

Gas analysis for photoelectrochemical water splitting

Fast, reliable and affordable: The advantages of a mobile GC system

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The investigation of photoelectrochemical water splitting requires the analysis of the evolved gases. Knowledge of the reaction products allows to determine the Faraday efficiency of the reaction and gives information about side reactions. Gas analysis has been carried out by mass spectrometry [1] or with electrochemical sensors [2], but the most common way is gas chromatography (GC).

Gas chromatographs are powerful tools for qualitative and quantitative analysis, but the integration in a photoelectrochemical lab is not easy. The machines require a stable gas supply (N_2 , Ar or He), which is not available in all labs. They are immobile and block sparse lab space. The connection with the electrochemical cell typically requires access to a mechanical workshop and is hampered by problems like leakages. The machines are sensitive and have to be operated by trained personal. Finally, the cost of a standard GC can be high.

Objectives

As part of our work on metrology solutions for photoelectrochemical applications it was our aim to:

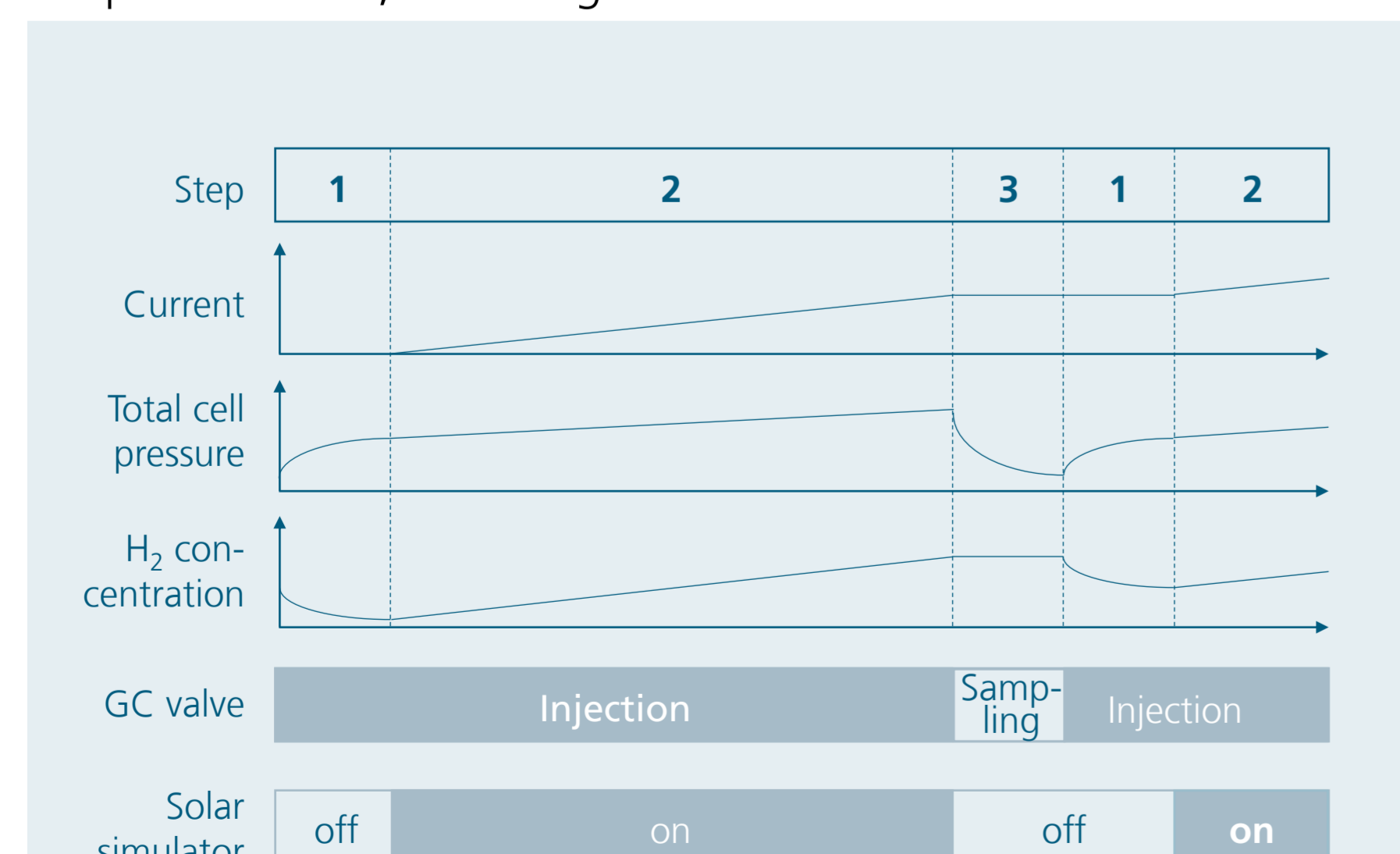
- integrate a mobile GC system in an existing metrological test platform
- develop and test a measurement routine
- carry out data and error analysis

Experimental approach

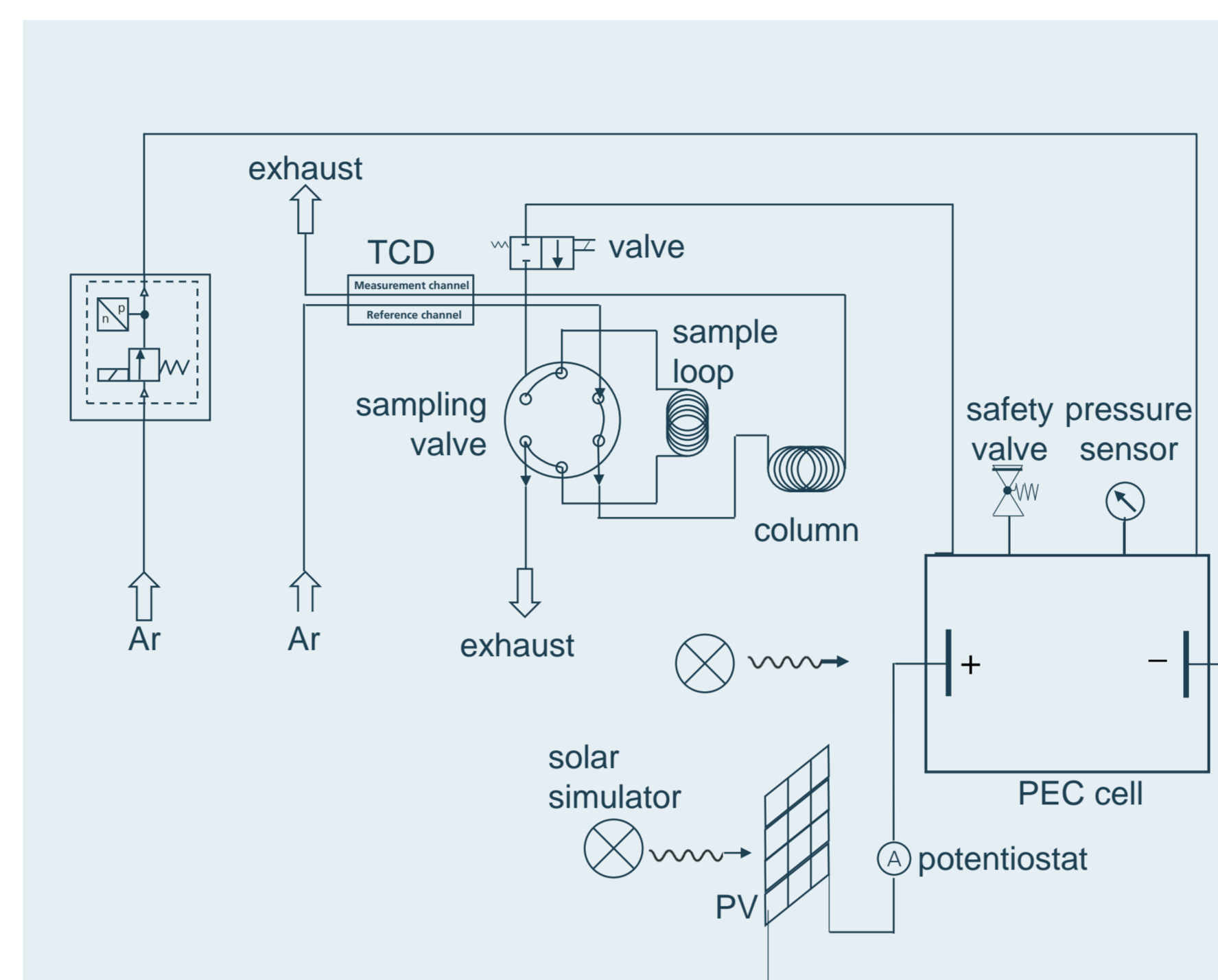
A Porto cell [3] is connected to a mobile GC from ECH, which is equipped with an integrated Ar tank. A pressure sensor and a pressure relief valve are connected as well. A potentiostat from Zahner records the current, illumination is done by an LED solar simulator from Wavelabs, and bias voltage for water splitting is provided by a photovoltaic module.

Every GC measurement consists of a series of cycles, each of which with three steps:

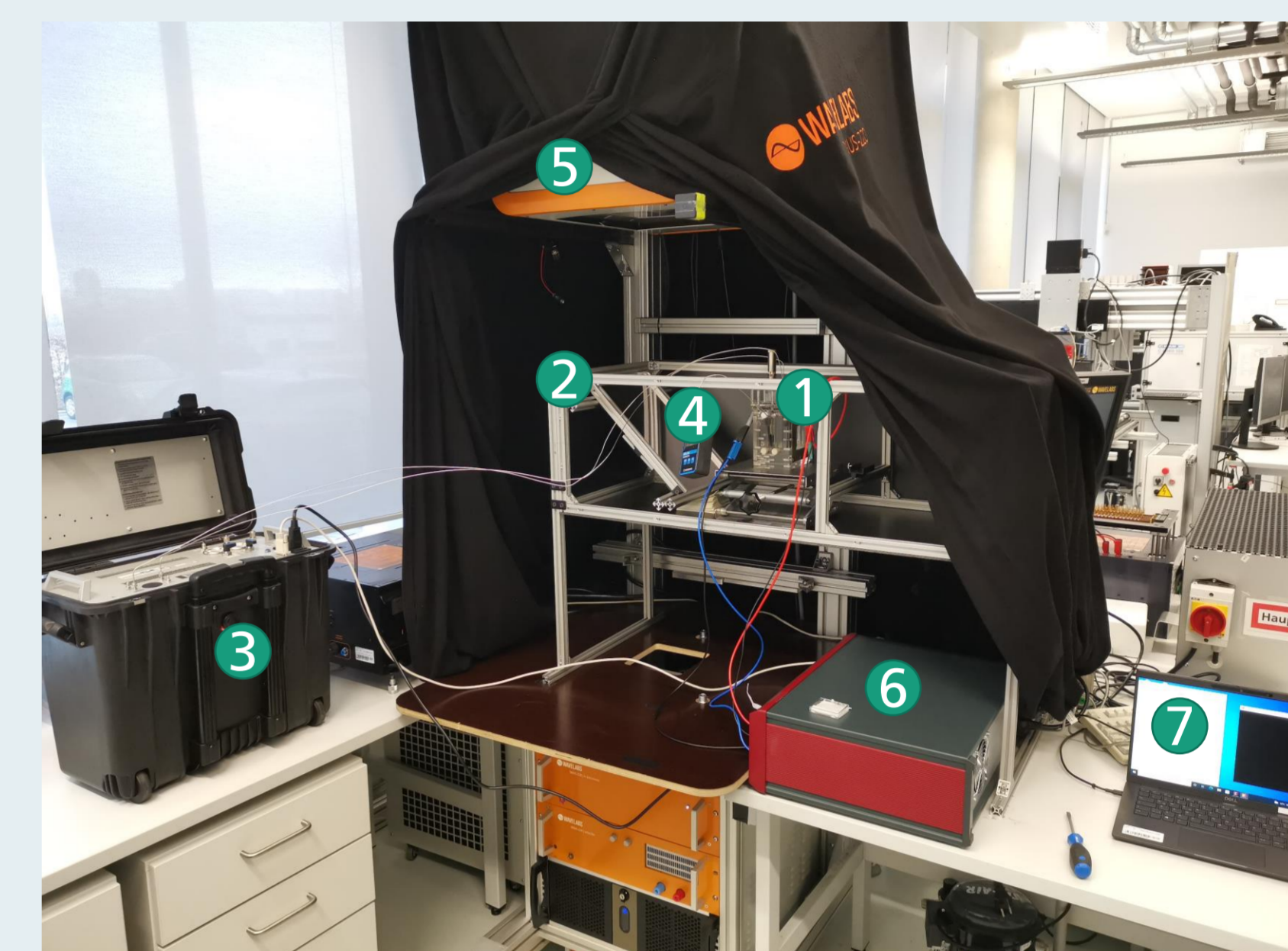
1. Setting the pressure of the photoelectrochemical cell to approx. 1.1 bar using Ar from the integrated gas tank of the GC. In this phase, the H_2 concentration in the cell falls.
2. A water splitting episode of 300 seconds, induced by switching on the solar simulator. At the same time the GC measurement of the previous cycle is running.
3. Sampling, which is done by releasing the atmosphere of the cell through the GC sampling valve. In this step, the cell pressure falls, but the gas concentrations remains constant.



Timeline of the three-step gas analysis process and changes in current, pressure and H_2 concentration (schematic; not to scale)



Process flow diagram of the experimental setup and photograph (1 Porto cell, 2 Fraunhofer test platform with removed cover, 3 GC, 4 pressure sensor, 5 solar simulator, 6 potentiostat, 7 computer with script for automated data analysis)



Data analysis

Once started, all individual devices operate continuously without user input. After the final measurement, all results are automatically imported into an Excel script. Further experimental parameters (eg, the gas volume of the cell) can be entered manually. For each completed measurement cycle, the program calculates the molar amounts of hydrogen and oxygen from their measured concentrations based on the ideal gas law and plots the Faraday efficiency and the solar to hydrogen efficiency as a function of time.

Automatic corrections are carried out for leakage (as determined from the pressure loss during an idle period), for the influence of the room temperature on the gas volume (by user input) and for the influence of the atmospheric pressure on the GC sample volume (automatic determination).

Results

For a 25.0 cm² photocathode of copper gallium selenide in 0.1 M H_2SO_4 , a Faradaic efficiency of (98.5±2.6) % was determined. The solar-to-hydrogen efficiency was calculated to be (1.9±0.1) %, when an additional area of 6.0 cm² for the PV module was considered. Both values agree with previous literature records [4].

Error analysis

For the example given above, a quantitative error analysis with consideration of the propagation of uncertainty showed that the free gas volume of the electrochemical cell is the most important contribution to the overall error. For this value, an individual measurement uncertainty of 0.2 cm³ results in an absolute error of 0.9 % in the Faraday efficiency.

Depending on the experimental setup, variations in reaction temperature, deviations in illumination (intensity, spectrum, spatial homogeneity) and non-ideal behavior of the gas/liquid system (trapped gas bubbles) can contribute significantly to the error. The GC measurement itself has a high accuracy with an error of less than 0.01 % but relies on the quality of the calibration.

Discussion and conclusion

The error analysis shows that the GC measurement is highly accurate and does not significantly contribute to the overall error. The developed GC system allows to solve a number of typical problems which are connected with this technique. Specific advantages are:

- A low internal volume and short columns allow **fast measurements** with one data point every 6 minutes (for other systems, 20 minutes are common) [5,6].
- The integrated gas cylinder allows an **easy setup** without the need for an external gas supply.
- **Automatic** determination of Faraday and solar to hydrogen efficiencies allows to correct leakage and environmental conditions. Human mistakes in data processing are avoided.
- The system is **more cost-efficient** than GCs which are designed for more demanding analytical tasks.

Literature

- [1] T. Takata *et al.*, *Nature* **2020**, 581, 411.
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