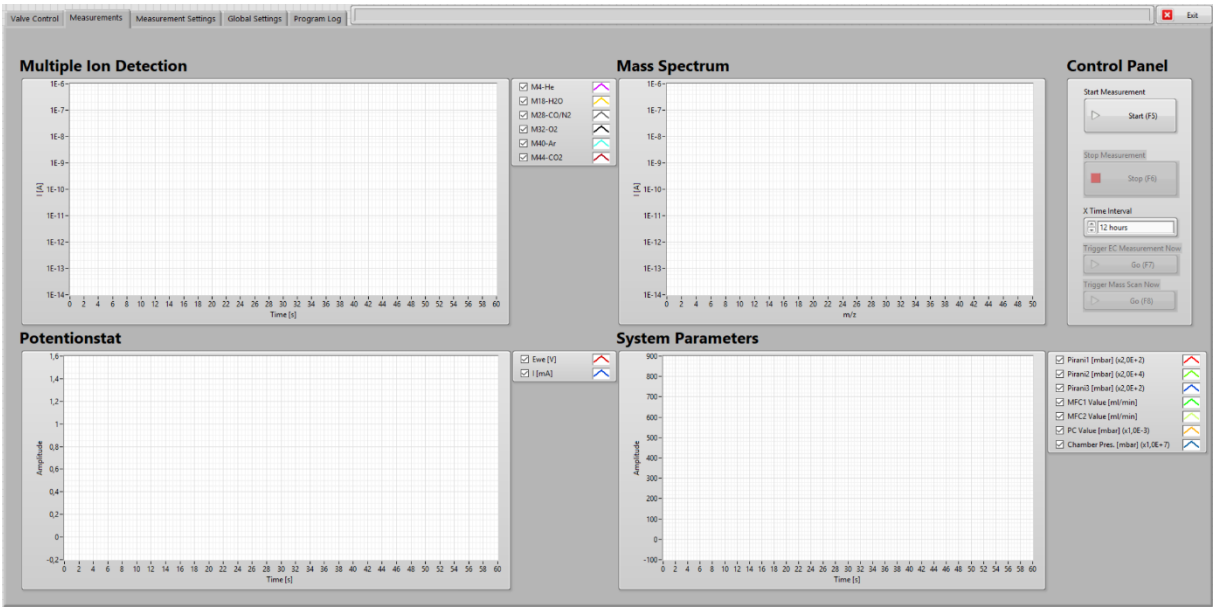

Figure 38. Measurements tab in Zilien. Here, synchronized MID, potentiostat, and system parameters data are shown. Acquisition of a full mass spectrum and electrochemistry recipes can be triggered at any time with a click.

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13 How to perform gas exchange

In a standard experiment, He is used as make-up gas. The Spectro Inlets system allows switching of the make-up gas with up to 3 different gases.

The user must exercise caution when using hazardous gases such as CO or H_2. Such gases must be flown only if a liquid is covering the chip surface, e.g. with the EC-cell mounted and filled with electrolyte, or if point suction is applied in proximity of the interface block. If the chip surface is exposed to air, gas will diffuse to the environment. Furthermore, the scroll pump exhaust must be connected to ventilation as well.

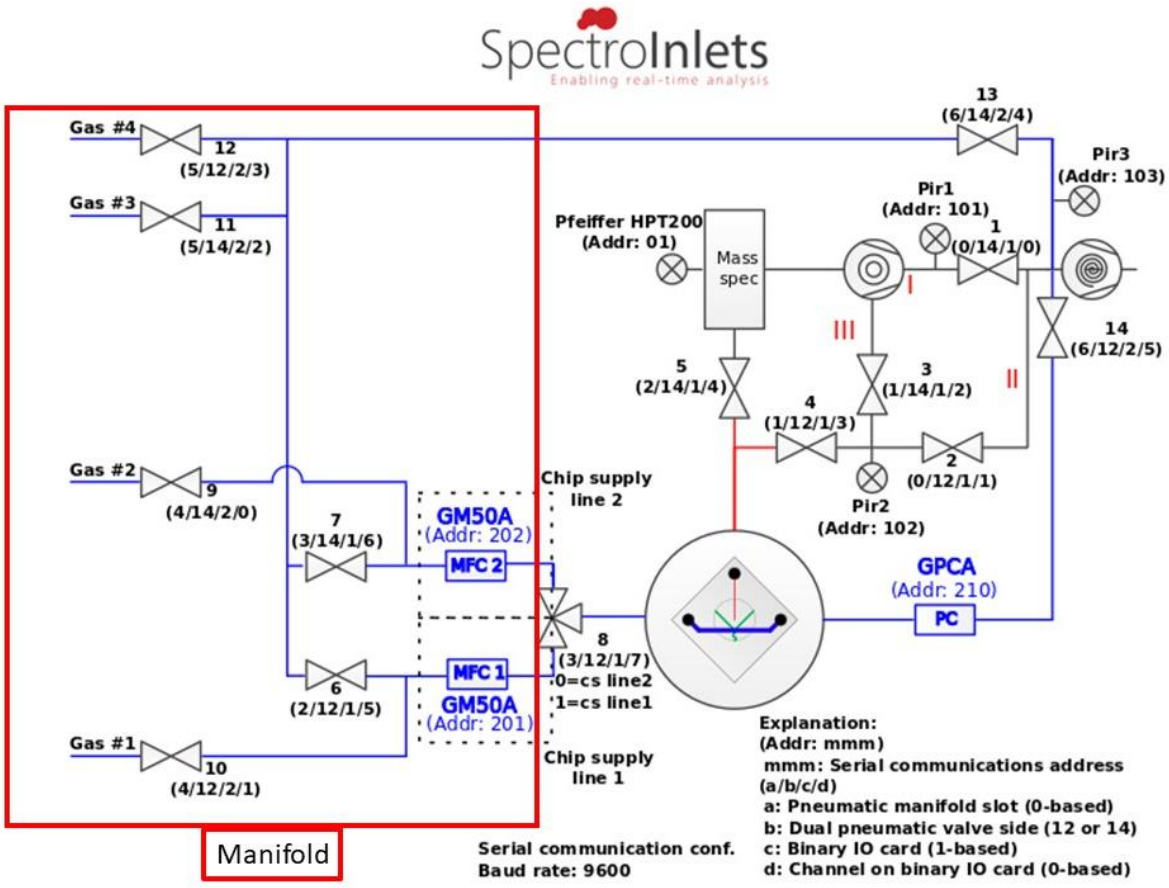

Figure 39. Gas system schematic. The gas manifold is highlighted in red on the left of the schematic.

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13.1 Pumping the manifold

This Section describes how to evacuate the manifold (highlighted in red in Figure 39). The manifold can be evacuated in order to pump the gas lines all the way to the bottles, or to prepare the manifold for new gas experiments.

WARNING: Pir3 can only tolerate an absolute pressure of 3 bar. Therefore, it is essential that the manifold is pumped without a line connected to an open gas bottle.

- Close V1, V2, and V14
- Switch V8 away from the line to be evacuated. For example, if line 2 must be evacuated, point V8 to line 1.
- Fully open the MFC of the line to be evacuated by selecting “purge” from the dropdown
- Open V6 or V7 depending on which line to pump
- Open V13
- Pump until Pir3 falls below 1E-2 mbar
- Close V13
- Set MFC back to normal mode, if appropriate
- Reopen first V14 (you never know if the line between V14 and the PC has built pressure)
- When Pir3 has fallen below 1E-2 mbar, open V1
- If necessary, flush the manifold with the desired gas by opening the corresponding inlet valve (either V9, V10, V11, or V12) for a short time, half a second should be enough to pressurize the manifold and prevent significant backflow in the gas line to preserve purity.
- Close the inlet valve after flushing
- Repeat the pumpdown procedure

13.2 Connecting a new gas to the instrument

This Section describes how to connect a new gas to the instrument.

Up to 4 gases can be connected simultaneously. Gas bottles can be connected to the instrument at any time, even during experiments. We recommend using pressure regulators with a purge valve on the high-pressure side of the regulator to allow for maximum gas line cleanliness. However, the Spectro Inlets system allows to pump the gas lines all the way to the gas bottle, through the regulator.

WARNING: Do not use absolute gas pressures higher than 3 bar from the bottles. We recommend using approximately 1.2 bar absolute (0.2 barg).

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- Connect the gas bottle to the VCR male bulkhead connector on the side of the instrument, for example Ar to Gas #2. Do not pressurize the line.
- For the highest purity, we recommend evacuating the gas line all the way to the bottle, via the regulator.
- To do so, close the main valve on the bottle and fully open the regulator, thus opening a direct pumpway to the bottle.
- Ensure that V6, V7, V10, V11, V12, and V13 are closed
- Open the valve corresponding to the connected gas. In this example, V10.
- Use the pumpdown procedure from Section 13.1 to pump the line all the way to the bottle main valve.
- As a rule of thumb, proper evacuation is attained when a Pir3 falls in the E-3 mbar range. When the pumpdown is complete, close V10. Now the manifold should be in vacuum with V13 shut.
- Fully close the pressure regulator on the bottle
- Open the main valve on the bottle
- Set the regulator to the desired working pressure (approximately 1.4 bar absolute).
- Before opening V10, make sure that V6, V7, V11, V12, and V13 are closed.
- Assign the appropriate label to V10 using the dropdown
- Open V10
- The gas is now connected to the manifold. Refer to the next section to prepare a line for operation.

13.3 Pressurizing a line via direct gas supply

This section describes how to prepare the manifold to flow gas through one of the two lines. Prior to this step, the user should have pumped the manifold and connected the desired gas as described in Sections 13.1 and 13.2, respectively. Each MFC is directly connected to a gas supply line (via V10 and V9, respectively). Besides, each MFC is connected to the two extra gas supply lines via the manifold (V6, V7, V11, and V12). Here, we will describe how to operate the MFC lines with direct supply. In the following section, we will describe how to use the extra supply lines.

WARNING: The section between the MFCs and V8 is not connected to a pressure gauge and can be closed off by the MFC and V8, thus creating a “dead volume”. If 1) such section is in vacuum, 2) gas is flown in the other line to the chip, and 3) V8 is switched, the vacuum in the dead volume will depressurize the gas present in the chip and may cause the chip to breach or fail.

- In this example we will prepare line 1 for He via V10.
- Go to Zilien main tab

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- V6, V7, and V13 must be closed
- Open V10
- Choose He from the MFC1 drop-down menu
- The volume between the MFC and V8 is under vacuum. To pressurize it with He, do as follows:
    - The dead volume is approximately 2.3 ml. Apply a flow of 10 ml/min for ~15 seconds to fill the volume at 1 bar. It is crucial that the MFC is set to the appropriate gas for this operation to be successful.
- The same procedure can be adopted for line 2, using V9 for gas supply.

13.4 Pressurizing a line via secondary gas supply

- In this example, we will prepare line 1 for Ar via V11. The same procedure is valid substituting V11 with V12 and viceversa.
- Go to Zilien main tab
- V7, V10, V12, and V13 must be closed
- Open V11
- Choose Ar from the MFC1 drop-down menu and set MFC mode to normal
- Fill the dead volume between MFC1 and V8 as described in Section 13.3
- The same procedure can be adopted for line 2, using either V11 or V12 for gas supply

13.5 Simple gas switching

This section describes how to change gas flown in the chip during experiments. In the simplest case, He will be flowing through MFC 2, whereas any gas can be selected for MFC 1. Switching between He and the chosen gas is described here. To exchange the gas in MFC 1, refer to the following section.

- The described procedure assumes that He is flowing in MFC 2, and that line 1 is prepared as described in Section 13.3
- Go to main tab in Zilien
- Set MFC 2 flow to 0 ml/min, thereby stopping the He flow
- Set MFC 1 flow to 10 ml/min but do not press enter or click outside of the setpoint field yet
- Click on V8 to switch gas line and simultaneously activate MFC 1
- MFC 1 flow can be set to 1 ml/min when the desired purity is achieved
- The effect of the gas switch can be followed plotting the respective gas signals in the MID tab

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13.6 Exchanging any gas between the lines

This section describes how to switch between gas lines using any gas in any line. Both lines can be used with any gas. Within the same experiment, the user can switch from gas 1 to gas 2 and then to gas 3, etc. without the need to revert to gas 1 in between. This application is thought for gas injection of short duration, i.e. pulse injection.

In this example, we will describe switching from He to Gas 2 to Gas 3. This procedure relies on using the gas contained in the section between V6 and MFC1 or V7 and MFC2. Such volume is approximately 3 ml, therefore filling this volume with 2 bar of any gas will result in

$$P_1 V_1 = P_2 V_2$$

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{2\ bar \times 3\ ml}{1\ bar} = 6\ ml$$

Where P_1 is the pressure in the manifold, P_2 is the desired running pressure in the chip (in this case atmospheric pressure, i.e. 1 bar), V_1 is the volume trapped between V6 and MFC1, and V_2 is the equivalent volume of gas contained in the trapped volume, once the gas is expanded at atmospheric pressure.

ATTENTION: Remember that most manometers (e.g. pressure regulators on gas bottles) show gauge pressures, i.e. pressures relative to atmosphere (their unit is bar*g*, where the *g* stands for *g*auge), so a pressure of 1 barg on the regulator indicates an absolute pressure of 2 bar. Most manometers report pressures in bar even if they actually display barg. Please check carefully about the pressure reading on your gauge before starting experiments.

This would allow to flow 1 ml/min for approximately 6 minutes. Using higher gas pressures, this time can be accordingly increased. This time should allow to switch gas with high purity while evacuating the manifold and preparing the other line.

Since analog pressure readouts may not be accurate, we recommend the user to directly measure the gas autonomy prior to experiment. Measurement can be carried out by pressurizing the trapped volume at the desired manifold pressure, then starting a flow of 1 ml/min and measuring the time it takes for the flow readout to drop below 1 ml/min. The flow starts dropping when the pressure in the trapped volume is the same as that in the chip.

- Assuming He is flowing in MFC 2
- Prepare Line 1 for Gas 2 following the procedures described in Section 13.3.
- Switch from He to Gas 2 as described in Section 13.4
- Close V6. From now, flow through MFC 1 will rely on the trapped gas between V6 and MFC 1, so it will have a limited autonomy.
- Open V7

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- Evacuate line 2 as described in Section 13.1
- Prepare line 2 for Gas 3
- Switch to line 2
- Here the user can either go on and switch to another gas in line 1 by repeating the last steps or revert to He directly. If He flow needs to be reestablished directly, do as follows:
    - Close V7
    - Prepare line 1 for Gas 3 (the same gas that is being flown in MFC 2)
    - Switch V8 to line 1. The same gas is present in the two lines, so this does not represent a gas switch.
    - Prepare line 2 for He
    - Switch V8 to line 2. He flow is reestablished.

13.7 Gas pulses

As an application example of the gas exchange system, this section will describe how gas pulses can be sent to the sample. In Figure 40, a plot of two Ar gas pulses is shown.

In order to minimize switching time, a few tricks are described in the following.

- The described procedure assumes that He is flowing in MFC 2, and that line 1 is prepared as described in Section 13.3 of the user manual. In this example, line 1 is prepared with Ar
- Go to main tab in Zilien
- Set MFC 2 flow to 0 ml/min by typing 0 but do not press enter or click outside of the setpoint field yet, so the new flow setting is not acknowledged yet
- The next two steps should be performed quickly in order to minimize switching time
- Set MFC 1 flow to 10 ml/min but do not press enter or click outside of the setpoint field yet. Note: setting MFC 1 (clicking on the MFC 1 field) automatically acknowledges the previously set MFC 2 value.
- Click on V8 to switch gas line. Clicking on V8 simultaneously activates the new flow setting on MFC 1
- Wait until the desired purity is achieved.
- As shown in Figure 40, when switching from He to Ar, it takes approximately 20 seconds for the m/q=4 signal to drop by two orders of magnitude

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- When switching from Ar to He, it takes approximately 50 seconds for the m/q=40 signal to drop by two orders of magnitude

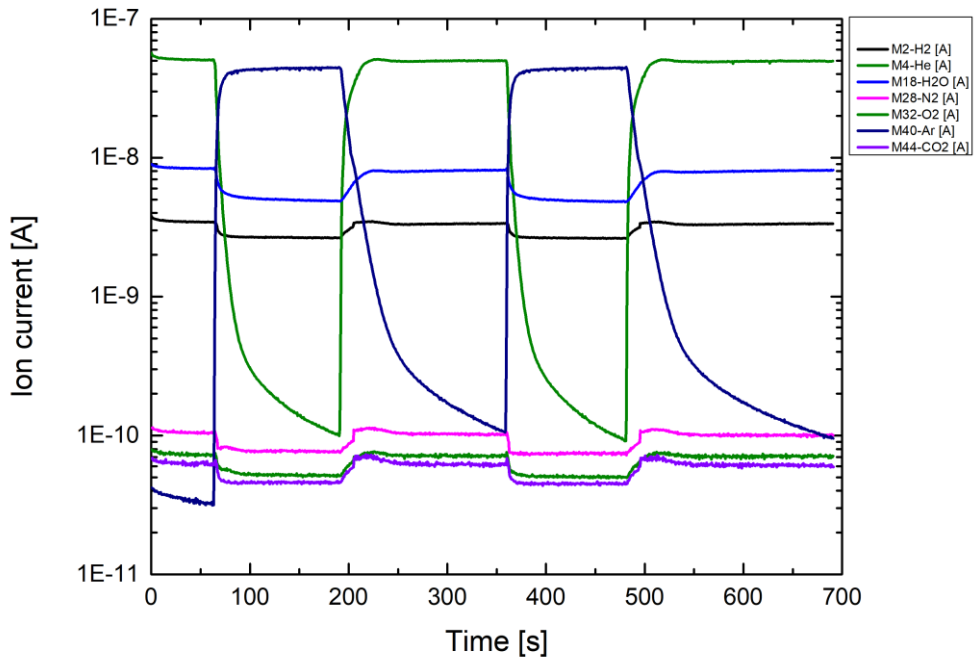

Figure 40. Argon gas pulses sent via the gas exchange system to the sample. EC-cell mounted and filled with 0.1 M aqueous perchloric acid electrolyte.

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14 How to tune the spectrometer

14.1 Tuning peak position and width

- Emission and multiplier should be on for at least 24 hours prior to calibration for best results
- Open PV MassSpec
- Refer to Help file “Best known methods for tuning”
- In Main tab, click “Tune” on the corresponding mass spectrometer (see Figure)

- Calibration can be performed either using a specialized gas mixture for calibration, or using air, as shown in Section 14.1.1 and below. When tuning an RGA, a low mass, a middle mass and a high mass calibration gas must be readily available.
- In the Tune tab, select the masses present in your calibration gas in the table on the right (see Figure)

Parameter	User 2
Dwell (ms)	32
Tune Masses (amu)	1, 2, 4, 28, 40, 86, 134
Emission Current (uA)	2000
Electron Energy (eV)	70
Anode (V)	250
Focus (V)	25
Ion Energy (meV)	8000
Rod Polarity	Reverse
EM (V)	890

- For a low mass, do not tune mass 1 or 2 if hydrogen is not available. Do not delete mass 1 or 2 from the tune table.
- When tuning higher masses, if there is no access to masses over 40 amu, tune with argon. If there is access to higher masses, tune one mass between 100–200 amu
- Tune individual masses starting with the extrema (lowest, then highest, then those in between), selecting them in the dropdown menu on the top (see Figure)

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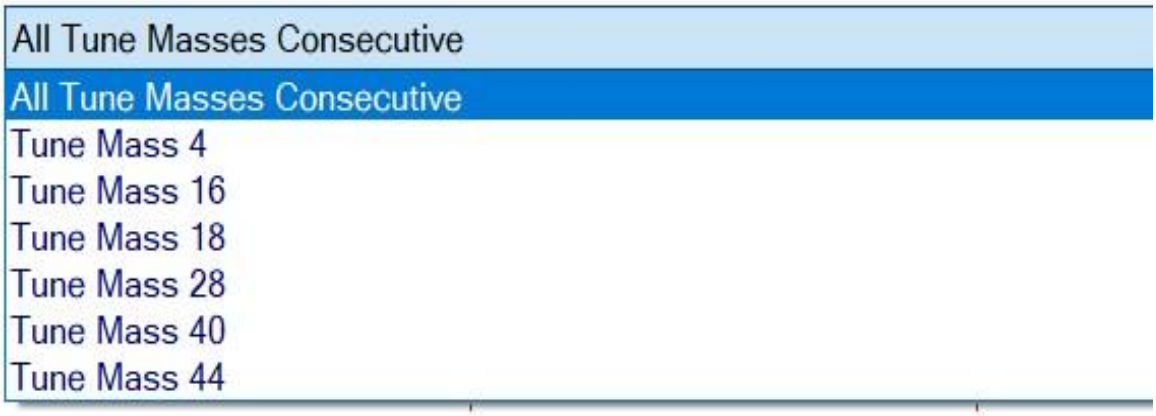

- Consider using an appropriate emission current to avoid double ionization. This can compromise data quality by increasing the background of certain signals. For example, double ionization of He generates a spurious background in mass 2 (hydrogen). The recommended emission current is 2000 µA.
- During individual mass tuning, aim at the desired peak width by clicking on the "narrow" and "widen" buttons on the bottom. The recommended peak width is 1 amu.
- Center the peaks clicking and holding the right mouse button
- A narrower peak width causes a loss of signal intensity/sensitivity. Such loss can be compensated for by increasing the multiplier voltage (see Section 14.2). However, be mindful that higher multiplier voltages will reduce its lifetime.
- We recommend the following tuning parameters, representing a good compromise between mass resolution and signal intensity.
    - Peak width = 0.7 AMU
    - Focus = 25 V
    - Ion energy = 8000 meV

14.1.1 Calibration using a specialized gas mixture

Use a calibration gas with components spanning the entire atomic mass spectrum from 0 to 200. We recommend using a mixture of 10% He, 10% Ar, 10% Xe, 70% N2. In the following, we will use this mixture as an example.

- Mount a chip and prepare for normal operation using the pumpdown procedure
- Flow 1 ml/min of the calibration gas through the chip
- Place a droplet of ultrapure water onto the chip, covering the entire membrane. This is done to let the calibration gas into the mass spectrometer

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14.1.2 Calibration using air

In lack of a dedicated calibration gas, air and He can be used.

- Mount a chip and prepare for normal operation using the pumpdown procedure
- Flow 1 ml/min of He through the chip
- To calibrate mass 4, place a droplet of ultrapure water onto the chip, covering the entire membrane. This is done to let He into the mass spectrometer
- Once mass 4 is tuned, remove the water droplet and proceed tuning first mass 28 (nitrogen) and subsequently mass 40 (argon).

14.2 Tuning the electron multiplier (EM)

The basic idea with this procedure is to tune the multiplier so that the highest signal read by the spectrometer has an intensity of 1E-7 A. This value is chosen to be as high as possible within the linear-response region of the mass spectrometer. The calibration should be performed in air, tuning on mass 28 (nitrogen). Please be mindful that as an electron multiplier ages, it will require more voltage to achieve the desired gain. The higher the EM voltage, the shorter the EM lifetime. As a rule of thumb, an amplification of about 100 is desirable. For a new EM, this is achievable with a voltage around 1000 V. When the EM voltage needs to be increased to 1500 V, the user should consider replacing the EM.

- From the Main screen, left-click the sensor name to select the sensor. A blue outline appears around the sensor bar on the main window.
- Click the Sensor Maintenance >> Calibrate Sensitivity and/or EM sensor control button.
- Alternatively, from the drop-down menu of the Main screen, click Maintenance >> Sensor Maintenance >> Calibrate Sensitivity and/or EM.
- From the What to Calibrate drop down menu, select EM voltage.
- Select a method for How to Calibrate. Choose Adjust EM voltage for target Signal.
- Check Start Calibration at the minimum EM voltage to produce a full calibration curve, this option takes more time. Do not check this option to begin the calibration at the current EM voltage.
- Sensitivity calibration uses either an external pressure gauge or the calibrated total pressure to derive the sensitivity. Check Use external Pressure measurement for calibration to use an external device.
- If using an external gauge (the more accurate method) enter the value in the Pressure setting.
- Verify that the Ionizer Presets, Mass Sensitivity, Mass EM, Dwell Time, and Target values are correct. If they are not, click Configure to open RGA Configuration.
- Choose mass 28 and target 1E-7
- Click Calibrate. PV MassSpec will automatically derive the EM values using the defined method.

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- If satisfied with the calibration, click Save to save and exit the calibration menu.
- If unsatisfied with the calibration, click Cancel to exit without saving the calibration.

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15 How to perform EC-MS data treatment

15.1 File format and how to open files

The sections will explain the file format and structure and how to open the files with different programs and extract metadata.

All data files are saved as TAB-separated CSV files (also referred to as TSV) with the file extension ".tsv". The character encoding is UTF-8.

For each measurement a folder is created, containing all the files pertaining to that measurement, both Zilien data files and raw data files from the potentiostat.

Data from a measurement is gathered into:

- One main data file which contains:
    - System parameters, mass spec MID values and potentiostat data and metadata for that data
- A set of mass spectra files which each contain one mass spectrum

For more details about the folder structure, see the Save file folder structure section. Each of the file formats are explained in the sections below.

15.1.1 Main file

The primary file format consists of a header for the metadata followed by the actual data. The header contains metadata both for the measurement and for the individual data series it consists of. Each metadata item is given in 5 columns, which contain the following:

1. **Metadata shortname**: A string which is unique within the data series it pertains to (see "The data ID" below) and whose value is limited to the lowercase characters a-z and "[]."
2. **Description**: A string with an explanation of what the metadata item is. (Its information content may be similar to the shortname).
3. **Data ID**: A string indicating which data series this metadata item pertains to. If it is empty, then the metadata item is for the whole measurement.
4. **Type**: A string which indicates the type of metadata. The type is useful for manually casting the string value into a native data type in a data treatment environment. Possible values are:
    - **int**: An integer
    - **double**: A double-precision floating point number
    - **bool**: A boolean, possible values "false" and "true"
    - **string**: A text string (NOTE: Because the TAB and NEWLINE characters are used for the format of the TSV, if these characters exist in the string to be saved it will be replaced with `<tab>` and `<newline>` placeholders, which

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makes it possible for a reader program to substitute back to get the original string.
    - **filepath**: A string that contains a file path
    - **timestamp**: A string that contains a timestamp in the format: "YYYY-MM-DD hh:mm:ss"
    - **color**: A string that contains a Hex HTML colour code on the form "#AABBCC"[2] (At present these colours are actually written out with a "string" type, but the colour type will be used in the future)
5. **Value**: The text representation of the value.

An example of a part of the metadata section is shown below:

num_header_lines	Number of header lines		int	75
num_data_header_lines	Number of data header lines (column description)		int	2
data_start	Line number of data start (0-based)		int	77
file_version	Save file version		int	1
Project	Measurement project		string	Project 1
Name	Measurement Name		string	Measurement 37
Comment	Measurement comment		string	Preparation procedure XYZ
minumum_save_interval	Minumum save interval [ms]	pirani1_[mbar]	int	1000
plot_color	Plot color (if plotted)	pirani1_[mbar]	string	#FF0000
Mass	Mass [AMU]	C0_M2	double	2
data_plotted	Data Plotted?	C0_M2	bool	true
plot_color	Plot Color	C0_M2	string	#0018FF
potentiostat_count	Number of points in the "potentiostat" data series	potentiostat	int	640

[2] https://en.wikipedia.org/wiki/Web_colors#HTML_color_names

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pirani1_[mbar]_count	Number of points in the "pirani1_[mbar]" data series	pirani1_[mbar]	int	7815

The first 3 lines are always the same and in the same order, since they can be used to parse specific sections of the file. The fourth line specifies the file version. If it is missing, the file version is assumed to be 1. The dataset format now depends on the file version number.

The data part of the file consists of first one row of Data ID's (as described above), one for each data set, then the data column headers and finally the data.

potentiostat				pirani1_[mbar]		C0_M2	
Time [s]	Voltage [V]	Current [mA]	Cycle [n]	Time [s]	Pirani1 [mbar]	Time [s]	M2-H2 [A]
2180,003	0,470768	0,00017218	1	2,194005	0,00371	3,925642	4,0057E-09
2179,873	0,4521361	0,00013289	1	2,753787	0,0037	4,740683	3,9122E-09
2180,79	0,4063033	6,9641E-05	1	3,336342	0,0037	5,556724	3,9026E-09
2181,703	0,3606729	1,6962E-05	1	3,893322	0,00371	6,371765	3,8507E-09
2182,619	0,3148057	-3,2055E-05	1	4,437942	0,00371	7,187514	3,6628E-09
2183,537	0,2688736	-8,9198E-05	1	4,96208	0,0037	8,001756	3,6395E-09
2184,451	0,2232279	-0,000141	1	5,506184	0,0037	NaN	NaN
2185,368	0,1773416	-0,00023316	1	NaN	NaN	NaN	NaN
2186,283	0,1316081	-0,00032585	1	NaN	NaN	NaN	NaN

All values are as function of experiment time. All data sets (except potentiostat data) consist of 2 columns (time, value), whereas the potentiostat data has 3 values for each timestamp. Potentiostat data is collected by Zilien from Biologic's EC-lab software. The unchanged original dataset from the EC-lab is appended as the last set of columns in the Zilien dataset, when an EC measurement has performed.

Since data is acquired at different frequencies, each of the data sets will have different lengths. The remaining slots for the shorter data sets are filled up with NaN values. NaN (or Not a Number) is a valid floating-point value, which means that by using this filling value, the entire table (all columns and as many rows as are in the datasets with most values), should be parseable as one big floating-point array. In order to know how many points are in the individual data sets look at the **[Data ID]_count** values in the metadata.

The Biologic data part of the Zilien dataset may consist of rows with NaNs in columns due to various data collected from different techniques. The data is kept chronologically in the dataset, so that they will match the sequence of the measurement execution.

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15.1.2 Mass scan files

The structure of the mass scan files is almost identical to that of the main file, but since there is only one data set, there are the following exceptions:

- The Data ID column of the metadata is empty for all metadata items
- The Data ID row in the data part is left out

One special item to notice, is that the mass_scan_started_at value of the metadata is the measurement timestamp when the mass scan was started.

15.2 How to open the data files

Formatting the data as TSV-files was specifically chosen because it is a are very general and widely used format clear text format. Because the format is widely used, it is also widely supported:

- TSV-files can be opened without anything extra by spreadsheet applications like Microsoft Excel and LibreOffice Calc.
- TSV-files can be imported into Python for data treatment via the **numpy.genfromtext** function or the standard library **cvs** module
- TSV-files can also be imported into Matlab® with different tools like e.g. **readmatrix**
- TSV-files can be imported into Origin® via the Import Wizard

15.3 How to quantify EC-MS data

For the simple case where each analyte of interest can be monitored at a unique $^{m}/_{z}$ ratio, absolute quantification entails knowing the calibration factors, F_M^i, such that

$$\dot{n}_{\mathrm{v}}^{i} = \frac{1}{F_M^i} S_M$$

where $\dot{n}_{\mathrm{v}}^{i}$ is the flux to the *v*acuum chamber of the mass spectrometer of analyte *i* and S_M is the mass spectrometer signal (minus background) at $^{m}/_{z} = M$. The flux $\dot{n}_{\mathrm{v}}^{i}$ has SI unit [mol/s], and

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for a mass spectrometer which records raw signal as an electrical current (e.g. from a Secondary Electron Multiplier) with SI units [A], the unit for the calibration factor is [A/(mol/s)] = [C/mol]. A higher value of F_M^i thus means a higher sensitivity at $^m/_z = M$ to analyte i, i.e., more signal for the same amount (note that if no set of unique primary masses exist for the set of analytes of interest, then the above equation has to be replaced by a system of coupled linear equations, i.e., a matrix equation).

The flux to the mass spectrometer, $\dot{n}_{\mathrm{v}}^i$, is not necessarily the same as the production rate at the electrode, $\dot{n}_{\mathrm{el}}^i$, which is what we are generally interested in. However, in the Spectro Inlets EC-MS system, 100% of the analyte produced at the electrode is eventually transported to the vacuum of the mass spectrometer. This means that it is straightforward to calculate the calibration factor for any analyte that can be produced at an electrode at a known rate by

$$F_M^i = \frac{\int_0^\infty S_M \mathrm{d}t}{\int_0^\infty \dot{n}_{\mathrm{el}}^i \mathrm{d}t}$$

This can be done for H_2, O_2, and CO_2, all of which can be produced with 100% Faradiac efficiency. In order to calibrate for these compounds a series of constant current (chronopotentiometry) measurements were used for greater control via

$$\dot{n}_{\mathrm{el}}^i = I/z\mathcal{F}$$

where z = -2, 4, and 2 for H_2, O_2, and CO_2, respectively, according to the stoichiometric coefficient of electrons in hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and CO oxidation reaction (COox), respectively. To minimize error, we recommend that chronopotentiometry experiments for each analyte are done at several absolute electrical currents from 50 mA to 500 mA. An example of such a measurement series is shown in Figure 41a-c.

This method of calibration is referred to as internal calibration

For more detailed information on quantification see [2].

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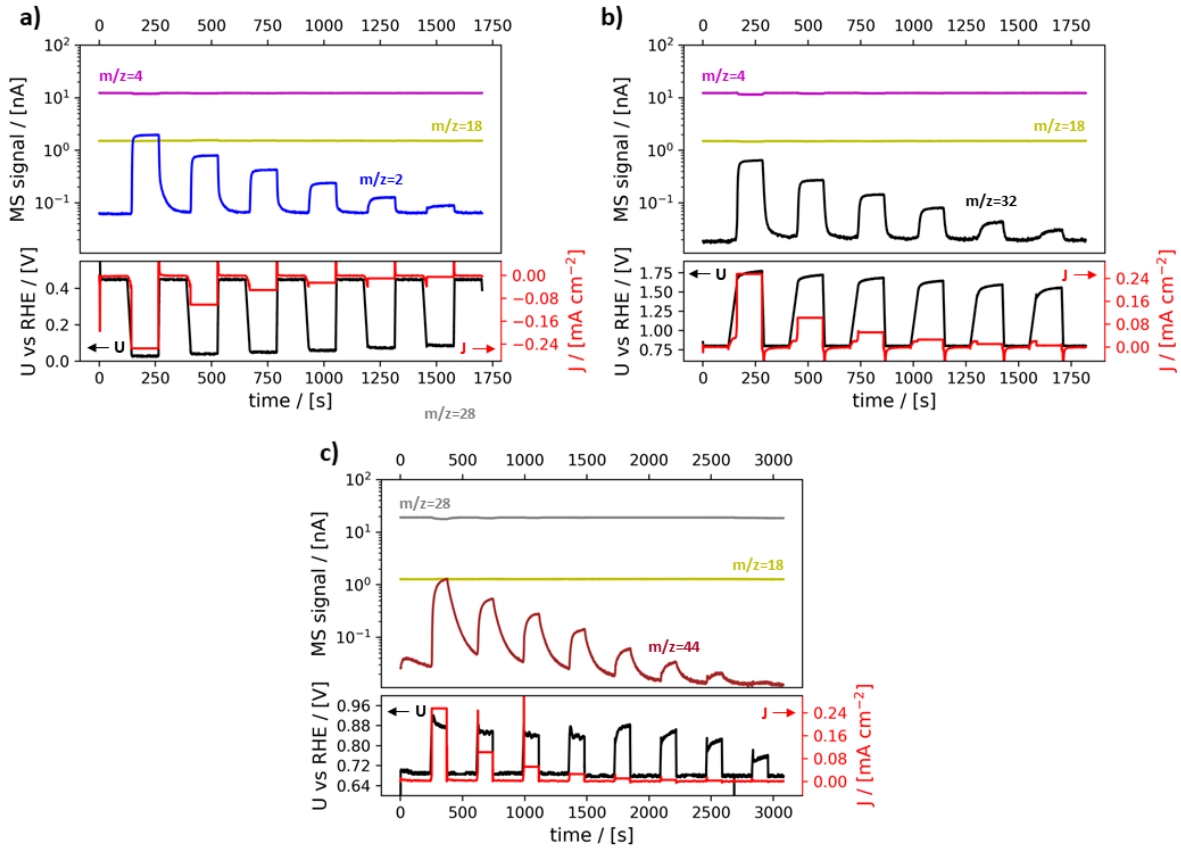

Figure 41. Measurement series to perform internal calibration

15.4 Plotting recommendations and best practices

In Figure 42a, an example of an EC-MS plot is shown. An EC-MS plot contains two panels, with the top panel showing mass spectrometry data and the bottom panel showing electrical potential (black) and current (red), all plotted on a shared time axis. On the left-hand side all inputs to the EC-MS system are plotted, i.e. the potential from the potentiostat and carrier gas signals (as they typically are of a different magnitude than analyte signals). On the right-hand side all response signals are plotted, i.e. current from the potentiostat and reaction product signals from the mass spectrometer.

In Figure 42b, selected MS signals as well as the current from the potentiostat are plotted as a function of electrical potential. This representation can be advantageous in order to visualize potential-dependent transient phenomena, such as a CO stripping event (shown in Figure 42). The recommended best practice though is to plot all data as a function of time in order to monitor the timely response of the electrochemistry in real-time.

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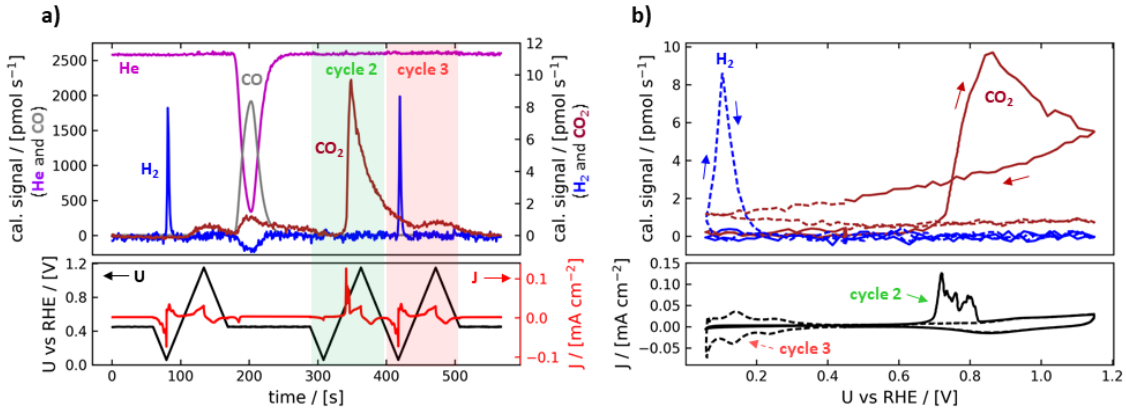

Figure 42. Two forms of experimental data representation. A) All data is shown as a function of time. This representation contains all information. B) MS data and current are shown as a function of applied potential. This information does not contain time-dependent information.

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16 Troubleshooting

16.1 How does hardware react to different events?

Event	Reaction
Computer dies or USB cable is unplugged	These two events have the same consequence on the system: All valves close, except for V1 and V14 which default to open. MFCs and PC stay as they are. V8 switches to MFC2
All power dies (but pressurized air stays on)	The power loss will have a first effect when the power is lost, then things will change when power is restored. In general, upon power loss, all valves except for V14 will close. V14 opens. V8 switches to MFC2. The pressure controller closes entirely, but the MFC status is unknown. The only way to know is to test it and we never got around to doing this test When power is restored, the PC will default to 0 mbar (i.e. fully open). MFCs will default to 0. All valves stay closed, except for V1 that reopens and V14 that stays open. V8 stays pointing to MFC2
Compressed air pressure drops to atmospheric (hose becomes disconnected, cylinder is exchanged…)	All valves except V14 close. V14 opens if it isn't already open. V8 switches to MFC2

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Some other communication error occurs	If there is any communication error, Zilien shows an error message and typically forces shutdown

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16.2 Most common faults and their solutions

Symptom	Possible causes	Solution
High pressure during pump down	The chip is cracked	Exchange the chip
	Dust on the O-rings	Clean or exchange the O-rings
	A connection is leaking	Check the connections with helium, and reconnect the leaking connection
	The chip is breached	Exchange the chip
	The packing surface under the O-rings is scratched	Re-polish the surface to a mirror finish
Sudden pressure increase in the vacuum chamber while liquid is over the membrane chip	The chip is breached	Exchange the chip
Low pressure after pump down / low QMS signals	The capillary in the chip is blocked	Exchange the chip
Chip breaks during installation	The O-rings are misplaced	Make sure that the O-rings are all correctly placed
	The interface block is dirty	Remove the spacer plates and the O-ring plate and clean the interface block.
	Glass residue from previously broken chip	Clean the sealing surface of the interface assembly with lens paper not leaving residue. If necessary, disassemble and reassemble the interface, clean or replace the O-rings.
Electrolyte leaks out at the bottom of the EC cell	O-ring is misplaced	Remove the EC cell, rinse it, dry it, place the O-ring correctly and remount the cell
	O-ring or chip surface dirty	Clean the O-ring with lens paper and ethanol. Clean the surface of the chip (sweep off dust, rinse).
	O-ring is worn / damaged	Replace the O-ring. See Figure 6 for ordering information.
Slow time response	Electrode is indented from the cell surface	Remount electrode and ensure that electrode, U-cup, and EC-cell are perfectly

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		flush using magnifying glass or microscope
	Bubble on electrode	As a result of electrochemistry or during mounting, a bubble may be trapped between electrode and membrane. Inject more electrolyte or remount the cell
Slow pumpdown	Liquid in the pumpway	In the unlikely event that a liquid leaks out of the cell and into the pumpway, disconnect the interface block and

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17 Appendix: First time setup of PC for Zilien

The following sections contain instructions for how to install the Zilien software. If it is the first install of Zilien on a computer, please follow the steps in Section 17.1. If the Zilien install concerns an update, please jump directly to Section 17.2.

17.1 Before first install

Before the first install of Zilien it will be necessary to install dependencies for Zilien (drivers and software runtime environments) and to setup the hardware.

17.1.1 Get dependencies

The following items are required to run Zilien on a new computer:

- Driver for USB to RS485 converter
- Labview runtime
- NI-DAQmx runtime

These components are all present in the "Extras" folder on the USB key delivered along with the setup. To download them from the internet, please follow the instructions below.

17.1.2 Download driver for USB to RS485 converter

Visit advantech-bb.com, go to support and search for the converter type: “USOPTL4DR-2” and select driver and download for Windows 10. When downloaded, unpack the downloaded file.

17.1.3 Download Labview runtime

Do an internet search for "download labview runtime engine" and follow the link to the "Labview Download – National Instruments" page, which should be for the download of the

Labview runtime engine. At present the link is https://www.ni.com/da-dk/support/downloads/software-products/download.labview.html#305508. Set:

- Supported OS: Windows
- Version: 2017 SP1
- Application bitness: 32-bit
- Included editions: Runtime

and press download.

17.1.4 Download NI-DAQmx driver runtime

Do an internet search for "download nidaqmx runtime" and follow the link to the "NI-DAQmx Download - National Instruments" (not the version-specific links). At present the link is: https://www.ni.com/da-dk/support/downloads/drivers/download.ni-daqmx.html#311818. Set:

- Version: 18.0
- Included editions: Runtime

and press download.

17.1.5 Install and setup equipment

The following sections describe first time connection of the equipment and install of drivers and software runtime environments.

17.1.6 First time connect status

ATTENTION: Currently the system has to be connected to a USB 2.0 port, otherwise the network adapter will not be recognized and Zilien cannot run. If there is no available USB 2.0 port on the computer, use a USB hub, with USB 2.0 ports.

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Connect the USB cable from the setup to the computer and open the device manager. Press “Win-R” to open the run dialog, enter “devmgmt.msc” and press enter. The device manager should show 3 or 4 unknown devices, depending on the generation of the electronics box (see section 17.1.7 for details), 1 or 2 USB to RS485 converters and 2 data cards. Besides that, there should also be a new network card named "ASIX AX88179 USB 3.0 to Gigabit Ethernet Adapter" as in Figure 43.

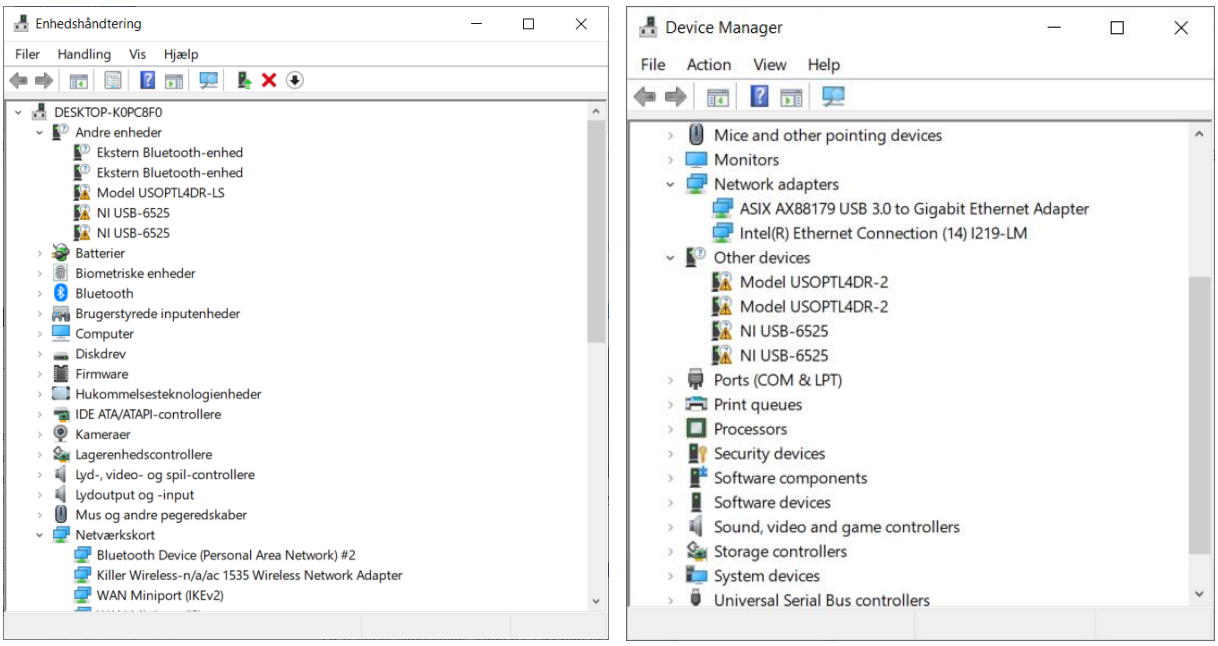

Figure 43. The list of unknown devices in the device manager. On the left, as it looks in the first-generation electronics boxes and, on the right, as it looks in the second-generation electronics boxes.

17.1.7 USB to RS485 converter driver installation and setup

Note: A revision to the electronics means that there are also small variations in the setup procedure, depending on whether you electronics box reports 1 or 2 USB-RS485 converters. The places where the setup procedure differs is highlighted with bold and prefaced with the text “2 converter version” in the rest of section 17.1.7.

First unpack the driver zip-file from the Extras folder or download it as described in Section 17.1.2. Open the device manager: Win-R: “devmgmt.msc” enter

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Right-click the “Model USOPTL4DR-LS” unit under “Unknown devices”, select “Update driver” and choose the bottom option to find the driver software on your computer. Then change the search path to the top folder of the unpacked driver zip archive, see Figure 44.

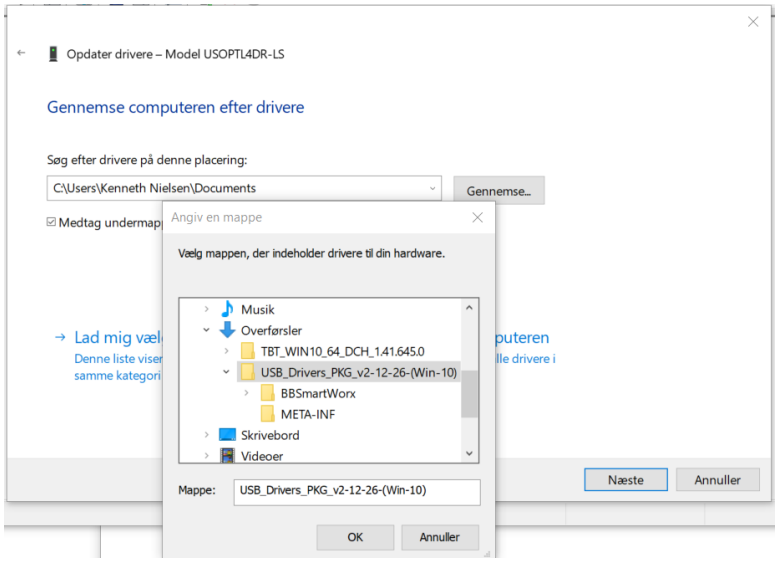

Figure 44. Select USB Serial driver folder

Then the “Model USOPTL4DR-LS” device under other devices should disappear and a “USB Serial Port” should appear in the same category. Then follow the same steps as before *one more time*. Update driver – Select on computer and select the same folder as before.

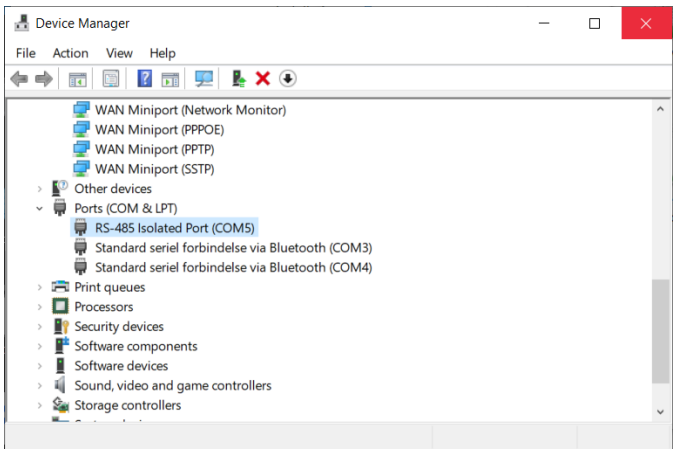

Figure 45. New COM port

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Now a new port “RS-485 Isolated Port (COM?)” should appear under “Ports (COM and LPT)” in the device manager, see Figure 45.

2 converter version: For the 2-converter version of the electronics box, simply repeat the procedure above for the other “Model USOPTL4DR-LS” unit under “Unknown devices” device as well, inputting driver path and installing drivers twice, until it also appears as an “RS-485 Isolated Port (COM?)” in the “Ports (COM and LPT)” section.

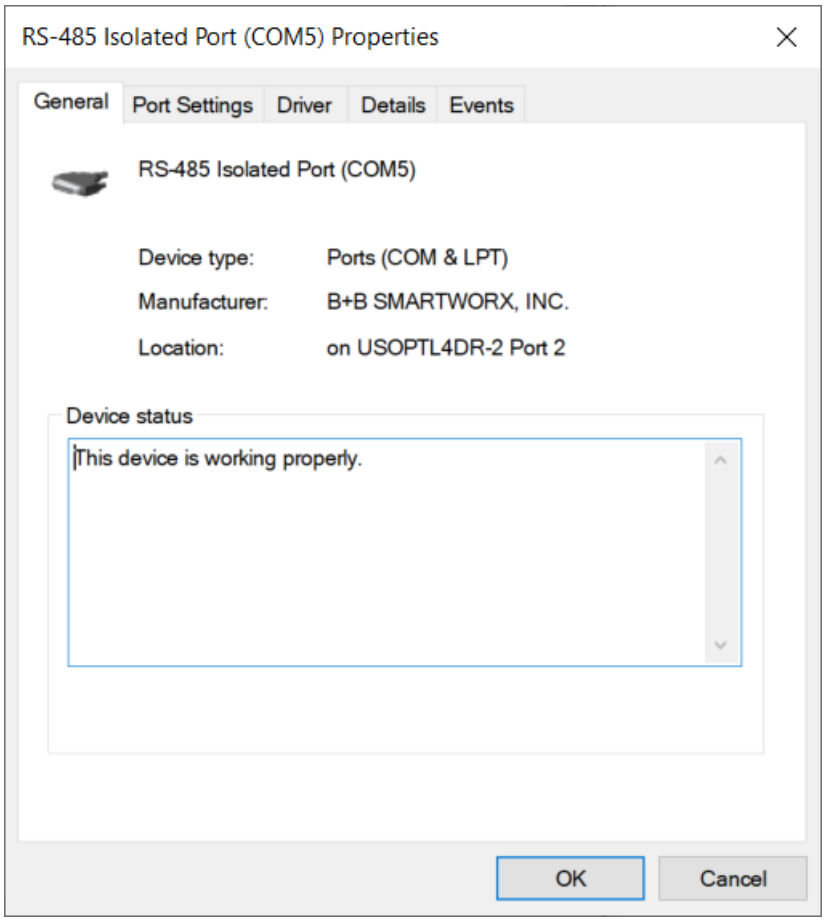

Figure 46: The General tab of the device properties. Note "Port 2" in the location.

2 converter version: In the next part of the setup procedure, one of the ports will be configured with a specific COM port number. For the 2-converter version we need to select the correct port to configure. To figure out which one it is, right click the “RS-485

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Isolated Port (COM?)" in the "Ports (COM and LPT)" on turn and select properties. Shift to the "General" tab and have a look at the "Location" field. The location will for one of the ports end with "Port 1" and for the other end in "Port 2" (see Figure 46). <u>The port that needs to be configured as outlined below, is the one that ends in "Port 2"</u>

Now right click this port and select "Properties". Select the "Port Settings" tab (see Figure 47 left) and click advanced. Then, at the very top where it says, "COM Port Number:" change the setting to "COM25", see Figure 47 right.

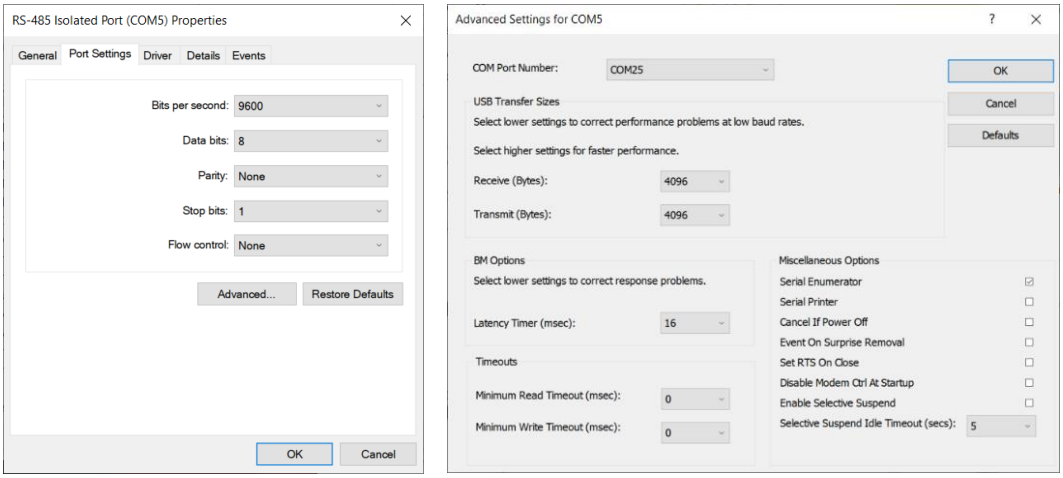

Figure 47. Left: COM settings. Right COM25.

Then press ok twice, first to close the "Advanced Settings" windows and then to close the settings window.

17.1.8 USB to ethernet converter

ATTENTION: In order to test the correct configuration of the network adapter as described in this section, Q2 switch on the electronics box (see **Figure 10** and **Figure 11**) has to be turned on for at least 30 s, i.e. pointing to the left and the LED should glow green. This is to ensure that the QMS electronics is on and can answer to queries

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The driver for the USB to ethernet converter should be installed automatically by Windows. Therefore, start by navigating to “Network adapters” in the device manager and make sure the “AXIS AX88179 USB 3.0 to Gigabit Ethernet Adapter” is present and does not report any errors.

Then open the “Network Connection” with Win-R: “ncpa.cpl” enter (Figure 48 left).

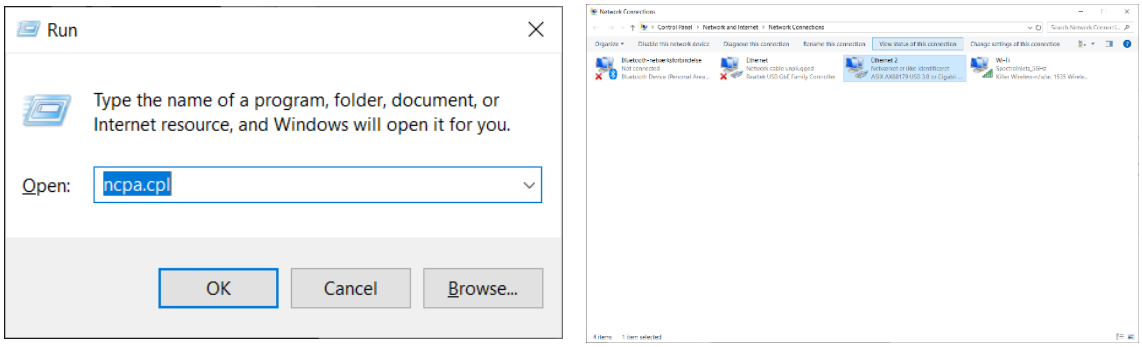

Figure 48. Left: start device manager with run. Right: Select network connection.

Select the network connections that runs on the AXIS device (see Figure 48 right). Right click and select “Properties”. Select “TCP/IPv4 (Internet Protocol Version 4)” in the center pane and click “Properties” (Figure 49 left).

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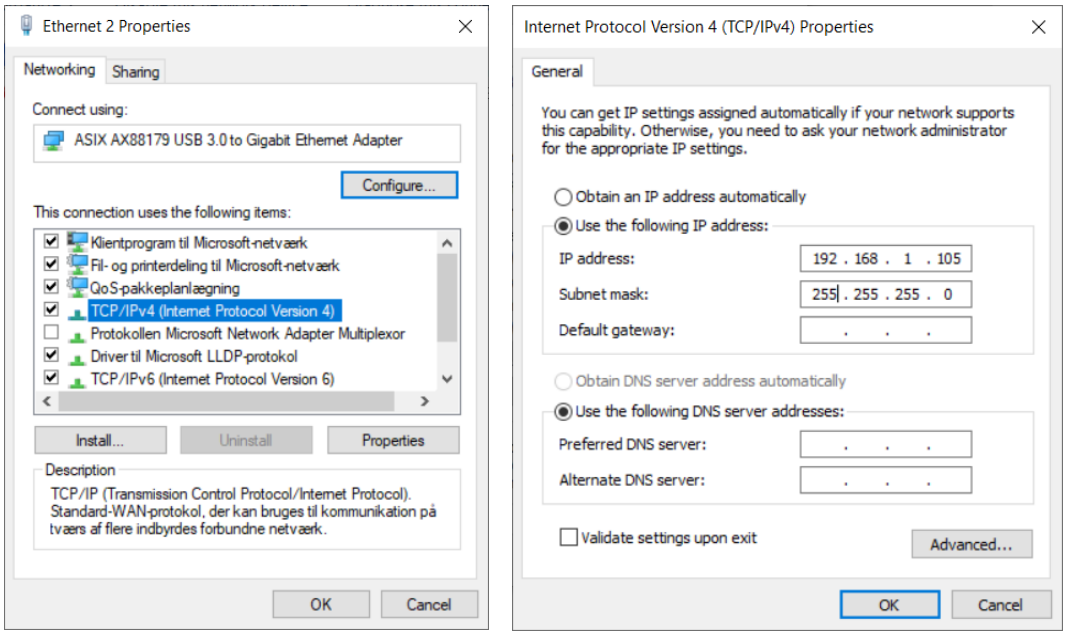

Figure 49. Left: select ipv4. Right: ipaddress and subnet mask.

In the top half, change to “Use the following IP address” and enter IP address “192.168.1.105” and subnet mask “255.255.255.0” (Figure 49 right). Note, you only need to enter the numbers, no dots. Then press “OK” to save the new settings and press “OK” again to close the general properties window. To confirm that the setup was correct, open a network browser and enter as the address 192.168.1.100. This should present you with the following status screen:

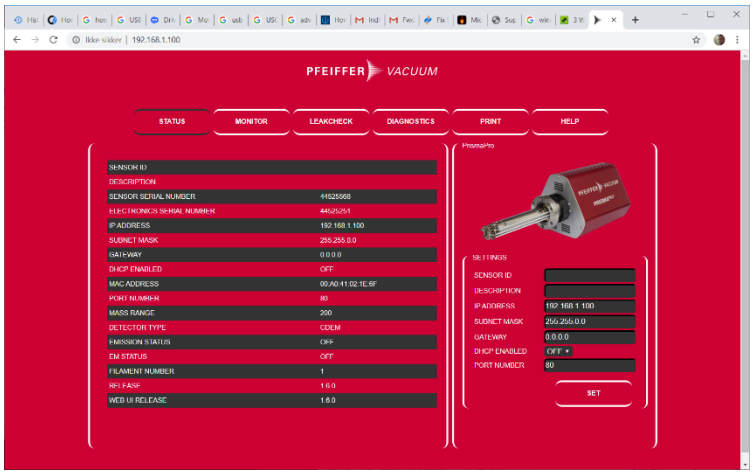

Figure 50. Status MS

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17.1.9 Setup Labview runtime and drivers

Labview runtime should be installed first, followed by NI-DAQmx runtime. Simply follow the instructions in the corresponding installers. After completed installation the "NI USB-6525" cards that were previously in the "Unknown Devices" category in the device manager should now show be located in a new "Data Acquisition Devices" category, see Figure 51.

ATTENTION: When prompted, disable Windows fast startup.

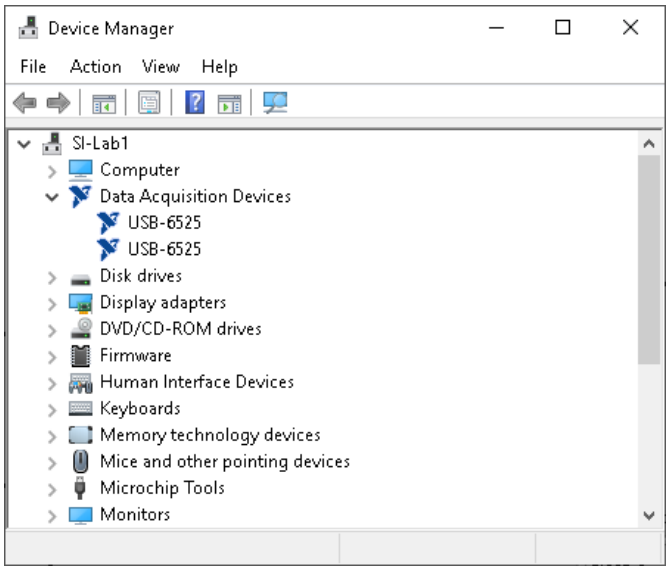

Figure 51. data acquisition devices

17.2 Installing or updating Zilien

To install Zilien simply unpack the content of the provided Zilien zip archive to the desired install location. NOTE: It is important that the contents of the folder is not moved around relative to each other, otherwise the software will not work. However, the entire Zilien folder can be placed anywhere except in the “Program Files” folders on the C: drive.

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17.3 Installing EC-Lab® and configure it for Zilien use

EC-Lab® is not provided in the Extras folder, as we do not have permission to distribute that installer. Please download EC-Lab® from the BioLogic® website using you own credentials and install the software.

For Zilien to be able to use EC-Lab® the COM interface needs to be activated. The steps for this are the following:

• Open the start menu and type "cmd". A result should show up as "Command Prompt". Right click it and select "Run as administrator".

• Navigate to the EC-Lab® install folder with the command:

cd "c:\Program Files (x86)\EC-Lab"

(HINT: The paths can be autocompleted by using the TAB key, so type "cd c:\Pro" and TAB should first show you "c:\Program Files" and then TAB once more and it should show "c:\Program Files (x86)"

• Once in the EC-Lab® folder (the prompt should read "c:\Program Files (x86)\EC-Lab>" run the following command:

EClab.exe /regserver

The command will not return any result but will now have registered EC-Lab for use from Zilien.

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References

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