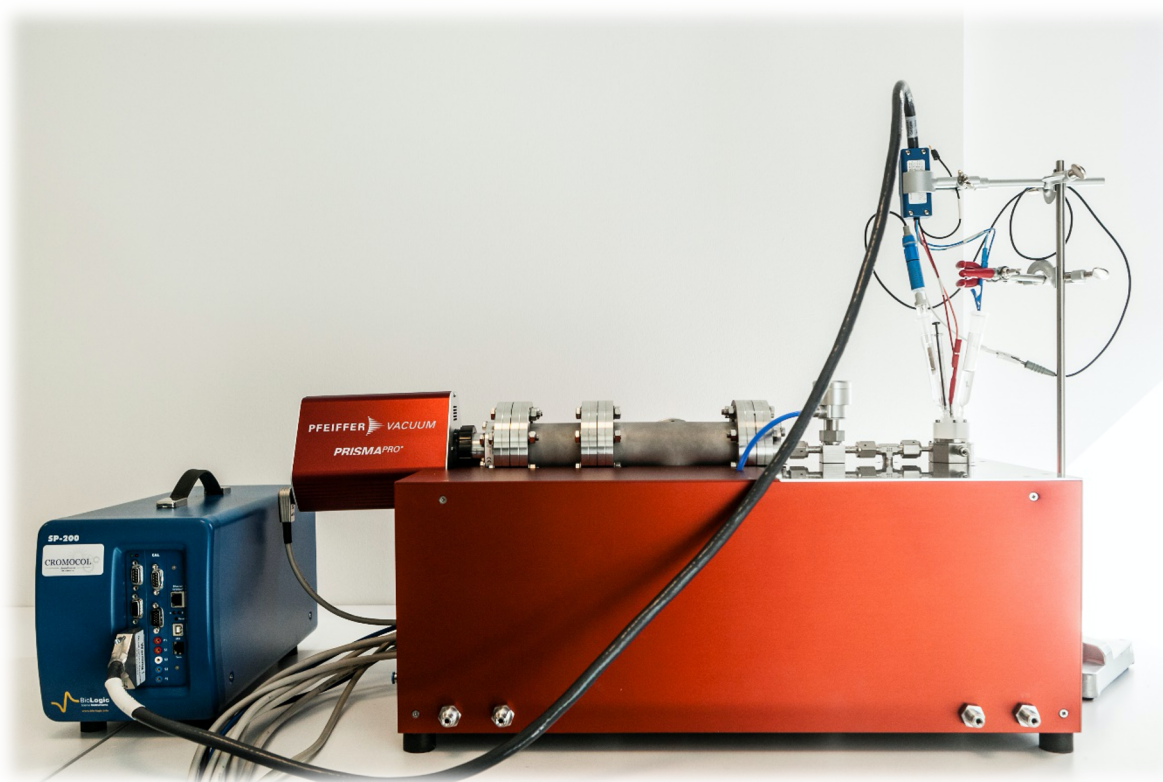


# SpectroInlets

Enabling real-time analysis

## WHITEPAPER



Quantitative real-time detection of volatile electrochemical reaction products  
with unprecedented sensitivity

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# 1. INTRODUCTION

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Beyond bare potentiostatic data: get the broader picture of electrochemistry with the Spectro inlets EC-MS system. 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 1 nA, corresponding to approximately 10 ppm of a monolayer 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.

The compact, tabletop instrument fits comfortably on standard laboratory tables. Upon installation, it operates straight out of the package with the embedded, fully functional 3-electrode EC cell and Bio-Logic SP-200 potentiostat.

In the following, the key features of the Spectro Inlets EC-MS system are explained, and some experimental results exploiting these features are shown. In the References section, the reader can find a selected list of scientific publications based on research conducted on a Spectro Inlets EC-MS system.<sup>1-6</sup>



## 2. FEATURES

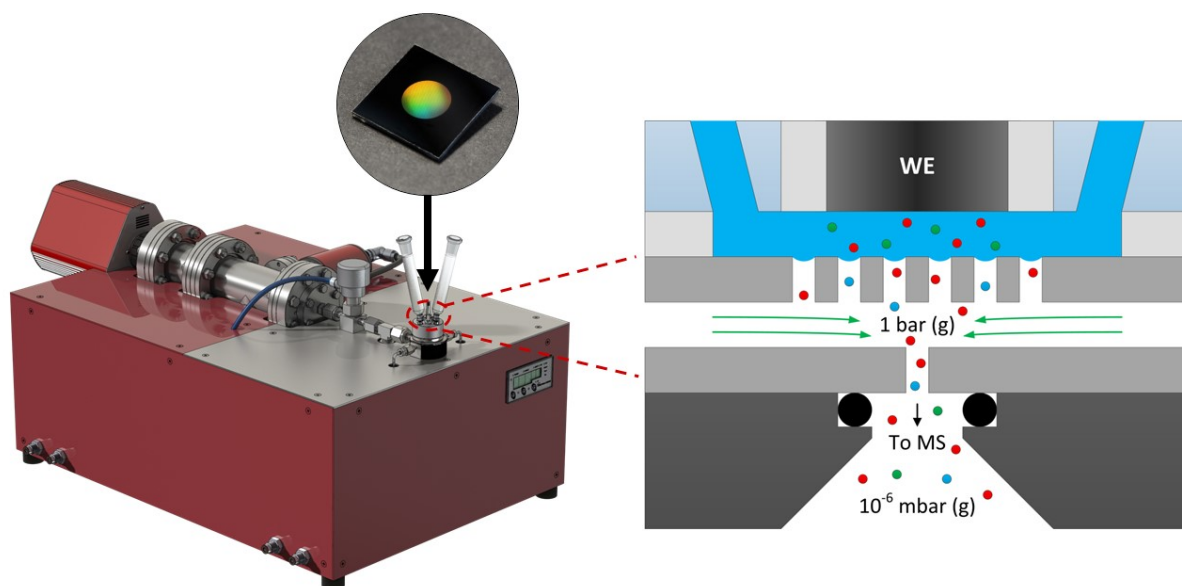
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- **Membrane chip:** Tailored analyte sampling and molecular flow for true quantitative analysis.
- **Standardized sample holder:** Piranha-cleanable stagnant thin-layer EC cell for standard 5 mm cylindrical electrodes, common in RDE.
- **Fast time-response:** Sub-second time resolution.
- **High sensitivity:** Measure the desorption of 10 ppm of a monolayer in 1 sec.
- **High dynamic range:** Measure from 1 mA down to 1 nA of continuous product formation.
- **Quantitative analysis:** 100% volatile species collection efficiency and tailored molecule flux to the detector.
- **Dosing of reactant gases:** Fully defined mass transport to and from the electrode.
- **Fast sample and chip exchange:** Integrated vacuum system for effortless chip exchange without interrupting instrument operation or venting.
- **Streamlined software solution:** Complete system control and synchronized EC-MS data acquisition and plotting. Full documentation is available for customization by the user.



### 3. 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 1).



*Figure 1. 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..<sup>3</sup>*

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 0 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.



## 4. STANDARDIZED SAMPLE HOLDER

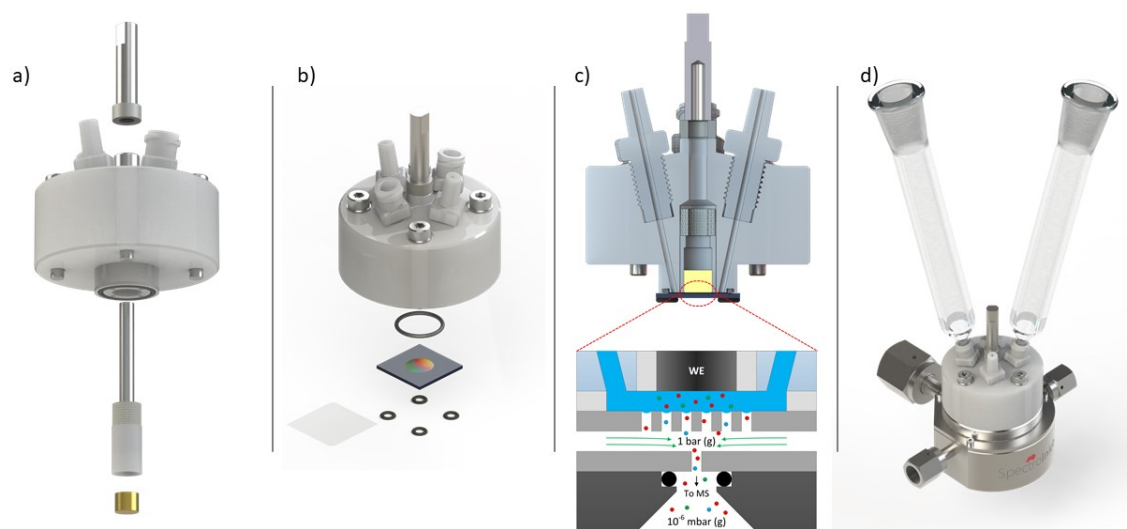
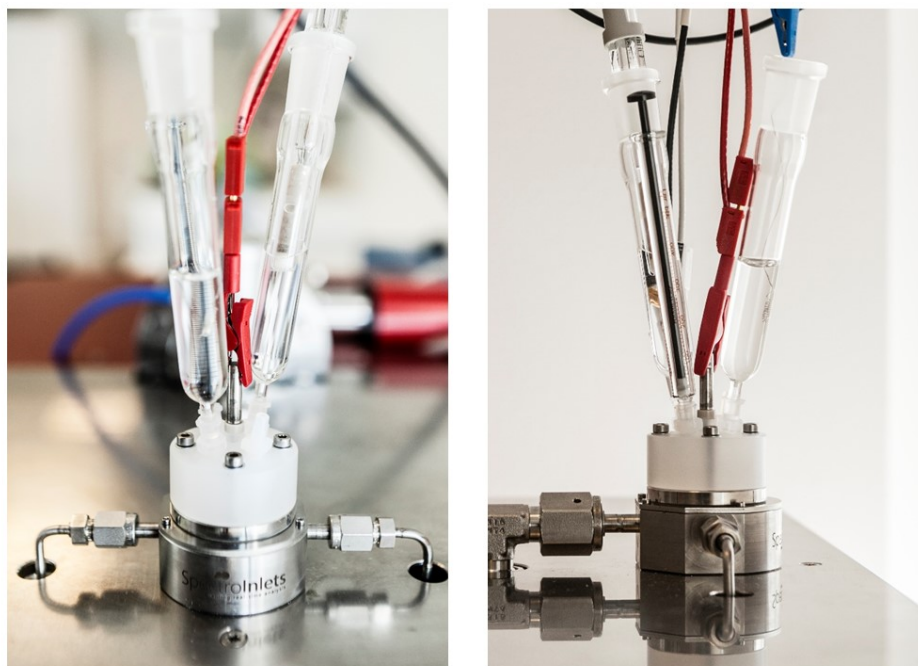


Figure 2: Schematics of the stagnant thin layer flow cell. a) Electrode assembly, with a disk contact core assembly from Pine Instruments used to retain the working electrode in the EC cell b) mounting of cell onto membrane chip, c) cross sectional view of the assembled flow cell. d) The electrochemical cell mounted on the interface block and equipped with two glass compartments for reference and counter electrode, respectively.<sup>4</sup>

The Spectro Inlets EC-MS system is provided with a tailored electrochemistry cell, ready for use immediately after installation (Figure 2). We developed the cell in collaboration with Pine Research Instruments and made it compatible with their standard 5 mm cylindrical electrodes used for RDE measurements. Most metals and glassy carbon supports are readily available off the shelf in this common electrode format, so the user does not need to waste time and money manufacturing custom electrodes. The electrode is retained in a typical disk contact core assembly from Pine Research Instruments (another inexpensive, standard, off-the-shelf component). Electrochemistry requires ultra-high levels of cleanliness, so we developed our EC-cell in PCTFE to make it chemically resistant and cleanable in piranha solution. The cell is equipped with four UNF 1/4"-28 threaded openings: two for the reference and the counter electrodes, and two for electrolyte inlet and outlet (Figure 2), where standard IDEX™ microfluidic fittings can be mounted. The thickness of the electrolyte layer is constrained to be precisely 100  $\mu\text{m}$ , providing a well-defined geometry yielding a well-defined mass transport to and from the electrode, excellent time-response, and 100 % collection efficiency for volatile electrochemical reaction products. The cell is coupled to glass cylinders made with a conical ground glass joint, a glass frit and a Luer connector at the bottom (Figure 2d), which can be used to connect a reference and a counter electrode. Such glass connectors are designed to perfectly fit e.g. an Ag/AgCl reference electrode B 3420+ from SI analytics. Any other reference electrode can be used as well.





*Figure 3. Photographs of the EC cell equipped with a B 3420+ Ag/AgCl electrode, a coiled Pt wire as counter electrode, and a gas-tight syringe to inject electrolyte in the cell.*

Mounting and removal of the EC cell can be carried out in seconds, and the same is true for working electrode exchange. This allows users to maximize productivity as several experiments can be performed in very short times. For example, a full activity volcano plot can be measured within one day.

We recommend operating the cell in stagnant configuration to fully exploit the sensitivity and quantifiability of the system. Because of the extraordinary control of experimental parameters obtained by chip design, in stagnant electrolyte the transport mechanisms of species from the electrode surface through the electrolyte and to the sampling volume are fully defined and modelled.<sup>4</sup> The thin-layer cell is designed so that *all* volatile molecules that are evolved at the electrode surface are transferred to the mass spectrometer and thereby quantified. This is a truly unique characteristic of the Spectro Inlets system and it allows to obtain e.g. the data shown in Figure 9-**Error! Reference source not found.**

The cell can also be operated in flow mode. However, in such configuration the total molecular yield information is lost.

## 5. FAST TIME RESPONSE

The system can measure composition changes of volatile species with a time resolution down to 0.1 seconds. This allows to effortlessly produce EC-MS plots, as shown in Figure 4, with EC and MS signal plotted against common time (a) and against applied potential (b). The software integration takes care of synchronization, so there is no need to manually (and somewhat inaccurately) record the time-zero when the EC technique is started with respect to the MS signal. For more information on software integration, see Section 11.





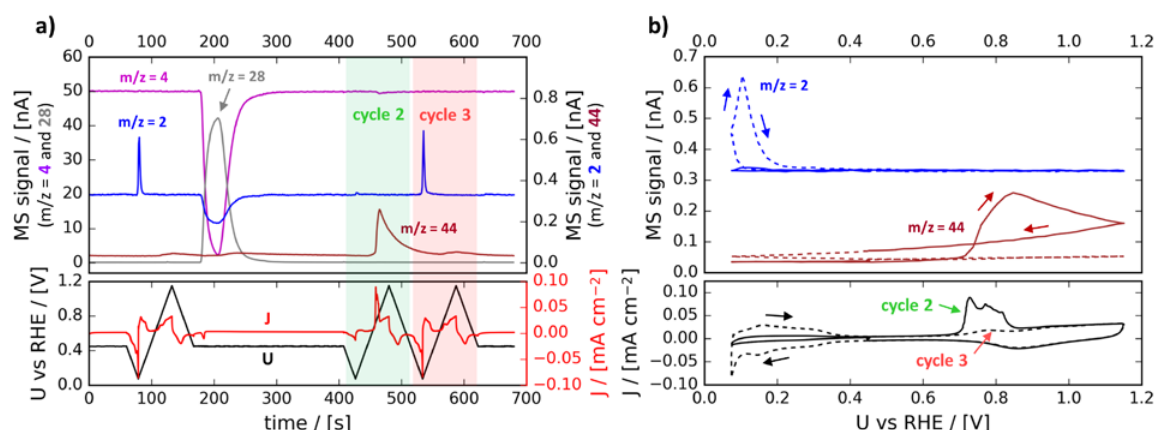


Figure 4.  $H_2$  evolution and CO stripping experiments using a 5 mm polycrystalline Pt electrode in 1M  $HClO_4$ . Potential sweeps are carried out at 20 mV/s. a) Different signals from the mass spectrometer corresponding to  $H_2$  ( $m/z=2$ ), He ( $m/z=4$ ), CO ( $m/z=28$ ) and  $CO_2$  ( $m/z=44$ ) along with the potential and current density as a function of time. b) MS signal as a function of applied voltage and CVs corresponding to the coloured sweeps in a).<sup>4</sup>

Figure 4 shows a CO stripping experiment performed with the Spectro Inlets EC-MS system. Starting from the left of Figure 4, one complete potential cycle is undertaken between 0.060 and 1.150 V vs RHE with a scan rate of 20 mV/s starting with a cathodic sweep from 0.45 V vs RHE to characterize the state of the electrode surface. Following the cycle, the potential is held at 0.45 V vs RHE while CO is injected through the chip from  $t = 180$  s to  $t = 240$  s (for further details on the gas exchange functionality, see Section 0). A cathodic CO displacement current is observed, centered around  $t = 185$  s. Following CO exposure, two cycles identical to the first one are carried out. The first cycle shows HER poisoning followed by the oxidation of the adsorbed CO at  $t = 340$  s, and the  $CO_2$  released is immediately observed as a signal at  $m/z = 44$ , which decays slowly thereafter. The last cycle is identical to the cycle before CO exposure, confirming that the electrode surface and setup have returned to their original state free of CO. The integrated CO stripping peak from the cyclic voltammogram corresponds to 370 pmol  $CO_2$ , or about 75% of a monolayer assuming a flat surface, in agreement with literature values. The integrated calibrated mass spectrometer signal for  $CO_2$ , after subtracting the background from oxidation of residual adventitious carbon, is 345 pmol, or about 70% of a monolayer assuming a flat surface, in good agreement with the electrochemistry data. In comparison, the amount of hydrogen produced at  $t = 420$  s in Figure 4 is 24 pmol, corresponding to 5% of a monolayer, i.e., 5% of a catalytic turnover assuming all surface atoms are active.

In addition to the remarkable signal-to-noise ratio for detection of a sub-monolayer of desorbed product, this is, to the best of our knowledge, the fastest full execution of a CO stripping experiment ever reported. By this, we mean the shortest total time required for surface area measurement by CO stripping including:

- a confirmation, by HER poisoning, that the surface has been completely covered by CO.
- a confirmation, by prior and subsequent cyclic voltammetry, that the surface has returned to its initial, completely uncovered, state.



## 6. HIGH SENSITIVITY

The chip is the secret behind the ultra-high sensitivity that allows the Spectro Inlets system to detect down to 10 ppm of a monolayer desorbing in a second. By design, the membrane chip is 3-4 orders of magnitude more sensitive than conventional DEMS systems for light substances.

The membrane chip was chosen to optimize the collection efficiency for those molecules that have a high volatility and that occur most often in electrochemical experiments, while lowering the uninteresting water signal. It should be noted that anything will be collected if the user is willing to wait long enough, but the time response depends on the solubility, volatility, and stickiness of the analyte.

## 7. HIGH DYNAMIC RANGE

With the Spectro Inlets system, you can measure from 1 mA to 1 nA of continuous product formation. We have worked in collaboration with Pfeiffer Vacuum to bring you the best-suited mass spectrometer for EC-MS measurements. The top-of-the-line Pfeiffer PrismaPro® mass spectrometer was chosen because of its ability to accurately resolve adjacent masses (e.g. 31 and 32 a.m.u.) exhibiting a signal difference of 7 orders of magnitude. This represents a key component to enable the extraordinarily high sensitivity that the Spectro Inlets EC-MS system guarantees.

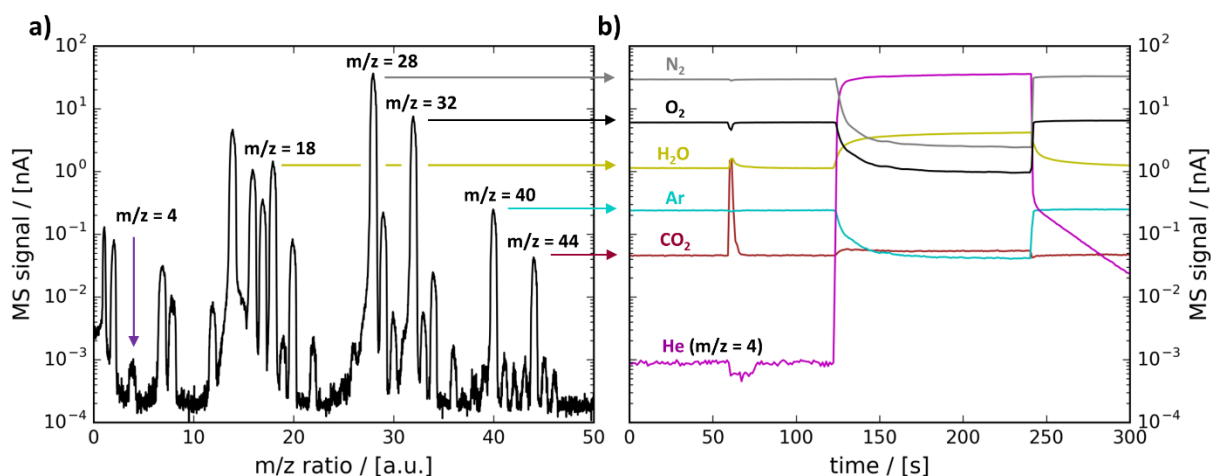


Figure 5. a) Mass spectrum of air being sampled through the membrane chip before a droplet of water is placed onto the membrane. b) Mass-time analysis of air with N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, Ar and CO<sub>2</sub> measured on m/z = 28; 32; 18; 40 and 44, respectively. At t = 60 s the user exhales on the chip, causing a spike in the CO<sub>2</sub> and H<sub>2</sub>O signals. At t = 120 s, a droplet of water is placed on the chip, after which the sampling volume equilibrates with water, with the He carrier gas making up the pressure to 1 bar, measured on m/z = 4.

With a 7-orders-of-magnitude dynamic range, the Spectro Inlets system can operate with gases with a 6.0 purity level. Furthermore, the entire system is constructed using VCR® metal gasket face seal components, which are rated for ultrahigh vacuum applications and are compatible with 6.0 gases.





## 8. QUANTITATIVE ANALYSIS

The Spectro Inlets system goes beyond bare detection of volatiles in liquids as it enables true real-time quantification of reaction product formation. This means the difference between just measuring relative amounts of substances and counting the molecules desorbing from an electrode surface as a result of an electrochemical event. In turn, this allows to study half-cell transient phenomena and get true mechanistic insight and fundamental understanding.

Quantitative analysis is enabled by the microchip geometry, in synergy with the gas and vacuum systems. Together, the system is designed to collect all the molecules desorbing from the electrode, as explained in Section 3.

## 9. DOSING OF REACTANT GASES

An accurately calibrated on-chip gas system allows rapid gas switching between up to 4 different gases. The system is compatible with 6.0 gases, and a 6.0 purity level is achieved during each pulse. Pulses or trains of pulses of different gases can be programmed by the user. The duration and composition of each pulse can be chosen separately.

Due to fast equilibration of the make-up gas with the small electrolyte volume, the chosen gas saturates the electrolyte immediately. Therefore, in stagnant configuration, there is no need to bubble gases in an external reservoir of electrolyte to pre-saturate it.

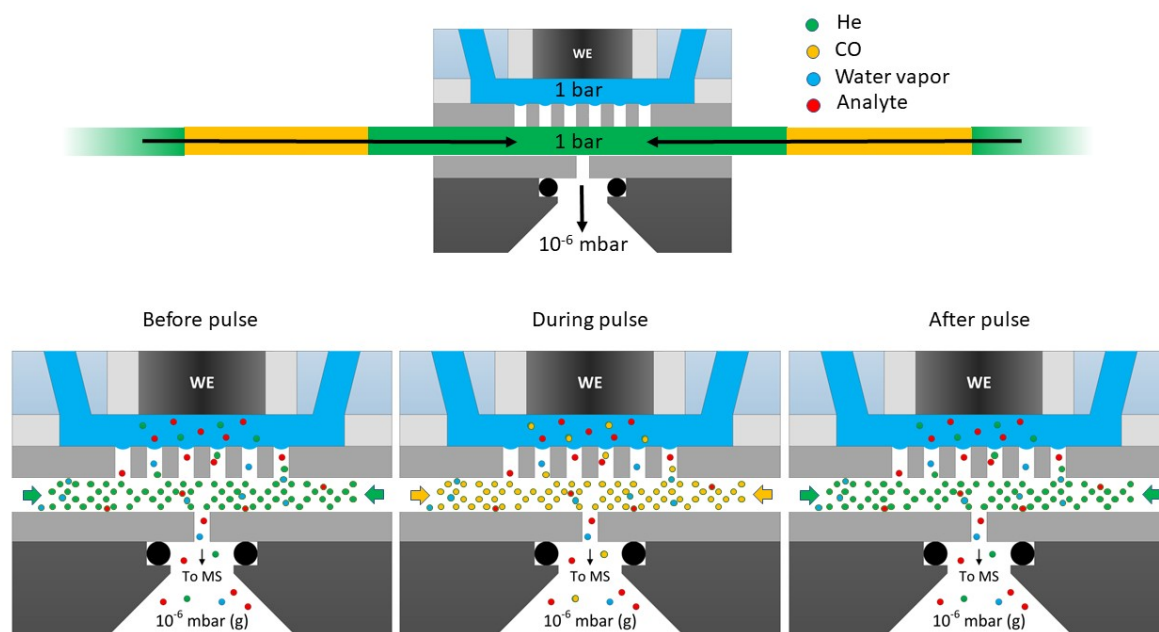


Figure 6. Schematic representation of a CO gas pulse sent via the gas exchange system.



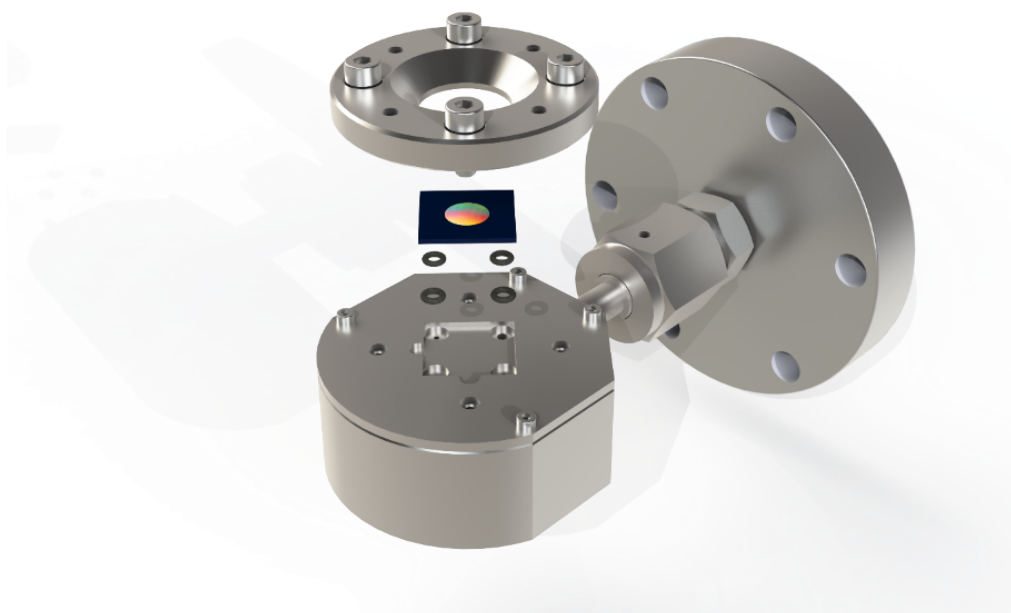
## 10. FAST SAMPLE AND CHIP EXCHANGE

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The system contains an integrated vacuum system, controlled by pneumatic valves via the user-friendly graphical user interface. Such system allows for rapid chip exchange with an automated pump-down procedure. A new chip can be installed in a few minutes without stopping pumps or turning off the spectrometer. This allows the user to dedicate different chips for experiments in special electrolytes or different electrode materials, and switch between such experiments in minutes.

If the system did not have an optimized, integrated vacuum system, the entire chamber would have to be vented every time a new sample or a new chip had to be exchanged. Not only is this a very time-consuming process, but it also dramatically compromises the vacuum quality in the MS chamber, increasing the baseline floor of the mass spectrum reading and, ultimately, compromising the high sensitivity of the instrument. Furthermore, venting requires the ionization filament of the mass spectrometer to be turned off, which is harmful and undesirable for multiple reasons. First, frequent power cycles of the filament shorten its lifetime. Second, degassing occurs each time the filament is turned on, deteriorating the vacuum level and wasting time. Third, the electron emission requires a few hours to stabilize each time the filament is powered up. Finally, pumping down a new chip via the main chamber would take too long to obtain proper evacuation of the chip.

Stability and control of these parameters are essential to enable reproducible and quantifiable EC-MS results. Our system avoids all this, ensuring fast and reliable operation and extended lifetime. It also avoids need for bake out, enabling rapid and reproducible chip and sample exchange without ever venting the chamber.



*Figure 7. Image of a chip mounted in the interface block. The chip exchange is effortless and quick.*



## 11. STREAMLINED SOFTWARE SOLUTION

We developed the Spectro Inlets EC-MS system in collaboration with Bio-Logic, so users can use the familiar EC-Lab software at its full capability to control EC experiments. The Spectro Inlets software directly communicates with EC-Lab and makes all the plots available inside the graphical user interface, together with the MS data.

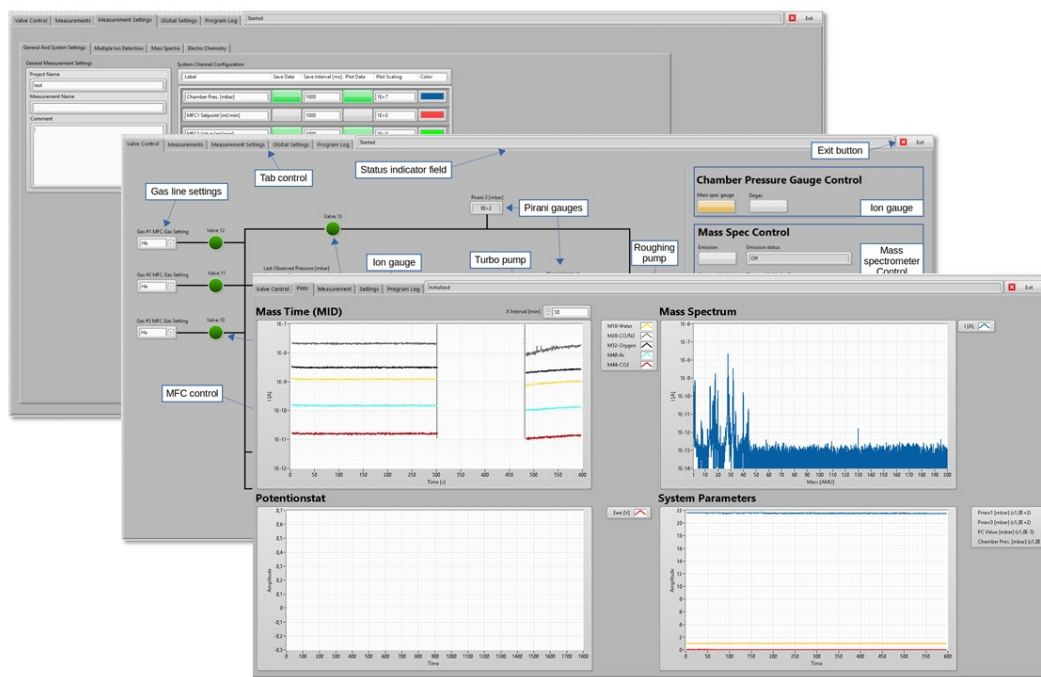


Figure 8. Screenshots from the user interface and a photograph of the software in action during a Pt cyclic voltammogram in acid electrolyte.

The software allows the full overview and control of the system with a user-friendly graphical user interface. Pneumatic valves, vacuum system, electronics, gas inlet system, and data acquisition are controlled via this interface. The user can manually control the individual components, or use the convenient automated procedures for e.g. chip pumpdown, timed gas pulsing, gas exchange, gas flow control, pressure control, etc.

The software streamlines synchronous acquisition, display, and storage of electrochemistry and mass spectrometry data with sub-second time resolution. The EC and MS data are acquired simultaneously, displayed side-by-side, and exported in a single ASCII text file, pre-synchronized. The file format is simple and well documented, helping with data analysis after experiments.

Automation enables the freedom to concentrate on the electrochemistry and obtain reproducible, standardized results. For example, the user can program a full CO stripping experiment as shown in Figure 4 with one or more gas switching events of arbitrary duration and timed exactly at a given time during the EC experiment (e.g. during the chronoamperometric hold in Figure 4).

The software is developed in LabView, and it is open source. Thus, the users are free and encouraged to modify the software and tailor the interface to their needs.



## 12. UNLOCKING A NEW CLASS OF EXPERIMENTS

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A representative experiment highlighting key features of the Spectro Inlets EC-MS is shown here.

### 12.1 EFFECT OF O<sub>2</sub> ON THE CO REDUCTION REACTION ON CU

In Figure 9, the effect of oxygen on CO reduction on Cu nanoparticles is shown. By exposing Cu nanoparticles to gaseous dioxygen (O<sub>2</sub>), while resting the working electrode at 0.0 V vs RHE, a reproducible, high transient production of CH<sub>4</sub> is seen at the onset of constant-potential CO electroreduction. Interestingly, this transient behavior is not observed on H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>, which indicates that only the reaction pathway towards single-carbon reaction products is affected. A two-minute pulse of gaseous O<sub>2</sub> was dosed into the carrier gas stream, replacing He. As a control, the same experiment was conducted with an Ar pulse injection prior to the introduction of O<sub>2</sub>.

Several key features of the Spectro Inlets system are highlighted in this experiment.

- **Gas dosing with reactant gases.** The system allows to control the gas saturation of the electrolyte and study the effect of different gases on electrodes. Electrolyte saturation is obtained within a second, thus avoiding the need of bubbling gas in external reservoirs for long time. See Section 9 for further details on the gas exchange feature.
- **Single turnover sensitivity.** Each molecule produced on the electrode is collected into the MS, so the total production can be easily quantified. Notably, while the EC signal is drowned in capacitance immediately after the change of potential, the MS signal provides unique insight into the transient behavior at the electrode surface. See Section 6 for further details on the high sensitivity of our instrument.
- **Quantification.** The signals are truly quantified in pmol/s.
- **Product detection.** The instrument can easily measure CO reduction products, including multi-C products such as ethylene, ethanol, propene, etc.
- **Real-time measurement.** The methane release lasts only a few seconds. The high time resolution together with the high sensitivity of the system allow to measure fast transient phenomena in a fully quantitative fashion.



## Effect of oxygen

**Electrode:** Cu nanoparticles  
**Electrolyte:** 0.1 M  $\text{KHCO}_3$

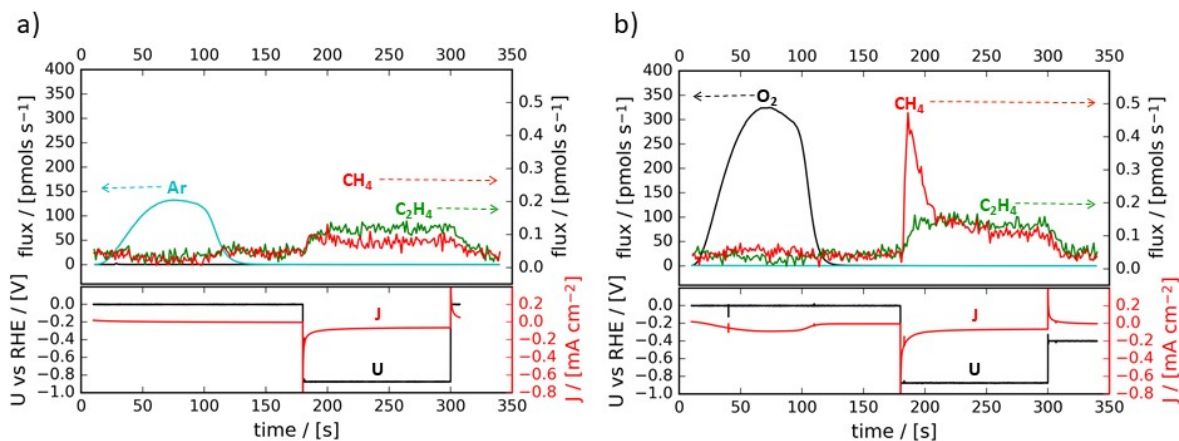


Figure 9. The effect of oxygen demonstrated by two consecutive constant-potential CO electroreduction experiments performed at  $-0.9\text{ V}$  vs RHE. Gaseous Ar (a) and  $\text{O}_2$  (b) are injected as 90 s pulse injections into the carrier gas stream of the membrane chip, while holding the potential at  $0.0\text{ V}$  vs RHE. This demonstrates that only gaseous  $\text{O}_2$  can activate the transient production of  $\text{CH}_4$ .<sup>3</sup>



## 13. TECHNICAL DATA

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	DESCRIPTION
MASS RANGE, AMU	0-200
SENSITIVITY	10 ppm of a monolayer in 1s, or 1 mA of continuous product formation
RESPONSE TIME	Down to 0.1 s (dependent on substance volatility)
SOFTWARE	LabView (open source)
INTERFACE	USB
DETECTOR	Faraday cup/Continuous Secondary Electron Multiplier
DIMENSIONS	450 mm x 790 mm x 337 mm
POWER	110/220/240 V AC, 50/60 Hz, 1.2 kVA

## REFERENCES

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