METROLOGY for
HYDROGEN VEHICLES 2

Deliverable 7

Good practice guide on measuring the impact of contaminants on FC stacks (with online analysis) with detailed description of parameters to monitor

Project name:	MetroHyVe 2
Grant agreement:	19ENG04
Lead partner:	VTT
Authors:	Jari Ihonen, Thor Aarhaug, Sylvie Escribano, Graham Smith
Due date:	30 September 2023
Submission date:	31 October 2023
Version:	1

This project “Metrology for Hydrogen Vehicles 2” (MetroHyVe 2) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union s Horizon 2020 research and innovation programme under Grant agreement No [19ENG04].

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

www.sintef.no/projectweb/metrohyve-2

Good practice guide on measuring the impact of contaminants on FC stacks (with online analysis) with detailed description of parameters to monitor

Funding European Metrology Program for Innovation and Research	**Grant agreement no:** 19ENG04
Project name Metrology for Hydrogen Vehicles 2	**Project short name** MetroHyVe 2
Author(s) Jari Ihonen (VTT) jari.ihonen@vtt.fi Thor Aarhaug (SINTEF) thor.a.aarhaug@sintef.no Graham Smith (NPL) graham.smith@npl.co.uk Sylvie Escribano (CEA) sylvie.escribano@cea.fr	**Pages** 18 pages

Summary

The purpose of this good practice guide is to provide guidance on measuring the impact of hydrogen impurities on PEMFC stacks. The recommendations focus on measurements performed with online gas analysis on short stack PEMFC representative of stacks for automotive use operating dead-end and with recirculation.

This good practice guide was written as part of activity 4.5.3 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit www.sintef.no/projectweb/metrohyve-2.

Confidentiality	Public

This project "Metrology for Hydrogen Vehicles 2" (MetroHyVe 2) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme under Grant agreement No [19ENG04].

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Deliverable D7

1. Introduction

1.1 Scope

This good practice guide (GPG) focuses on measuring the impact that trace impurities in hydrogen have on the performance of polymer electrolyte membrane fuel cell (PEMFC) stacks. The measurements performed in MetroHyVe2 which underpin this GPG focused on short stacks of ca. 10 cells with 150 - 350 cm^2 active area representative of stacks for automotive use, operating in dead-end mode with recirculation. The measurements also featured online gas analysis to characterise the composition of anode gas in the recirculation loop. Many of the recommendations herein are general but several relate to measurements using this specific configuration. This Good Practice Guide should be read with MetroHyVe2 Deliverable 8: *Report on standard test protocols concerning FC measurements with stack to determine threshold limits of critical contaminants in hydrogen.*

1.2 Aims & Objectives

PEMFC are prone to poisoning by impurities and automotive PEMFC require hydrogen with a very low level of impurities to ensure high performance and durability. The quality of hydrogen at refuelling stations is specified by the ISO 14687:2019 standard, which limits the maximum permissible levels of hydrogen impurities by specific compounds or type of compound. As fuel cell technology develops and the hydrogen supply chain becomes more complex introducing new impurities, robust experimental evidence of the behaviour of impurities inside stacks operating under normal conditions is required to underpin decisions about the permitted levels of impurities. If the limits are too conservative, the price of hydrogen is increased unnecessarily, and if too relaxed, fuel cell vehicles may be damaged. This GPG aims to communicate the best practices developed in the MetroHyVe2 project to others seeking to measure and characterise the impact of specific impurities on PEMFC.

2. Parameters that should be monitored and controlled.

Test protocols for measuring the impact of impurities on stacks are provided in MetroHyVe2 D8; this section provides recommendations for parameters that should be monitored and reported to ensure that the measurements performed following D8 are understood and can be repeated.

2.1 Anode composition

Understanding the composition of the gas at the anode is vital to understanding the impact of deliberately introduced impurities. The composition of the fuel should be monitored on the operating test station either during or before measurements are made, as trace changes in the composition may alter the impact of impurities. Furthermore, when measurements with anode recirculation are performed the composition of the gas can vary as a function of sample location so measurement of anode gas from several different points during operation may be necessary to fully characterise the composition and how it changes as a result of the introduction of impurities. The possible points for analysis are illustrated in Figure 1 and the rationale behind each measurement point is explained in the following sections.

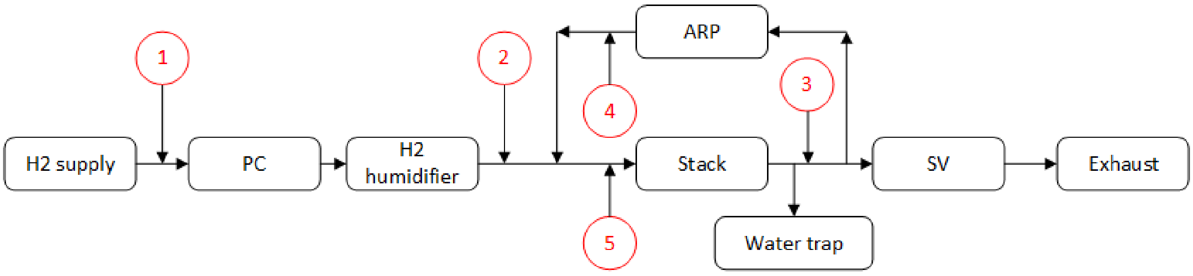


Figure 1. Illustration of sampling points. PC=Pressure controller, ARP=Anode recirculation pump, SV=solenoid valve.

2.1.1 Gas feed from hydrogen supply (Point 1)

The hydrogen gas quality should be controlled and monitored before the test station (1). The quality of the 'pure' hydrogen, used for baseline testing, and the impure hydrogen, used for assessing the impact of the impurity, should both be known, with a particular focus on the presence of any impurities specified in the ISO 14687 standard. Hydrogen produced electrolytically in the laboratory using a hydrogen generator avoids the introduction of many potential impurities, however the oxygen concentration must still be quantified.

Cylinders containing high concentrations of impure hydrogen are often diluted with pure hydrogen due to the relatively high gas consumption of stacks. This is often accomplished by the use of decaded mass flow controllers (MFC). MFC dilution often adds considerable uncertainty to the final composition of the fuel, particularly during dynamic operation, such as during purges and dynamic load cycling. If MFCs are used it is recommended to verify the composition of the hydrogen before measurements using gas analysis at flow rates that span the expected operational range. Alternatively, analysed cylinders containing the target concentration can be used directly which eliminates this uncertainty.

2.1.2 Inlet gas feed (Point 2)

The composition of the gas after passing through the test-station and before mixing with recirculated hydrogen should be monitored (2) either before or during measurements. This measurement should be performed after any MFC, tubing and humidifiers.

This measurement is to confirm that the impurity of interest is not lost inside the test station. Water soluble species can be lost to humidifiers while other species can be adsorbed onto pipes, valves etc. See section 3 for additional recommendations when using reactive gasses.

This measurement should also confirm that additional impurities are not introduced. Humidifiers can introduce impurities as gases dissolved in the humidifier water supply; this particularly applies to oxygen which is known to mitigate the impact of other impurities and is not removed during the typical deionisation methods used to make Type I water. This issue is pronounced if the humidifier has a bleed function active so that the amount of water passing through the humidifier is larger than that used for humidification. Where possible it is recommended that humidifiers be avoided.

2.1.3 Composition of recirculated gas at the anode exit (Point 3)

Depending on the measurement being performed monitoring the composition of the recirculated gas at the anode during operation may be important. During operation of a stack with dead-end and recirculation, the concentration of components that are not consumed by or adsorbed to the stack will build up (enrich) as the hydrogen supplied to the stack is consumed. Such compounds may include impurities (such as nitrogen, argon), the products of reaction of impurities, deliberately introduced tracer gases (such as methane) and compounds that crossover from the cathode to the anode (principally oxygen, nitrogen, argon and carbon dioxide). The degree of enrichment is a function of the utilisation of the hydrogen and subsequently the dead-end purge parameters, as inert components are only lost by crossover to the cathode or during the purge.

2.1.3.1 Monitoring carbon dioxide

Carbon dioxide permeability through the membranes used in PEMFC is high so after a short period of operation the carbon dioxide concentration at the anode will approach that on the cathode. The time taken for this enrichment depends on the area of the stack relative to the recirculation loop volume but for 10 cell short stacks with an active area of ~ 200 cm^2 and a ~ 5 L recirculation loop volume an equilibrium concentration was reached within 2 h of operation, the limit to this is stable equilibration of the membrane so this may vary between stacks. The presence of carbon dioxide at the anode has been reported to have a detrimental impact on the performance of PEMFC [1]. Though the impact is small at relevant concentrations it may add additional uncertainty to measurements of the impact of other fuel impurities.

2.1.3.2 Monitoring oxygen

Like carbon dioxide, oxygen crosses from cathode to anode. Most oxygen is consumed by chemical reaction with hydrogen in the anode catalyst layer where it is catalysed by the anode catalyst. However, it may also react chemically with impurities adsorbed on the anode catalyst, oxidising and removing them and mitigating the impact of impurities. A typical reaction may be the oxidation of carbon monoxide to carbon dioxide. Matsuda et al. [2] could observe 5 times higher carbon monoxide tolerance (in ppm) when oxygen was applied added to the recirculation loop.

Low concentrations of oxygen may also remain unreacted, particularly when a substantial fraction of the anode catalyst is poisoned and is therefore catalytically inaccessible. In this case high levels of oxygen may pass through the anode exhaust. In a study by Matsuda et al. [2] the oxygen level in the absence of poisoning was 30-40 ppm, during mild poisoning, when cell voltage drop was 40 mV, over 100 ppm oxygen could be measured in the anode exit, and during severe poisoning, when the cell voltage dropped by about 200 mV, the oxygen concentration at the exhaust was over 200 ppm.

When measurements were performed in the MetroHyVe2 project, oxygen at the anode exit was below the detection limit of microGC with argon as carrier gas (approximately 10 ppm). When oxygen level at the anode exit was measured during mild poisoning, corresponding to a cell volage drop of less than 50 mV, the oxygen concentration was still under the detection limit (10 ppm). However, when a severe poisoning, corresponding to a voltage drop over 200 mV, happened, then over 50 ppm oxygen could be measured in the anode recirculation gas. The results of the MetroHyVe2 project therefore confirm the observations of Matsuda et al. [2]., even if the level of oxygen in the stack level measurements was lower than in the single cell measurements of Matsuda et. al.

2.1.3.3 Monitoring enriched impurities

The enrichment of a deliberately applied impurity may be important to monitor when it is expected that the impurity, or a product formed by the impurity, may have an impact on the cell performance as its concentration increases. This is the situation e.g. with toluene [3] hydrogenating to methylcyclohexane which may have a poisoning effect at high concentrations.

When the concentration of the deliberately applied impurity does not increase during the measurement, then monitoring is not needed. As an example, it was observed in the MetroHyVe2 project that the carbon dioxide level at the stack exit is very small and starts to increase only after very severe poisoning has already taken place. It could be concluded that monitoring carbon dioxide level is not necessary when Pt is used as anode catalyst as no enrichment occurs. This result, however, is catalyst dependent and may also be stack dependent. If new carbon dioxide tolerant catalysts are studied, then carbon dioxide level at the anode exit should be measured at least in the beginning to see if carbon dioxide is enriching in the anode recirculation loop or not.

2.1.3.4 Fuel utilisation calculation

When operating a stack with dead-end operation there are several possible methods to calculate the utilisation. Two of the most accurate methods involve monitoring the composition of the anode gas at the outlet of the stack. The methods are i) monitoring the enrichment of inert gas that crosses from the cathode (argon, nitrogen) or ii) monitoring the enrichment of an inert tracer gas (e.g., methane) that is deliberately supplied as an impurity.

Monitoring the composition of methane at the stack outlet is straightforward, with a target utilisation of 99% the enrichment of the methane is 100 fold. In MetroHyVe2 a concentration of 0.05 µmol mol^{-1} methane was added to the inlet hydrogen with the concentration monitored by methaniser. The principal source of uncertainty on measurements of utilisation using this method was that introduced by the MFC dynamically diluting the impurity at the inlet.

To avoid adding methane it is also possible to monitor utilisation via enrichment of nitrogen and argon which cross from cathode to anode. In practical PEMFC systems that have operated long enough to reach equilibrium there is approximately 10-30% nitrogen and about 0.1-0.3% argon in the anode recirculation gas on a dry gas basis. Therefore, measuring nitrogen or argon concentrations is a straightforward method of assessing fuel utilisation. Alternatively, hydrogen concentration may be monitored, with the 70-90% expected for real PEMFC system operation. The main uncertainty on these measurements is that gas permeability is a function of operating conditions and different for different types of membrane and may change over a stack's lifetime. Crossover therefore needs to be adequality characterised before using this method to estimate utilisation. Measurements of nitrogen, argon or hydrogen concentrations also verify that the anode purge is working consistently such that gas volumes between different purges are not too different. Measurement of this is important since gas volumes in purges are strongly dependent on the operating conditions as well as stack hydration state.

Enrichment may also be monitored via the carbon dioxide concentration in the anode loop, however several laboratories in MetroHyVe2 observed that the carbon dioxide concentration in the cathode air supply varied though the day and is known to be different at different locations (e.g. urban air). It is therefore necessary to monitor or control the concentration of carbon dioxide at the cathode too.

2.1.4 Composition of gas after the recirculation pump (Point 4)

Measurement of gas mixture composition after the recirculation pump is recommended to verify that oxygen is not being added by the recirculation pump. In measurements in the MetroHyve2 project one partner could measure additional oxygen (tens of ppm), which was due to operation of the recirculation pump (double diaphragm type).

2.1.5 Composition of gas mixture of inlet feed and recirculated gas (Point 5)

Comparison of the anode composition at the stack outlet and after mixing the fresh hydrogen with recirculated hydrogen is one method to measure the recirculation rate. This is done via a simple mass balance.

2.2 Measurement and control of fuel utilisation

If operating dead-end with or without recirculation it is important to measure or estimate fuel utilisation and if possible, control it. Measurements in MetroHyVe2 suggested the utilisation impacted stack tolerance to carbon monoxide with higher utilisation resulting in lower tolerance.

The recommended methods for fuel utilisation measurement or estimation are based on gas analysis. These are:

1. Measurement of inert tracer gas, that has been added in hydrogen fuel. Methane is one possible tracer gas.
2. Measurement of enriched nitrogen, argon or carbon dioxide levels or hydrogen level in the anode recirculation loop.

Direct measurement of consumed fuel is also possible using well calibrated mass flow meters, which have a fast response time. However, MetroHyVe2 results showed that fuel utilisation can fluctuate significantly during a single measurement and between measurements as the volumes in purges are strongly dependent on the operating conditions as well as stack hydration state. Due to this, separate measurement of purge volumes is not a reliable way to estimate fuel utilisation. This means that fuel utilisation cannot be estimated based on a single measurement, in which high data sampling frequency for mass flow meters during hydrogen purges can be used. Instead, flow measurement during hydrogen purge should be used in every measurement all the time and may still introduce significant uncertainty.

Control of very high (>99.5%) fuel utilisation using laboratory setups was found to be difficult during MetroHyVe2. The loss of control may lead to excessive nitrogen level in the anode loop, causing large differences between measurements, and in the worst case, local fuel starvation leading to accelerated degradation. Fuel utilisation of about 98-99% is still easy to control according to experiences from the MetroHyVe2 project. This fuel utilisation seems to be sufficient for the measurements.

2.3 Stack temperature and gas dew point temperatures

Stack coolant inlet and outlet temperatures, as well as gas dew point temperatures at the inlet should be measured. Since typical humidity sensors used in test stations tend to drift, these sensors should be calibrated frequently.

The measurement of stack coolant inlet and outlet temperatures is straightforward. However, the *control* of these temperatures is very challenging when stack power levels are changing, as in rapid measurement of a polarisation curve or during a dynamic load cycle (DLC). When a DLC is applied, the changes of stack temperature and gas dew point temperatures are different for every test station, and for every real fuel cell system. This is due to the different thermal masses of the components, different methods of controlling humidity as well as coolant flow rates. In addition, the design and programming of the control systems are different. Furthermore, the response time of most humidity sensors is longer than the shortest step times in common DLC. Due to this, measurement and control of real humidity levels of gases becomes impossible during the DLC.

Changes to the stack temperature and gas dew point temperatures can affect impurity tolerance, in addition to different base level performance without contaminants. The effect of DLC is dependent on the contaminant studied. If it can be shown, by single cell measurements, that DLC does not have a major influence on the impact of contamination, it should not be used in the stack level, as uncertainties due to different stack temperature and gas dew point temperatures are larger than the benefits gained.

2.4 Anode gas recirculation rate

Results in MetroHyVe2 showed that the anode gas recirculation rate changed the impact of the carbon monoxide on stack performance at all fuel utilisation rates. Therefore, the control and measurement of anode recirculation rate is important.

Based on the MetroHyVe2 results and previous experiences, the recirculation rate can be measured relatively simply by using humidity sensors and humidity balance [4]. However, using this approach requires well calibrated and stable humidity sensors. If the gas composition is measured before and after the mixing point for recirculated and mixed gasses, then the recirculation rate, on a dry gas basis, can be obtained from the mass balance of nitrogen, argon, hydrogen, carbon dioxide or a tracer gas. Measuring the total flow rate of gas also requires the humidities to be monitored.

Another option to estimate the anode gas recirculation rate is to monitor the anode pressure drop. However, in practice this was found out to be problematic with both flow resistance and gas viscosity changing during an experiment introducing significant uncertainty.

2.5 Stack anode active surface loss

To report results in way that allows a full understanding of the impact of impurities on the stack requires key details of the stack to be reported. One of the most important parameters is the anode electrochemically active surface area – this is a measure of the amount of area of catalyst that is available to perform electrochemical reactions; a stack with a higher area requires longer to poison. Another key parameter is the membrane thickness as this has an influence on crossover behaviour. Finally, the presence of any additives to make the stack more resistant to impurities, such as recombination catalysts should be reported. A proxy to these parameters was used in MetroHyVe2 where a baseline experiment assessed the length of time taken for a 50 mV cell voltage loss when 0.8 µmol mol^{-1} impurity was applied.

2.6 Anode volume, pressure and inlet flow rate

To convert from concentrations to absolute quantities e.g., from µmol mol^{-1} to µmol, and to calculate mass balances it is necessary to have a measure of the anode volume, anode pressures and in the flow rate of hydrogen to the stack. It is also worth noting that the pressure of the anode in many test bench experiments using recirculation and dead-end is lower than is typical during operation as the pressure is limited by the maximum operating pressure of recirculation pumps. Where this is the case, it is recommended to maintain the same anode-cathode pressure differential as would be found in a real system to maintain the same crossover dynamics; however, note that lower cathode pressures will lead to reduced performance for most stacks.

3. Recommendations for gas analysers

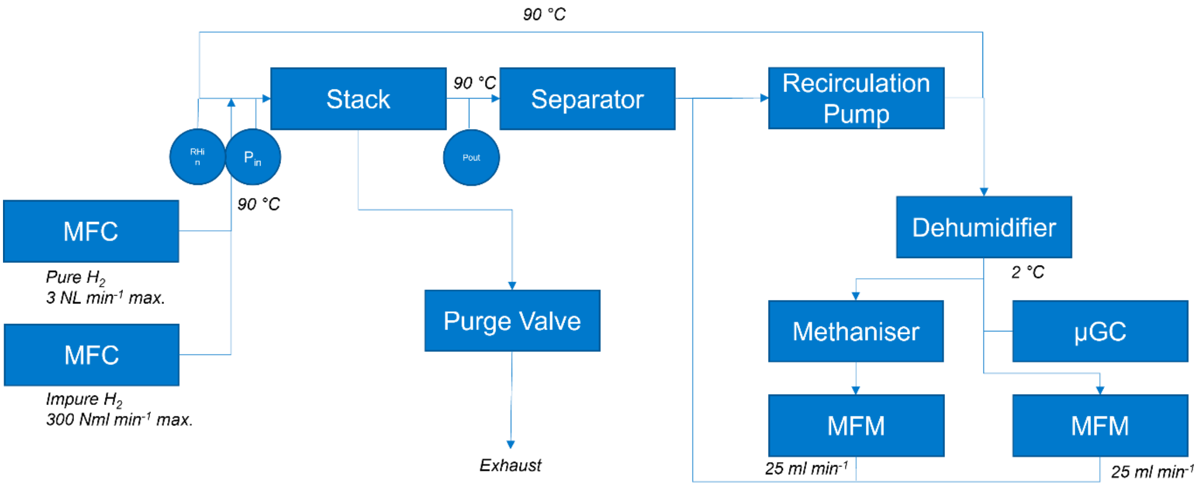
3.1 Introduction

This section considers gas analysers suitable for online analysis, specifically on hydrogen in the recirculation of a PEMFC system or test bench. Operation in such an environment places additional constraints on the analysis equipment relating to gas conditions and sample volumes. The advantages, disadvantages and advice on the installation of various types of analyser are discussed.

Making online gas measurements is complex and requires careful consideration of the fuel cell and the gas analysis systems, and how they are coupled together. There are several factors that must be considered for high quality measurements and often a balance must be struck between properties such as gas consumption, sampling time and limits of detection. There are numerous options for gas analysers when the anode gas composition is measured. The choice of gas analysis instrument is always a compromise of several parameters.

3.2 General considerations

Recirculation vs single pass: In systems with a single pass of hydrogen through the anode, it is straightforward to connect analytical instrumentation after the fuel cell stack or back pressure controller, with the exhaust acting as an overflow. In systems where the anode gas is recirculated, as in many experiments in MetroHyVe2, the situation is more complex, and gas must be sampled from the recirculation loop. In practice, this often requires a bypass to the recirculation loop that can pass a fraction of the recirculated anode gas over the instruments in overflow. If the bypass has a low pressure drop then it is often possible to use the pressure difference over the recirculation pump to drive flow through the bypass though this limits the sampling locations, Figure 2



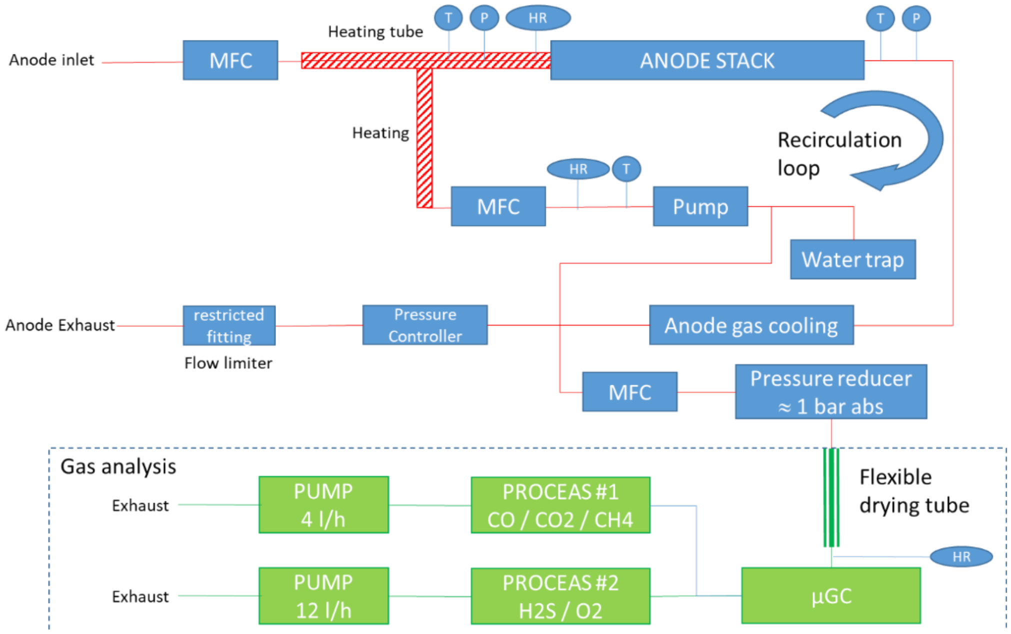


Figure 2 A simplified P&IDs of the anode line including sampling and analysers of short stack measurements in MetroHyVe2.

Fuel utilisation: When operating with dead-end, it is common for 1-5% of all hydrogen supplied to the stack to be lost through the exhaust and ideally the gas analysis equipment will not change this. Depending on the stack's size, operating conditions and current drawn, the quantity of gas that instruments may be permitted to consume may be small if fuel utilisation is expected to impact the measurements. Furthermore, it may be necessary to adjust purge cycle timing to adjust for the extra volume of gas lost to the instrument. For the same reason, even small leaks are not permissible.

Sampling frequency: While instruments may have fast response times, the anode flow rate and the total volume of any exhaust system, sampling system, recirculation loop and stack and anode will determine how quickly steady state is reached and how quickly changes to behaviour will be detected by gas analysis equipment.

Limits of detection, accuracy and range: The concentrations of impurities that may impact PEMFC often are low necessitating low limits of detection and high accuracy. The lowest concentration in the ISO 14687 standard is 0.04 µmol mol^{-1} total sulphur content. However, nitrogen is often present in the anode at concentrations of >30 %; the analyser must therefore be chosen with a realistic assessment of likely concentration ranges and more than one may be required.

Water solubility: If the impurity is water soluble, its loss into liquid water produced by the fuel cell must be considered. In recirculation loops, droplet traps are employed to collect the excess water, and thus, to ease the circulation pump performance and maintain good purge performance and repeatability. Water drainage affects the accumulation of water-soluble impurities.

Gas drying: Many analysers require low humidity to function reliably, or else quantification/ calibration factors change as the relative humidity changes. Often, chilled condensers are used to dry gas before analysis which may remove impurities from the analysed gas, impacting quantification.

Latent oxygen / air species: The presence of oxygen, nitrogen, argon or carbon dioxide from crossover through the membrane or from insufficient purging before starting experiments may prevent straightforward quantification of some compounds. For example argon and oxygen have similar retention times on common µGC instruments which often prevents quantification of oxygen.

Sticky impurities: Many impurities of interest stick to tubing and connections preventing their accurate quantification. The use of specially coated tubing and components is often required to mitigate this problem.

Pressure: At realistic stack operating conditions, around 1.5 bar_g, the pressure may need to be reduced to safely operate certain instruments. Changes in pressure may also affect the calibration constants of analytical equipment, for instance changing the amount of gas in sample loops.

Stability: Gas analysers need regular calibration; however, with many PEMFC experiments spanning several days common calibration times and practicality must be considered.

Economics: Gas analysers are available at a range of price points and with varied operational costs, especially the cost of high-grade helium.

Number of components: Many gas analysers can monitor several components simultaneously, particularly gas chromatographs; this has many operational benefits when these compounds are the permanent gases commonly found in PEFMC anodes – oxygen, nitrogen, carbon dioxide, argon.

3.3 Review of gas analysis equipment

Gas analysis equipment suitable to use online on a PEMFC test bench is listed in Table 21 along with approximate detection limits in Table 2. The listed equipment is limited to instruments that the partners have experience operating. More details are provided in MetroHyVe report 4.2.1 where each type of equipment is addressed in turn. In FTIR all gas can be returned to recirculation loop leading to zero gas consumption.

Table 1 Summary information for the different analysis techniques; figures are indicative and depend on the specific instrument, experimental configuration, and other parameters.

Technique	*Gas consumed by analyser and not returned to system*	*Drying Required?*	*Recirculation Possible?*	*Time Resolution*[1]
GC - methanizer - FID	<1 ml min^{-1}	Y	Y	300 s
GC - PDHID	<1 ml min^{-1}	Y	Y	300 s
GC - TCD	<1 ml min^{-1}	Y	Y	300 s
GC - MS	<1 ml min^{-1}	Y	Y	300 s
FTIR	0 ml min^{-1}	Y	Y	< 10 s
OFCEAS	>50 ml min^{-1}	Y	N	< 10 s
CRDS	<1 l min^{-1}	Y	N	< 300 s
SIFT - MS	>10 ml min^{-1}	N	N	< 10 s

---

[1] Time resolution does not consider the time to replace gas in the sample loop or the instrument which in the case of techniques like FTIR might reduce the real temporal resolution significantly.

Table 2. Online gas analysis equipment for PEMFC systems showing detection limits in μmol mol^{-1}.

	Ammonia	Argon	Carbon dioxide	Carbon monoxide	Formaldehyde	Formic acid	Halogenated compounds	Helium	Methane	Nitrogen	Oxygen	Total hydrocarbons	Total sulphur compounds	Water
Chromatography														
GC - methanizer - FID			0.020	0.020					0.020			0.020		
GC - PDHID with He carrier		0.1	0.1						0.3	0.3	0.1			
GC - TCD with He/H_2 carrier		1	2	TBC					TBC	1	1			
Spectroscopy														
FTIR	0.05		0.01	0.002	0.05	0.05	0.01[2]					0.05	0.025[3]	
OFCEAS	0.1		0.002	0.001	0.001	0.005	0.05[1]		0.01		1		0.001[4]	0.01
CRDS	0.0003		0.320	0.05	0.006				0.0075		0.003			0.005
Spectrometry														
SIFT - MS	0.020		0.5		0.020	0.020	<0.1[5]					<0.1[4]	0.002[4]	

---

[2] HCl, freon unknown

[3] SO_2, COS, CS_2 not H_2S

[4] H_2S

[5] For specific compounds

3.4 MetroHyVe2 Experience

In MetroHyVe2 measurements the following two gas analysis instruments were studied in detail.

1. Gas chromatograph (GC) with thermal conductivity detector (TCD) from Agilent (490 Micro GC). With this instrument all common components in the anode recirculation gas could be measured. However, the limit of detection (LoD) for carbon monoxide was not sufficient for the experiment performed. For measuring the oxygen concentration in the anode loop, a measurement channel using molecular sieve and argon as a carrier must be used. The argon content in the recirculation loop is so large that the smaller oxygen peak cannot be separated from the argon peak if helium is used as a carrier. The main disadvantage of GC-TCD is its limited sampling rate. In principle the absolute minimum sampling interval is 2 minutes but in practice 3-4 minutes is needed. Gas consumption of GC-TCD is negligible, which means that it does not affect fuel utilisation during measurements.

2. Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) from Ap2e (ProCeas®). With this instrument continuous monitoring of numerous relevant components (methane, carbon monoxide, carbon dioxide, hydrogen, water, oxygen) is possible. From these components oxygen, carbon monoxide and methane were studied in MetroHyVe2 measurements using two ProCeas® instruments. Based on the results of MetroHyVe2 project, OFCEAS has an excellent limit of detection as well as response time for the PEMFC measurements. However, relatively high gas consumption of the instruments (67 ml min^{-1} and 200 ml min^{-1}, respectively) is an issue for fuel utilisation, when short stacks and low current densities are measured.

Based on the MetroHyVe2 measurements, GC-TCD (Agilent 490 Micro GC or similar) can be recommended with 5 Å molecular sieve and Poraplot U (PPU) channels or columns. For the measurement of oxygen in the recirculation loop argon is needed as a carrier gas for 5 Å molecular sieve column. For more precise measurements of gas components and for higher sampling rates a ProCeas® or comparable laser instrument may be suitable.

4. Recommendations for testing with reactive contaminants

Inert species exit the anode though the anode purge and to a lesser extent by crossover from anode to cathode. Water-soluble species may exit with condensed water, which in recirculation loops is separated from the recirculated hydrogen in the loop. Reactive species, however, may decompose in the loop, either through reaction with other gas constituents or by decomposition over the anode catalyst, for example the fate of formic acid and formaldehyde has been extensively studied [5]. A recent review of recovery procedures for PEMFCs also addressed some mechanisms and regeneration methods regarding catalyst poisoning by air contaminants or fuel impurities [6].

Experiments with reactive impurities should come with a strategy for cleaning up the stack and the fuel line. Studying the tail-off concentration after stop of impurity feed could provide valuable information about the clean-up efficiency and time needed.

The measurements with reactive and strongly adsorbing contaminants differs significantly from those where carbon monoxide or similar contaminants are used. Generally, adsorbing gas species like hydrogen sulphide, sulphur dioxide and ammonia will not enrich in the recirculation loop as loop walls and the stack itself will accumulate the impurities. The effect of reactive and/or adsorbing contaminants can nevertheless show dependence on other gases enriched in the loop, as shown with carbon monoxide and increased oxygen concentration.

4.1 Adaptations required to experimental set-up

The adaptations required will depend on the physico-chemical nature of the impurity to be tested. For example, both hydrogen sulphide and toluene are reactive but both have very different interactions with materials used in recirculation loops and differing impacts on fuel cells. The following general recommendations should be considered when planning an experiment.

Passivate tubing: some species are known to adsorb onto tubing material reducing the concentration in the gas phase and potentially desorbing later contaminating otherwise pure hydrogen. It is therefore necessary to check that the compound of interest does not appreciably adsorb to the tubing. In experiments in MetroHyVe2 it was found that there was no detectable time for hydrogen sulphide to pass through PFA tubing or SilcoNert® coated 316 stainless-steel but there was for uncoated stainless steel. However, there was no detectable retention for toluene or ammonia on any of the tubing materials. Passivation is recommended on gas supply lines, and gas analysis lines when it is suspected that impurities may adsorb.

Pre-treatment of tubing: where adsorption is particularly strong or the concentration of interest is transient and low it may be necessary to pre-saturate gas supply lines and recirculation loops. It may also be necessary to remove adsorbed water on supply lines especially when using water soluble species such as ammonia. It is also necessary in nearly all cases to thoroughly remove residual air from all tubing, due to the influence of oxygen.

Actively heat recirculation loop components: where used recirculation loops are usually heated to prevent condensation of water; heating also prevents adsorption of impurities.

Minimise water volume and assess dissolved concentrations: many impurities are water soluble; it is therefore necessary to bypass any humidifiers present at the inlet and minimise the water volume in the recirculation loop. If accurate quantification is desired, then it will likely be necessary to perform analysis on the water.

Reduce the tubing length and recirculation loop surface and volume: reducing the surface available for impurities to stick to is recommended.

4.2 Adaptations required to experimental method

For absorbing and reactive species, feeding accurate concentrations to the fuel cell can be challenging due to interaction of gas with piping, valves etc. It is therefore necessary to add an experimental step that compares the expected, set, concentration of the impurity with the actual concentration at the stack inlet. Due to equilibration/saturation of surfaces, there may be a significant time delay before stable concentration is provided. It is therefore also necessary to establish knowledge about equilibration times (e.g. T_{90} response time). Depending on the configuration for online monitoring of gases in the recirculation loop, the gas concentrations in the recirculation loop should be investigated without the stack installed to check absorption to absorption in the recirculation loop and check the impurity concentration tail-off after it has been shut-off to validate clean up.

4.3 Methods to remove impurities

After testing with reactive and sticky impurities it may be necessary to apply additional cleaning protocols to remove adsorbed impurities or their reaction products. These methods may be applied to the stack or to the recirculation system.

4.3.1 Methods to remove impurities from stack

During experiments in MetroHyVe2 with carbon monoxide it was found that simply operating a stack for an extended period (> 12 h) did not fully remove the impurity from the stack and it was necessary to apply air to the anode after shutdown to recover repeatable impurity impact measurements. The following stack clean-up procedures can be applied to clean up the stack. Unlike in single cell measurements it is not possible to control the potential of the individual electrodes during operation, so techniques rely on chemical methods to increase the potential and oxidise impurities or physical methods to maximise desorption. Note that in any process where the anode potential increases above ~0.6 V vs RHE there is the potential for oxidation of the anode catalyst and catalyst support with a probable penalty on fuel cell durability. The possible techniques are:

1. Purging with large volumes of clean hydrogen at elevated temperatures
2. Load cycling to clean up catalyst surfaces
3. Heating of components
4. OCV (start/stop) exposure to aid impurity oxidation
5. Supply of air / oxygen to anode during shutdown protocol to aid impurity oxidation
6. Ozone treatment [7]
7. Deliberate starvation to cause potential excursions
8. High humidity operation

To illustrate, sulphur clean-up procedures include voltage excursions higher than OCV in order to oxidise sulphur species to sulphate. Further, low voltage (i.e. high load) excursions below 0.3 V may then be required in order to remove sulphate from the catalyst surface [7]. Cycling of the cell voltage through such a range will have a durability impact on the fuel cell, with high potentials well known to cause corrosion of cell components. It is possible to chemically increase the potential and remove impurities [6]. . Such an approach was shown to be more effective than cycling to voltages as high as 1.6 V. However, work in the HYDRAITE project showed that such methods caused significant stack damage.

4.3.2 Methods to remove impurities from test station

If impurities are persistent, it may be necessary to remove them from the test station and recirculation loop as well as from the stack. The technique applied will depend on the physical nature of the impurities. For easily oxidised compounds exposure to warm air will may be sufficient for oxidation to occur and for non-easily oxidised but volatile materials high temperature high volume purging may be required. For persistent water-soluble impurities such as ammonia purging with heated water is likely to be highly effective but time consuming. Non-easily oxidised, non-volatile impurities may require harsh chemical treatments such as ozone purging or replacement of the loop.

5. References

[1] Erbach S, Epple S, Heinen M, Toth G, Klages M, Gaudreau D, et al. CO2 Enrichment in Anode Loop and Correlation with CO Poisoning of Low Pt Anodes in PEM Fuel Cells. Fuel Cells 2018;18:613–8. https://doi.org/10.1002/fuce.201700216.

[2] Matsuda Y, Shimizu T, Hashimasa Y. Effect of Carbon Monoxide on Polymer Electrolyte Fuel Cell Performance with a Hydrogen Circulation System. J Electrochem Soc 2020;167:044509. https://doi.org/10.1149/1945-7111/ab732c.

[3] Viitakangas J, Auvinen S, Costantino M, Viik S, Ihonen J. Effect of Toluene on PEMFC Performance. Fuel Cells 2020;20:245–52. https://doi.org/10.1002/fuce.201900075.

[4] Nikiforow K. Optimization of polymer electrolyte membrane fuel cell systems-Applied study of hydrogen recirculation. MSc. 2010.

[5] Viitakangas J, Ihonen J, Koski P, Reinikainen M, Aarhaug TA. Study of formaldehyde and formic acid contamination effect on PEMFC. J Electrochem Soc 2018;165. https://doi.org/10.1149/2.1381809jes.

[6] Mitzel J, Zhang Q, Gazdzicki P, Friedrich KA. Review on mechanisms and recovery procedures for reversible performance losses in polymer electrolyte membrane fuel cells. J Power Sources 2021;488:229375. https://doi.org/10.1016/j.jpowsour.2020.229375.

[7] Kakati BK, Kucernak ARJ. Gas phase recovery of hydrogen sulfide contaminated polymer electrolyte membrane fuel cells. J Power Sources 2014;252:317–26. https://doi.org/10.1016/j.jpowsour.2013.11.077.