D5: Validation report of a metrological chain for gas quality measurement at a H_2 demonstration platform level

Project	19ENG03 MefHySto
Due date	2023/11/30
Release date	2024/01/29
Leading partner	CEA
Status	FINAL VERSION
Authors	CEA Fabrice Micoud
	CEA Basile Brault
	UDC Soledad Muniategui
	UDC Jose Andrade
	UDC Purificación López-Mahía
	UDC María Fernández-Amado

Dissemination level:

PU Public

PP Restricted to other programme participants

RE Restricted to a group specified by the consortium

CO Confidential, only for members of the consortium

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

Document history

Version	Date	Description
1	29/01/2024	Released version

Table of Contents

List of acronyms

ALPIX	Laboratory test bench for PEMFC system at CEA (1 kW)
ATD	Automated Thermal Desorber
ATIS	Adsorbent Tube Injector System
CEA	Commissariat à l'Énergie Atomique et aux Énergies Alternatives
EEA	European Environment Agency
IS	Internal Standard
ISO	International organization for standardization
ITEX-DHS	In-tube extraction dynamic headspace
GC	Gas chromatograph
GC-MS	Gas chromatography-mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantitation
MetroHyVe	Metrology for hydrogen vehicles, EURAMET research project (16ENG01)
PEMFC	Proton-exchange membrane fuel cell
PFSA	Perfluoroalkyl sulphonates
RH	Relative Humidity
RSD	Relative standard deviation
TD	Thermal desorption
UDC	Universidade da Coruña
VOCs	Volatile organic compounds
NMR	Nuclear Magnetic Resonance

Executive Summary

This report describes the developed protocols for gas sampling (air and H_2) and the validation of the subsequent analysis by in-tube extraction dynamic headspace coupled to gas chromatography-mass spectrometry (ITEX-DHS-GC-MS) carried out at the University of A Coruña (UDC) for the determination of halogenated volatile organic compounds (VOCs). These compounds, if present in the input gases of the fuel cell, can affect its efficiency and durability. Their monitoring at the outlet of the test bench could also have potential to be a useful tool to evaluate the membrane degradation.

The developed methodology has been applied to different gas lines, and to ambient air, in the demonstration H_2 platform at CEA called “SENEPY”. The results are presented and discussed in this report, which also includes a literature review about expected levels of the VOCs in ambient air in sites of diverse typologies and from different countries.

Besides and in the frame of WP1 activities, humidity measurements in the H_2 stream produced by a commercial electrolyzer have been carried out using a state-of-art humidity sensor equipped in our hydrogen platform. The results obtained as a function of the production rate and time are presented and compared to the electrolyzer specifications. For further details and comparison with WP1 results, the reader is invited to consult the dedicated D1 and D2 deliverables of the Mefhysto project.

1 Introduction and literature review

The key for the performance and durability of the proton-exchange membrane fuel cells (PEMFC) is the membrane, whose function can be affected by impurities present either in the hydrogen or in the air supplies. Most of these impurities can affect the catalysed chemical reaction between H_2 and O_2 by poisoning the required catalysts.

In the A3.1.1 internal report (Hydrogen and Air Impurities Definition, reported in the 1st Interim Technical Report delivered in month (M) 09 to MSU) it was stated that two major sources of pollutants exist: exogenous (e.g. from air impurities) and endogenous (e.g., degradation of fuel cell components). A literature search was undergone to identify major pollutants of each source and it was decided in a Consortium meeting that the degradation compounds that might exit from the cells due to the degradation of the polymer membranes should not be studied in Mefhysto. Major reasons were that their analysis would require some advanced analytical techniques and resources that had not been budgeted nor allocated in the project. On the contrary, a suite of common atmospheric contaminants that affect the cell performance were identified from literature. Those were included by NPL in gas cylinders and subjected to study. This was the major objective of **Deliverable D4**, in this same Work package and the reader is kindly forwarded to that specific report.

Out of the many atmospheric pollutants, it was decided that halogenated compounds (in particular, fluorinated ones) would be evaluated in air supplies to the fuel cells. This was accomplished in the SENEPY platform, at CEA and it is a main issue of **Deliverable D5**.

Following, a protocol was developed by UDC, with the collaboration of NPL and CEA, to sample air and hydrogen in order to analyse halogenated volatile compounds (in particular, fluorinated ones). Also, an analytical methodology was implemented to quantify them, details can be found in the present report.

Halogenated volatile organic compounds present in air (VOCs) decompose in halogens and eventually poison catalysts [1]. These compounds are present in ambient air and come from several sources. However, they are usually present at trace levels. Halogenated compounds are not included in ambient air regulations, so the information about their concentrations is very limited.

Further, it must be stressed that most of the information/data that can be gathered do not proceed from 'usual' literature sources (papers and published official reports) but from regional or national databases related to air pollution. In recent years, published papers refer to Asiatic data (mostly China) and a few to North America (Canada and USA), and, likely, they are not of direct application here due to differences in vehicles, fuels, traffic volume and, also, climatology.

Hence, scarce data have been found in a specific literature research undergone in the initial months of the project, corresponding to some few sites of only 2 countries. Further, different compounds were analysed, at different years and time resolutions. Compounds like 1,2-dichloroethane, chlorobenzene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane,1,2-dichloroethylene, tetrachloroethylene, tetrachloromethane and trichloroethylene have been reported in Europe in recent years, with individual daily or annual concentrations below 2.0 µg/m^3 even at traffic sites (see Table 1).

Table 1: Concentration (µg/m^3) for halogenated VOCs in ambient air, from Air quality statistics calculated by the EEA [2]

Halogenated compound	Annual mean[a]	Day levels range in urban background stations[b]	Day levels range in sub-urban back-ground stations[c]	Day levels range in sub-urban traffic stations[d]
1,2-dichloroethane[e]		0-1.4	0-3.5	0-2.0
Chlorobenzene[f]		0.02-0.6	0-1.49	
1,1,1-trichloroethane	0.54			
1,1,2-trichloroethane	0.77			
1,1-dichloroethane	0.23			
1,2-dichloroethylene	0.13			
Tetrachloroethylene	0.21			
Tetrachloromethane	0.91			
Trichloroethylene	0.36			

[a] 2019 data from an urban background station in France (GPS coordinates: 45.16190, 5.73560)
[b]Data from 2 stations in Belgium (GPS coordinates: 51.05833, 3.72930; 50.84967, 4.33382)
[c]Data from 9 stations in Belgium (GPS coordinates: 50.98158, 5.72562; 51.01628, 2.58232; 50.97758, 4.83762; 51.20966, 4.43182; 51.20316, 3.80837; 50.87966, 4.69113; 50.79663, 4.35854; 50.85658, 4.42570; 50.93971, 5.36838)
[d]Data from 1 station in Belgium (GPS coordinates: 50.82513, 4.38472)
[e]Data of 2019
[f]Data of 2018-2019

These levels are at least one order of magnitude below the limit set by ISO 14687:2019 for halogens, and therefore the impact of halogens from the air supply over PEMFC may be expected to be quite low. More important sources for these compounds would be, for example, cleaning products. Nevertheless, the scarcity of available data (and, so, of dedicate studies) do not allow us to dismiss their possible effect. Mostly because high variations between sites may be possible (because of the different types of cars, fuels, regulations, etc.), and emission peaks of much higher concentration during a very little time may exist and are undetected by pollution sensors because of their usual time resolution to yield data – daily or annual.

Despite being information from USA, it is worth noting the work of Bigazzi et al. [3], who studied VOCs uptake from urban cycling. In the study, ATD cartridges filled with Tenax TA and Carbotrap B sorbents were attached to the bikes' handlebars and sampled air from the middle of the traffic during different riding segments (22–38 min each) in Portland, Oregon. Therefore, their results have better time resolution and more 'real' traffic conditions than daily-anual data from air quality stations. Further analysis of the air samples comprises a lot of VOCs, including 6 halocarbons: trichlorofluoromethane (CFC11), methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113), chloroform, carbon tetrachloride and tetrachloroethylene. Individual values of these compounds ranged from 0.07 to 3.49 µg/m^3, which are equivalent to 0.04–1.98×10^{-3} µmol/mol (halogen basis). Even the sum of the maximum values for all the six compounds (0.0047 µmol/mol) is one order of magnitude lower than the limit set by ISO 14687:2019 for halogens. Despite the differences suggested above between Europe and USA, the findings reinforce the idea of the air supply not being, likely, a major contribution of organic halogens for PEMFC.

Despite this, it is important to develop tools to monitor the presence of halogenated VOCs in air in order to verify that their concentrations can be dismissed. In addition, the H_2 input has also to be analysed as it can introduce this kind of impurities in the fuel cell as well.

On the other hand, and despite endogenous impurities (those that arise from degradation of the fuel cell components or fuel cell system itself) are out of scope of MefHySto. However, monitoring halogenated organic compounds at the outlet of the fuel cells has potential to be a useful tool to evaluate the membrane degradation. This is because among the endogenous compounds from the degradation of the membrane of the fuel cells/stacks, there are some halogenated organic compounds already identified. There is consensus nowadays on the identity of the most common degradation molecules [4–11], which arise mostly from PFSA side-chain degradation; namely: trifluoroacetic acid; 1,1,2,2-tetrafluoro-2-(1,2,2,2)tetrafluoroethoxy-ethanesulfonic acid; perfluoro(3-oxapentane)-1-sulfonic-4-carboxylic diacid (from Nafion membranes); perfluoro(2-ethoxyethane) sulfonic acid and perfluoro(4-sulfonic butanoic) acid (from 3M membranes).

They have been identified in water exhausts either after intensive use or after ex-situ studies (mainly using NMR, Nuclear Magnetic Resonance) but they have not still been studied in the gaseous phase. Their potential risk is that they decompose further under the FC working conditions and affect the catalysts. They appear as both anode and cathode membrane degradation products. These compounds would deserve more attention in future and may be sampled and analysed in the gaseous phase with a methodology similar to the one described in this report.

2 Protocol for gas sampling

2.1 Tests for the optimization and validation of the sampling protocol

Automated thermal desorption (ATD) systems are widely used to analyse VOCs, and the ATD tubes (Figure 1), containing sorbents of different types, are used for air sampling. There, a known volume of gas or interest, usually air, is passed through the ATD tube and the target analytes are retained onto the sorbent. Later, the ATD tube is heated in the ATD system and the analytes are thermally desorbed into the analytical system (usually a gas chromatograph, GC).

Figure 1. Stainless steel sorbent tubes with different caps (from left to right: brass, PTFE and long term storage caps).

Despite the working scheme depicted above is applied widely to sample air, there were some doubts on whether the different physical characteristics of hydrogen (when compared to air) may affect its sampling. The main concern here was that the hydrogen may desorb the previously retained target compounds when it continues to flow through the tube until the sampling volume is completed. Thus, sampling flow and time are critical. To ascertain this, tests were carried out by UDC to check the suitability of the use of ATD tubes for H_2 sampling.

For the tests, the sampling flow was fixed at 40 mL/min (slightly lower than for air sampling, for which 50 mL/min was used, to minimize the possibilities of desorption). The ATD tubes with 200 mg of Tenax® TA (see section 3.3 for details about sorbent selection) were spiked with 5 ng of VOCs (see section 3.2 for details about spiking the tubes) and then pure H_2 was passed through during a period that would correspond to the sampling time. Two sampling times were tested: 1 h and 3 h. The tests were carried out also for air (with pure air from an Ultra Zero Air Generator, PerkinElmer) for comparison. Then, the sorbent in the ATD tubes was analysed (see section 3 for details) and the obtained results were compared with tubes spiked with the same amounts of VOCs but without either air or H_2 passed through after spiking. The average recoveries for the 38 halogenated VOCs used in the test are shown in Table 2.

Table 2. Average recovery, as percentage (100x[ng of analyte after blowing gas/ ng of analyte without blowing gas]) for the 38 halogenated VOCs at different times for pure air and H_2. Four replicates of each experimental setup were carried out.

	Average recovery (%)
After 1h of pure air at 50 mL/min	88 %
After 1h of pure H_2 at 40 mL/min	84 %
After 3h of pure air at 50 mL/min	78 %
After 3h of pure H_2 at 40 mL/min	58 %

Recoveries for 1 h are acceptable and it is noticeable that there is not a big difference between the performance for air and H_2. On the contrary, the passage of a gas for 3 h reduces recoveries, and some compounds are even completely lost. It also increases uncertainty between replicates. This effect can be seen even for air, but it is really significant for hydrogen (with only 58 % of average recovery for 3 h, and as mentioned above, the loss of some target analytes). Therefore, 1 h was selected as the sampling time, and it was proved to be suitable for a 40 mL/min flow of H_2.

2.2 Sampling protocol to measure halogenated VOCs in air and H_2

An internal document with the derived protocol from the previously described tests has been written and shared with the other partners. The protocol is divided into 6 sections:

1.- Preparation of the sorbent tubes before submission, including information about type and amount of sorbent, preparation (if commercially packed tubes are not used) and cleaning procedure.

2.- General precautions to be considered during transport and storage to avoid contaminations and/or losses of analytes.

3.- Sampling protocol, with the possibility of performing active sampling with a pump (for ambient air) or sampling from a gas supply system (e.g. a compressor, a tank or a hydrogen line), using its own pressure to make the gas flow through the ATD tube.

The setup parameters were those derived from the tests presented in section 2.1: flow rate of 50 mL/min for air and 40 mL/min for H_2, and 1 h of sampling time in all cases.

4.- After sampling: storage, identification and preservation.

5.- Quality control tasks, including field blanks and the control tubes for transport and storage.

6.- Submission of the samples back to UDC for further ITEX-DHS-GC-MS analysis.

The complete protocol is attached as **annex** of this report.

2.3 Presentation of the SENEPY H_2 Platform at CEA

The SENEPY H_2 Platform at CEA is equipped with a commercial PEMWE Electrolyser HOGEN from PROTON (see Figure 2). The main technical specifications are:

- Maximum H_2 production : 530 Nl/h (500 Nl/h as maximum set point in SENEPY)
- 10 cell-stack (around 130-140 cm² as active area)
- No internal H_2 purifier
- Drying by 2 zeolite units (regenerated with dry H_2 bypass by alternative operation)
- Asymmetrical stack operation: atmospheric pressure at the anode (O_2) / 15 bar abs at the cathode (H_2, 200 psig)
- Gas analysis for %H_2 in O_2 by catharometer equipment but not really precise (drifts in time due to “wet gas”)

Figure 2: HOGEN S20 Electrolyzer installed on SENEPY Platform

Regarding gas quality for HOGEN S20, PROTON specifies a purity of H_2 at 99.9995% with H_2O < 5 ppm, N_2 < 2 ppm and O_2 < 1 ppm without any other compounds detectable.

The humidity measurements were carried out with a DMT152 sensor from Vaisala with customized range from -100 to 0°C for dew point (frost point) with a precision ± 2°C in our humidity range. The RH sensor was placed at the electrolyser H_2 outlet after a pressure regulator at low pressure (between 1.0 and 1.3 bar abs) in a dedicated measurement chamber close to pressure and temperature sensors as well as a flowmeter. For the sake of simplicity, the RH sensor was checked for calibration by NPL with their gas standards after the measurement campaign. The sensor was still under the validity of manufacturer calibration. The values in ppmv (per volume) are calculated via the Sonntag formula which can be found in British Standard 1339:1, 3.2.2.

In this test campaign, the first step consisted in flushing and drying the H_2 pipes on the platform for several hours until the humidity level remains stable (frost point below -85°C) at 70% of H_2 maximum production before any specific humidity measurements.

First, increasing and decreasing current steps (between minimum and maximum stack operation, 10 min per step) were applied progressively. The impact of fast transitions between minimum and maximum electrolysis current (47 A / 140 A, 10 min per step) was also studied. Finally, a steady-state phase at 70% of maximum production (100 A) was applied before shutting-down the equipment.

The corresponding results are presented in section 3.6.2

The SENEPY Platform is also equipped with a home-made open-system for PEM Fuel Cell testing named “ALPIX” (see Figure 3~~Figure 3~~). This equipment is well-suited to test different PEMFC system architectures in terms of H_2 supply modes such as dead-end or recirculation in a wide range of operating conditions. The air circuit is based on compressed technical air supply to replace the compressor, which allows a wider range of operating conditions. The nominal stack power on this bench is 1 kW.

Typical pipes, valves and actuators of this bench are representative of the components used on more powerful systems. Thus, the relative contamination coming from these sub-parts can be studied on our bench to look for possible VOC contaminations by comparing the purity between the gas supply before the bench inlets and at the outlet of the gas circuits of ALPIX. In our cases, we used N_2 flow to characterize the possible contamination by VOCs instead of technical air (based on ambient air sampling) to avoid possible fluctuations in terms of contaminations during the different sampling campaigns.

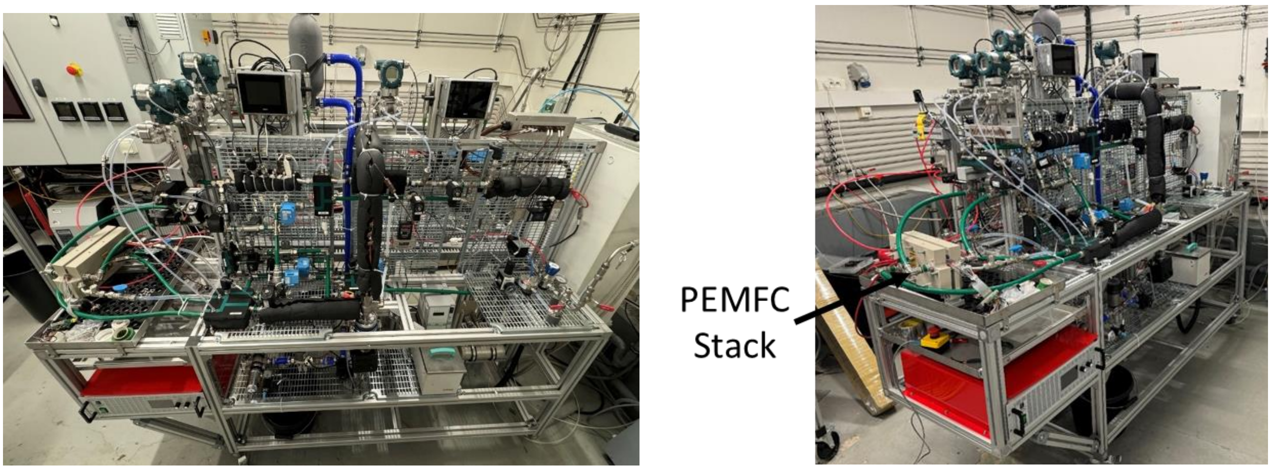

Figure 3: ALPIX Test bench for 1 kW PEMFC stack installed on SENEPY Platform (air circuit side on the left, front side on the right)

3 Optimization and validation of the analytical method for halogenated volatile organic compounds

As commented previously, classical thermal desorption (TD) is a widely used technique to analyse VOCs. But for MefHysto, the suitability of the novel in-tube extraction dynamic headspace coupled to gas chromatography-mass spectrometry (ITEX-DHS-GC-MS) technique has been tested as an alternative to TD.

ITEX-DHS performs an enrichment of the volatile and/or semivolatile compounds present in the sample. For this, a microtrap filled with an adsorbent material (or mixture of adsorbents) is placed between the syringe and the syringe needle of the chromatograph. Using the syringe as a pump, a part of the gaseous phase of the samples (headspace) is pumped repeatedly through the microtrap. Then, the microtrap is rapidly flash-heated into the GC injector for thermal desorption. The GC is coupled to a triple quadrupole mass spectrometer (MS), allowing for the identification of VOC compounds (also for screening). Very good sensitivity and limits of detection are usually obtained.

The main disadvantage of ITEX-DHS-GC-MS for this application is that the first desorption (to pass the analytes from the sorbent used for sampling to the gaseous phase, i.e, headspace, to be extracted by the microtrap) is limited to 200 ºC. That temperature is quite low for sorbents like Tenax® or different carbons used commonly for sampling of VOCs, whose recommended desorption temperatures are in the 300-350 ºC range. Nevertheless, if the transference from the sorbent to the gaseous phase is reproducible, even if it is not complete, the method can be applied advantageously in routine thanks to its good performing characteristics, like the detection (LOD) and quantitation (LOQ) limits.

UDC has carried out the development of a method to analyse 39 halogenated VOCs (see list of compounds in section 3.5) using this novel technique.

3.1 Cleaning sorbent tubes

The ATD tubes are cleaned usually in an ATD system or in a tube conditioner, whose operation principle is the same: the sorbent tubes are heated while a stream of a pure inert gas (He or N_2) passes through it to remove the impurities that could be retained onto the sorbent.

UDC has tested an alternative procedure for cases when the abovementioned systems (quite specific and relatively expensive) are not available. It consists of a two-stage cleaning procedure by which the sorbent tubes are heated in a furnace and then a N_2 stream is passed through, at room temperature. Comparing the Tenax® TA sorbent blanks obtained after conditioning them for 4 h at 300 ºC under a He stream (60 mL/min) in an ATD *vs* heating conditioning for 4 h at 330 ºC followed by 1 h of a N_2 stream (60 mL/min), the results were quite similar for halogenated VOCs.

Apart from dichloromethane, which had to be dismissed because of its wide presence as a common solvent in laboratories, which leads to non-reproducible and aberrant results when analysing it, halogenated VOCs were not present in blanks cleaned with ATD. For the 2-stage cleaning procedure, only a few halogenated VOCs (8 out of 39) were present in the blanks (Table 3), and their levels were usually very low. Thus, despite not being the best option (as it can lead to higher detection and quantitation limits), the two-stage alternative procedure can be applied for halogenated VOCs.

Table 3: Occurrence of halogenated VOCs in blanks cleaned with the alternative two-stage procedure.

Halogenated VOC	Occurrence in blanks
2,2-Dichloropropane	60 %
trans-1,2-Dichloroethylene	40 %
Chloroform	60 %
Bromodichloromethane	60 %
1,1,2-Trichloroethane	20 %
Dibromochloromethane	60 %
Chlorobenzene	80 %
Bromoform	60 %

3.2 Preparation of standards

The standards required to optimise and validate the method were prepared in the laboratory using an ATIS (Adsorbent Tube Injector System) device shown in Figure 4. A solution of the target compounds in methanol was injected manually with a syringe in a hot glass chamber (125 ºC), where immediate vaporization is produced. Meanwhile, a N_2 stream is passed through the system, transferring the gas-phase VOCs to the sorbent tube connected at the end of the system, where the analytes will get retained.

Figure 4: ATIS system used for the preparation of the standards.

3.3 Selection of sorbent

Many types of sorbents can be used to sample VOCs. In a previous hydrogen-related project, MetroHyVe, a three-bed sorbent was proposed to determine “total species”: “TCC” (Tenax TA, Carbograph 1TD and Carboxen 1003) [12]. However, as indicated at the beginning of section 3, the limitation of the desorption temperature in the ITEX system can lead to precision problems if the target analytes are not reproducibly released from the sorbent at that relatively low temperature. For this reason, some tests comparing Tenax® TA alone *vs* TCC multi-bed were carried out.

Results showed that 200 ºC were not enough to desorb the VOCs efficiently from the carbonaceous sorbents. Even if clean carbonaceous sorbents are added to a vial with the analytes retained onto Tenax® TA, the presence of those carbonaceous sorbents during the ITEX procedure affects the results, decreasing the number of VOCs found and the levels of those that still appear (with respect to the same analysis without the presence of the carbonaceous sorbents). Therefore, for this method, the use of carbonaceous sorbents like Carbograph 1TD or Carboxen 1003 has been discarded.

In addition, it was verified that for a spike of the halogenated VOCs (containing 25 ng of each compound), and using a traditional ATD system with desorption at 330 ºC, results were very similar when tubes of Tenax® TA and TCC were used. Therefore, for the expected levels of VOCs in the samples, Tenax® TA seems good enough to retain all the target compounds and the use of additional sorbents is not necessary.

3.4 Use of internal standards

Opposed to ATD, where the tube with the sorbent is analysed directly, ITEX-DHS-GC-MS requires the sorbent to be in a small glass vial. For this reason, just before the analysis, it is necessary to open the sorbent tube, remove the glass wool and pour the sorbent with sample in a vial. Before the measurement step itself an internal standard solution (IS) containing dedicated compounds should be added over the sorbent before the vial is closed and placed in the system for its analysis.

The use of IS in gas chromatography is widely recognized by the scientific community to correct for variations during injection. In this particular case, the IS works as a surrogate standard for the ITEX-DHS part, thus correcting also the variations produced in the desorption from the Tenax® and in the subsequent extraction onto the ITEX microtrap. The ratio (area of target analyte / area of the IS) for each analyte has been used for quantitation.

Three internal standards have been added to all the samples and standards: 4-bromofluorobenzene, 1,2-dichlorobenzene-d_4 and fluorobenzene; namely, EPA 524.2 Fortification Solution (Supelco). After checking their performance, fluorobenzene was selected for all the target analytes as it gave the best results regarding precision and linear regression.

3.5 Validation and figures of merit of the final methodology

A scheme of the whole procedure is shown in Figure 5.

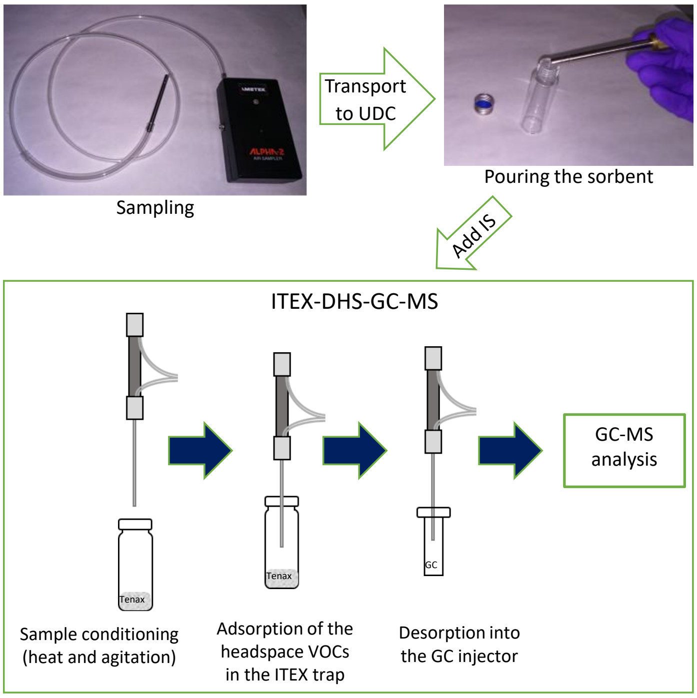

Figure 5: Scheme of the method developed to analyse halogenated VOCs.

The final method allows for the quantitation of up to 39 halogenated VOCs, and also for a qualitative screening to identify more compounds. As an example, a chromatogram of a standard is shown in Figure 6. The method has been validated in terms of precision, linear ranges and limits of detection and quantitation.

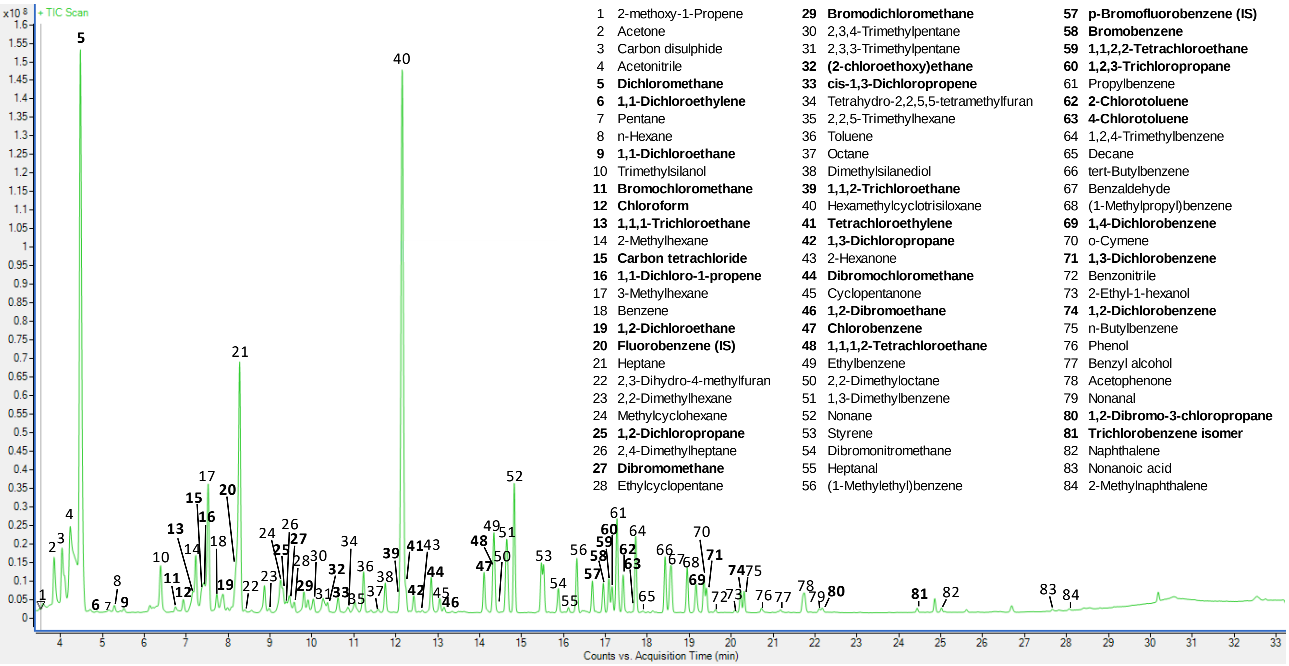

Figure 6: Chromatogram of a standard (25 ng of each VOC). Peaks identified with match factor > 85 %. Chemicals in bold letter are halogenated VOCs present in the standard. Note that most of the other peak components are also present in the standard, but they are not halogenated compounds. Some of the chemicals that are not in bold letter correspond to impurities.

Precision was evaluated at 2 levels of mass of each compound (5 and 25 ng), obtaining good results (RSD <10 % for most VOCs in repeatability and RSD <15 % for most VOCs in reproducibility). Results are shown in Table 4. Dichloromethane was the only tested halogenated VOC with poor precision (RSD up to 40 %) and it had to be dismissed from the method. The most probable explanation for this behaviour is that it is often used as solvent in the laboratories where the sample preparation and the final analysis are carried out, and the ambient concentrations contaminate the sorbent tubes (yielding a lack of reproducibly).

Table 4: Repeatability and reproducibility (as RSD) of the method at two different levels (5 and 25 ng), with n=3.

	Repeatability (% RSD)		Reproducibility (% RSD)	
	5 ng[a]	25 ng[b]	5 ng[a]	25 ng[b]
1,1-Dichloroethylene	2.2-11.3	4.4-4.6	7.3	14.1
Dichloromethane	2.1-31.1	20.9-26.0	38.5	40.0
cis-1,2-Dichloroethylene	4.6-6.4	2.1-4.4	5.1	8.6
1,1-Dichloroethane	4.5-7.9	5.4-5.8	6.8	11.7
2,2-Dichloropropane	2.2-6.3	3.2-4.8	5.4	8.1
trans-1,2-Dichloroethylene	1.8-8.0	4.2-7.2	6.5	13.8
Bromochloromethane	14.1-17.6	6.2-15.1	16.5	14.9
Chloroform	4.8-5.4	3.6-7.0	4.6	11.3
1,1,1-Trichloroethane	3.4-5.3	1.1-3.5	5.9	9.2
Carbon tetrachloride	9.4-10.7	2.9-5.7	9.3	8.4
1,1-Dichloro-1-propene	3.8-10.8	4.8-11.3	8.7	11.7
1,2-Dichloroethane	3.1-8.2	6.4-10.0	10.0	12.8
Trichloroethylene	3.3-7.0	3.2-9.3	6.8	11.8
1,2-Dichloropropane	11.9-12.7	3.5-8.2	12.7	12.4
Dibromomethane	2.0-5.0	3.0-4.8	5.4	9.3
Bromodichloromethane	5.8-16.9	3.6-4.4	12.2	7.9
cis-1,3-Dichloropropene	1.4-7.0	4.1-7.0	6.0	11.2
trans-1,3-Dichloropropene	3.4-7.7	5.4-8.3	6.8	10.6
1,1,2-Trichloroethane	5.0-5.9	4.2-8.2	7.5	10.9
Tetrachloroethylene	2.1-6.0	4.4-8.1	5.7	11.2
1,3-Dichloropropane	3.5-7.4	5.1-9.6	7.7	11.5
Dibromochloromethane	15.1-16.0	3.6-8.9	14.1	6.5
1,2-Dibromoethane	2.6-7.2	5.1-9.5	7.1	10.4
Chlorobenzene	3.3-7.3	6.5-11.3	7.4	12.5
1,1,1,2-Tetrachloroethane	0.9-8.3	4.1-7.1	6.8	9.5
Bromoform	6.3-7.6	5.1-10.3	6.7	9.6
Bromobenzene	6.3-9.1	8.0-14.5	10.3	14.2
1,1,2,2-Tetrachloroethane	4.5-8.5	7.5-12.1	9.1	12.3
1,2,3-Trichloropropane	5.8-9.7	7.7-13.8	10.8	13.6
2-Chlorotoluene	3.7-9.9	8.0-13.4	10.7	13.7
4-Chlorotoluene	7.1-8.9	9.0-16.2	11.6	15.2
1,3-Dichlorobenzene	9.0-9.4	9.5-17.2	22.7	17.0
1,4-Dichlorobenzene	10.2-10.4	8.0-15.7	13.2	15.6
1,2-Dichlorobenzene	9.2-10.3	8.3-15.0	12.1	15.0
1,2-Dibromo-3-chloropropane	11.4-12.4	10.3-15.4	13.7	14.9
1,2,4-Trichlorobenzene	14.9-17.0	14.5-20.2	17.7	18.4
Hexachloro-1,3-butadiene	5.7-6.2	4.9-8.7	6.1	8.8
1,2,3-Trichlorobenzene	14.7-17.1	13.5-19.3	16.3	17.8
1-Bromobutane	6.6-13.2	2.6-6.6	9.6	10.0

[a] 5 ng correspond to 1.7 µg/m^3 for air and 0.000319-0.001302 µmol/mol (halogen basis) for H_2

[b] 25 ng correspond to 8.3 µg/m^3 for air and 0.001595-0.006511 µmol/mol (halogen basis) for H_2

The linear ranges have been tested up to 25 ng, taking into account that the expected levels in the samples are low. All the compounds show good linear behaviour within this range. Exemplary plots for two compounds are shown in Figure 7.

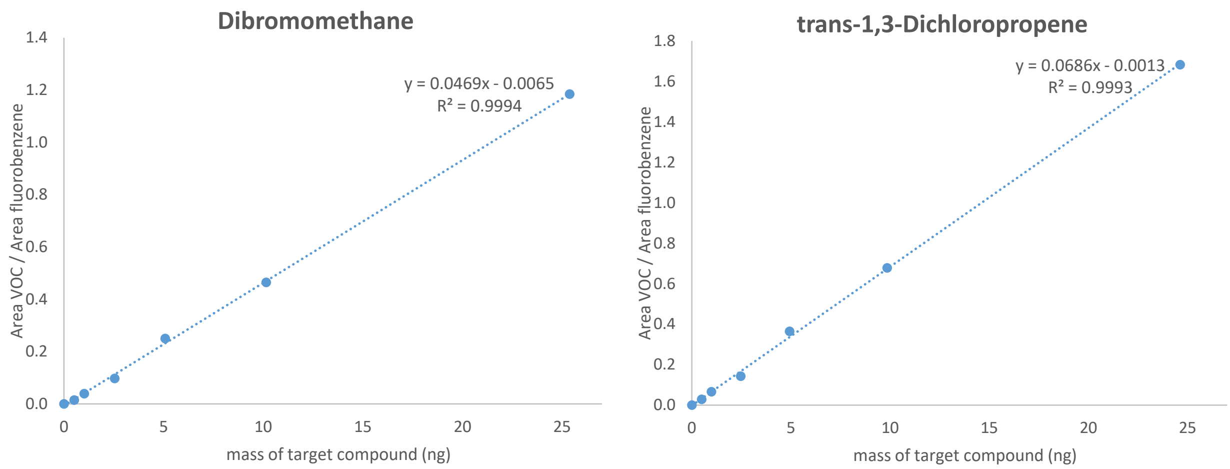

Figure 7: Calibration lines for two exemplary halogenated VOCs.

Table 5 displays the data for the calibrations of all the target VOCs and the calculated limits of detection and quantitation. Levels lower than 0.5 ng have not been tested for, but for some compounds the calculated LODs and LOQs are lower, and there are peak signals when 0.5 ng are used high enough to detect lower levels (so, likely, the real limits are lower for many analytes). For air, the limits are given in µg/m^3, considering the flow rate for air sampling (50 mL/min). For H_2, the limits are given in µmol/mol on halogen basis (thus, calculating the µmol of halogens) and, for the conversion from sampled volume (in this case, 40 mL/min) to mol, 20 ºC and 1 atm were used, as those are the conditions used for the standardization of gaseous pollutants according to the air quality legislation [13]. Most compounds have LODs ≤ 0.17 µg/m^3 or 0.12 µmol/mol and LOQs ≤ 0.33 µg/m^3 or 0.25 µmol/mol.

Table 5: Data for the calibrations of all the target VOCs and limits of detection (LOD) and quantitation (LOQ).

	LOD air (µg/m³)	LOQ air (µg/m³)	LOD H_2 (·10³) (µmol/mol)[a]	LOQ H_2 (·10³) (µmol/mol)[a]	Slope ± error[b] (·10³)	Intercept ± error[b] (·10³)	R^2
1,1-Dichloroethylene	≤0.33	≤0.33	≤0.207	≤0.207	12.5±0.3	3.3±3.9	0.9973
cis-1,2-Dichloroethylene	≤0.17	≤0.33	≤0.103	≤0.207	16.5±0.4	1.5±3.7	0.9977
1,1-Dichloroethane	≤0.17	≤0.33	≤0.101	≤0.202	29.3±0.5	3.0±4.8	0.9988
2,2-Dichloropropane	≤0.83	≤0.83	≤0.443	≤0.443	48.9±1.8	37.6±22.4	0.9959
trans-1,2-Dichloroethylene	≤0.33	≤0.33	≤0.207	≤0.207	34.7±0.5	37.6±6.3	0.9990
Bromochloromethane	≤0.17	≤0.33	≤0.077	≤0.155	18.1±0.3	3.1±3.5	0.9983
Chloroform	≤0.17	≤0.33	≤0.126	≤0.252	51.9±1.2	29.1±12.7	0.9973
1,1,1-Trichloroethane	≤0.17	≤0.33	≤0.113	≤0.225	62.6±1.6	13.4±17.1	0.9966
Carbon tetrachloride	≤0.17	≤0.33	≤0.130	≤0.260	59.4±1.4	19.7±14.9	0.9971
1,1-Dichloro-1-propene	≤0.17	≤0.33	≤0.090	≤0.181	27.6±0.5	4.4±5.8	0.9986
1,2-Dichloroethane	≤0.17	≤0.33	≤0.101	≤0.202	41.3±0.8	9.3±8.6	0.9980
Trichloroethylene	≤0.17	≤0.83	≤0.114	≤0.572	37.8±1.3	15.7±13.5	0.9942
1,2-Dichloropropane	≤0.17	≤0.33	≤0.089	≤0.177	34.1±0.8	7.9±8.2	0.9973
Dibromomethane	≤0.17	≤0.17	≤0.058	≤0.058	46.9±0.5	-6.5±5.4	0.9994
Bromodichloromethane	≤0.17	≤0.33	≤0.092	≤0.183	86.8±1.4	10.5±14.0	0.9988
1-Bromobutane	≤0.17	≤0.33	≤0.037	≤0.073	32.3±0.9	19.8±10.9	0.9969
cis-1,3-Dichloropropene	≤0.17	≤0.33	≤0.090	≤0.181	66.3±1.4	8.9±14.7	0.9977
trans-1,3-Dichloropropene	≤0.17	≤0.17	≤0.090	≤0.090	68.6±0.8	-1.3±8.2	0.9993
1,1,2-Trichloroethane	≤0.33	≤1.43	≤0.225	≤0.967	85.5±2.8	55.4±31.2	0.9958
Tetrachloroethylene	≤0.17	≤0.17	≤0.121	≤0.121	92.4±1.6	-8.3±16.2	0.9986
1,3-Dichloropropane	≤0.17	≤0.33	≤0.089	≤0.177	63.3±1.6	13.6±16.8	0.9967
Dibromochloromethane	≤0.17	≤0.33	≤0.072	≤0.144	81.6±1.0	11.1±10.0	0.9993
1,2-Dibromoethane	≤0.17	≤0.33	≤0.053	≤0.107	55.5±0.9	2.3±9.4	0.9987
Chlorobenzene	≤0.17	≤0.33	≤0.044	≤0.089	155.2±3.3	28.7±34.4	0.9977
1,1,1,2-Tetrachloroethane	≤0.17	≤0.17	≤0.119	≤0.119	83.9±0.8	-13.7±8.4	0.9995
Bromoform	≤0.17	≤0.17	≤0.059	≤0.059	57.7±1.2	-1.1±12.5	0.9979
Bromobenzene	≤0.17	≤0.33	≤0.032	≤0.064	64.9±1.1	4.7±11.4	0.9985
1,1,2,2-Tetrachloroethane	≤0.17	≤0.17	≤0.119	≤0.119	99.7±1.2	-1.7±12.1	0.9993
1,2,3-Trichloropropane	≤0.17	≤0.17	≤0.102	≤0.102	73.3±1.2	-0.6±13.7	0.9989
2-Chlorotoluene	≤0.17	≤0.17	≤0.040	≤0.040	161.7±0.4	5.1±4.8	1.0000
4-Chlorotoluene	≤0.17	≤0.17	≤0.040	≤0.040	163.1±2.3	17.0±25.2	0.9992
1,3-Dichlorobenzene	≤0.17	≤0.33	≤0.068	≤0.136	91.5±1.1	7.6±12.7	0.9994
1,4-Dichlorobenzene	≤0.17	≤0.33	≤0.068	≤0.136	84.6±0.9	9.6±9.8	0.9996
1,2-Dichlorobenzene	≤0.17	≤0.33	≤0.068	≤0.136	82.1±1.1	6.5±12.2	0.9993
1,2-Dibromo-3-chloropropane	≤0.33	≤0.33	≤0.127	≤0.127	17.4±0.0	0.3±0.3	1.0000
1,2,4-Trichlorobenzene	≤0.17	≤0.33	≤0.083	≤0.166	25.3±0.5	7.4±5.7	0.9984
Hexachloro-1,3-butadiene	≤0.17	≤0.33	≤0.115	≤0.230	35.4±0.5	-11.9±5.2	0.9991
1,2,3-Trichlorobenzene	≤0.17	≤0.17	≤0.083	≤0.083	18.0±0.3	3.1±3.1	0.9991
1,2,3-Trifluorobenzene	≤0.17	≤0.83	≤0.114	≤0.569	139.5±4.6	47.8±48.0	0.9946

[a] Halogen basis
[b] The term error refers to the standard error derived from the calibration

3.6 Results from the demonstration H_2 platform “SENEPY”

3.6.1 Results of gas analysis by chromatography

The methodology developed so far has been applied to different gas lines and to ambient air, in the demonstration H_2 platform at CEA called “SENEPY”. Two short sampling campaigns were carried out, in July and September 2023, with a total of 8 samples covering air, Hydrogen and Nitrogen supplies. They comprised ambient air (outdoor, near the test rooms and with influence from the Grenoble free highway; and indoor, in the fuel cell stack assembly room), compressed air (from the system fuel cell stack test bench inlet), H_2 (produced by the electrolyzer and that used for PEMFC tests) and N_2 from the Alpix bench (inlet and outlet for both air and H_2 sides). For each sample, a field blank was obtained.

For quality control, two control ATD tubes (one blank and one spiked with 5 ng of each target compound) were sent in the transport container of each campaign, to act as transport/storage controls. Another pair of tubes was prepared at the same time and stored at the UDC lab for comparison. In the blanks, all compounds were below LOD except for chloroform in 3 of them. The UDC blank of July presented a slight contamination by chloroform (2.5 ng) that could be subtracted to the respective spiked control. On the contrary, both transport blanks (July and September) presented high levels of chloroform (103 and 28 ng respectively), being that of July even higher than the level found in the spiked control. A contamination during storage in the freezer at CEA, where chloroform was stored, is the most probable cause of this contamination, which also affected some samples. The average recoveries and the ranges for all the analytes are shown in Table 6.

Table 6: Obtained average recoveries (range in brackets) for the spiked controls, in percentage. The spiked level was 5 ng of each VOC. Only chloroform had to be subtracted as the other compounds were not found in the blanks.

	Control CEA July 2023	Control UDC July 2023	Control CEA Sept 2023	Control UDC Sept 2023
% R	108 (66-145)[a]	104 (65-136)	118 (99-139)[a]	93 (58-125)
% R Chloroform	1455[b]		242	

[a] Without chloroform
[b] The blank could not be subtracted as it was higher than the level obtained for the spiked control

In the field blanks, only chloroform was found, usually with higher levels than the corresponding samples. As indicated above, there was a contamination affecting this VOC and therefore it could not be quantified. Only a few halogenated VOCs were detected in the samples, and only some of them had concentrations high enough to be quantitated. Results are shown in Table 7 and Table 8. The obtained levels are low, in the order of ppb. For the sample with higher levels (N_2 outlet Alpix bench, air side), the sum of all the quantitated halogenated VOCs is < 4 ppb, one order of magnitude lower than the limit set by ISO 14687:2019 for halogens (0.05 ppm). For air, the equivalent levels should be < 1.2 ppb and lower concentration levels were obtained. In particular for Hydrogen, with both samples #4 and #5 presenting levels < 0.2 ppb. Likely, the halogenated VOCs are not affecting the neither the performance nor the durability of the fuel cell significantly in the demonstration H_2 platform “SENEPY”.

Table 7: List of VOCs detected in some samples but not quantifiable.

Chloroform	Contamination problems have been found, high levels were detected, not only in the samples but in the field and control blanks
Carbon tetrachloride	Only detected at outdoor air sampling (near the fuel cell stack test rooms and the Grenoble freeway), its concentration < LOQ
Bromobenzene	Below LOD for all samples. A signal < LOD in the N_2 outlet Alpix bench sample (air side) was detected
4-Chlorotoluene	< LOD for all samples. A signal < LOD in the ambient air in the fuel stack assembly room was detected
1,3-Dichlorobenzene	Only detected at Ambient air in the fuel cell stack assembly room, but < LOQ

Table 8: Results for the field samples. Only halogenated VOCs that could be quantitated are shown, in µg/m^3 for air samples (#1-3) and in nmol/mol (halogen basis, assuming 1 atm and 20 ºC for gases) for H_2 (samples #4-5) and N_2 samples (#6-8). Sample 1: Outdoor air sampling near the fuel cell stack test rooms and the Grenoble highway, Sample 2: Compressed air system fuel cell stack test bench inlet, Sample 3: Ambient air in the fuel cell stack assembly room, Sample 4: H_2 produced by the electrolyzer, Sample 5: H_2 used for PEMFC tests, Sample 6: N_2 inlet Alpix bench, Sample 7: N_2 outlet Alpix bench (air side), Sample 8 (no compounds were quantified): N_2 outlet Alpix bench (H_2 side).

	Sample 1 (µg/m^3)	Sample 2 (µg/m^3)	Sample 3 (µg/m^3)	Sample 4 (ppb)	Sample 5 (ppb)	Sample 6 (ppb)	Sample 7 (ppb)
2,2-Dichloropropane	2.188						
Trichloroethylene		< 0.83	1.814				
Tetrachloroethylene			0.376			0.189	0.460
Chlorobenzene				0.142	0.175	0.165	1.920
1,4-Dichlorobenzene							0.954
1,2-Dichlorobenzene							0.630
∑ halogenated VOCs	2.188	< LOQ	2.190	0.142	0.175	0.354	3.964

3.6.2 Measurements of water content in H2 produced by PEM Electrolyser

This section presents the methodology and the results obtained by CEA regarding the measurements of water content in the H_2 stream produced by a commercial electrolyzer. This work is shared with WP1 and Deliverable D2 of the Mefhysto project. Other methods are presented in deliverables D1 and D2 of the project.

The RH sensor used here is usually installed on our test platforms and test benches. For sake of reliability, the sensor calibration has been checked and validated at NPL. This verification has been made after the measurement campaign at CEA.

The detailed operating phases are listed in Table 9 and the overall view of the test is presented in Figure 8. The dew point measured initially is already below -65 °C (< 5 ppmv, corresponding to the HOGEN specifications) and progressively decreases. After 20 hours of drying, the humidity level reaches -80 °C (*ca*. 0.5 ppmv) and continue to drop slowly down to -88 °C (*ca*. 0.1 ppmv).

Table 9: Detailed operation phases for the humidity measurement campaign

	Time	H2 production [%]	Stack Electrolysis current [A]	Description
1	~41h	70	100	Pipe flushing and drying
2	~1h	100	140	Max. power test
3	~10min	50	71	Intermediate load
4	~2h	~ 25 (minimum flowrate allowed)	47	Stabilization at minimum current (33% of maximum current)
5	~10min	40	57	Polarization curve test
6	~10min	60	85	
7	~10min	80	113	
8	~10min	100	140	
9	~10min	80	113	
10	~10min	60	85	
11	~10min	40	57	
12	~30min	~ 25	47	Stabilization at minimum current (33% of maximum flowrate)
13	~10min	100	140	Minimum/Maximum Current tests
14	~10min	~ 25	47	
15	~10min	100	140	
16	~10min	~ 25	47	
17	~10min	100	140	
18	~30min	~ 25	47	Stabilization at minimum current (33% of maximum current)
19	~17h	70	100	Test at intermediate current (70% of maximum current)
20	~10h	~ 25	47	Stabilization at minimum current before shut-down

The humidity variation during current cycles are presented in detailed in Figure 9. Some pressure variations at high electrolysis current can be observed due to the pressure regulator and the pressure drop within the H_2 gas network. The humidity value is influenced by the electrolysis current. The higher current, the dryer H_2 gas: at minimum current the dew point reaches *ca*. -86 °C and -94 °C for the maximum current during the maximum current step. We can observed some delay in the RH sensor probably due to the volume buffer between the electrolyser and the sensor.

These humidity variations are also observed during minimum/maximum current cycles but in a lesser extent between -86 and -92 °C as dew point which corresponds to a concentration of water between 0.2 (considering 0.1 barg at minimum H_2 flowrate) and 0.03/0.04 ppmv (considering 0.1/0.3 barg for the maximum current). For information, when the pressure of H_2 is considered into the calculations, the results are in the same range of the precision of the RH measurement sensor (± 2 °C).

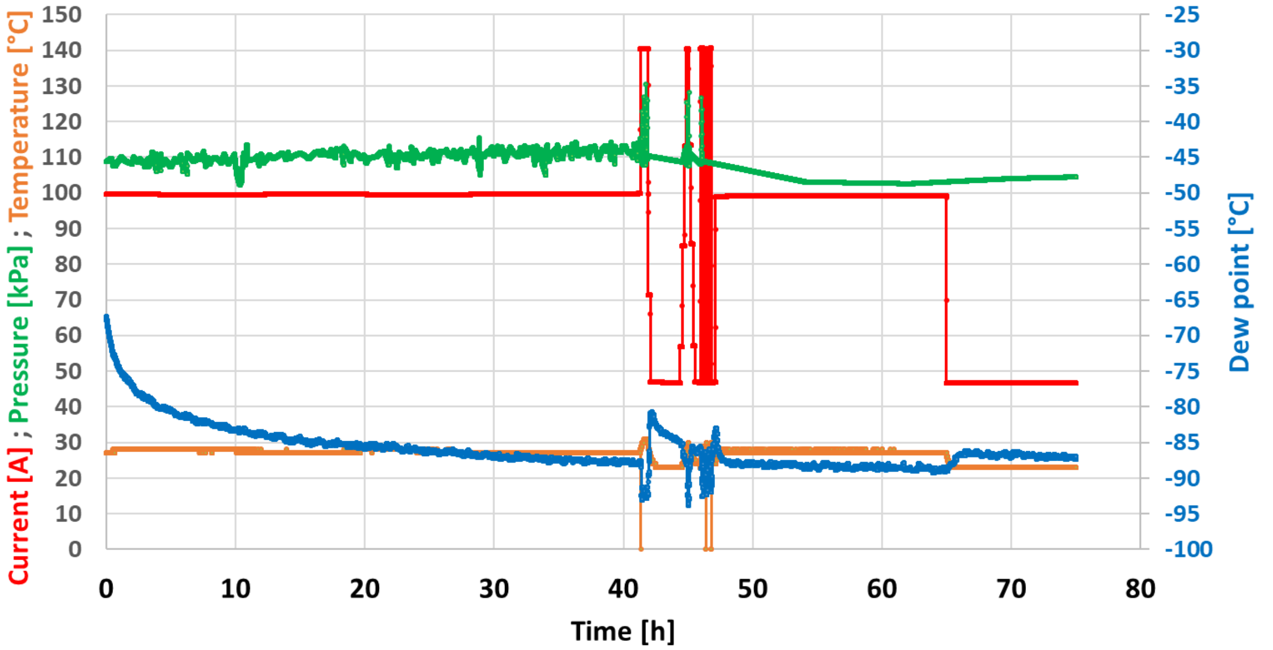

Figure 8 : Overall view of the humidity measurement test on SENEPY platform. Main operating parameters are detailed: Stack current, Pressure and Temperature (close to RH sensor) (left axis) and dew point (right axis)

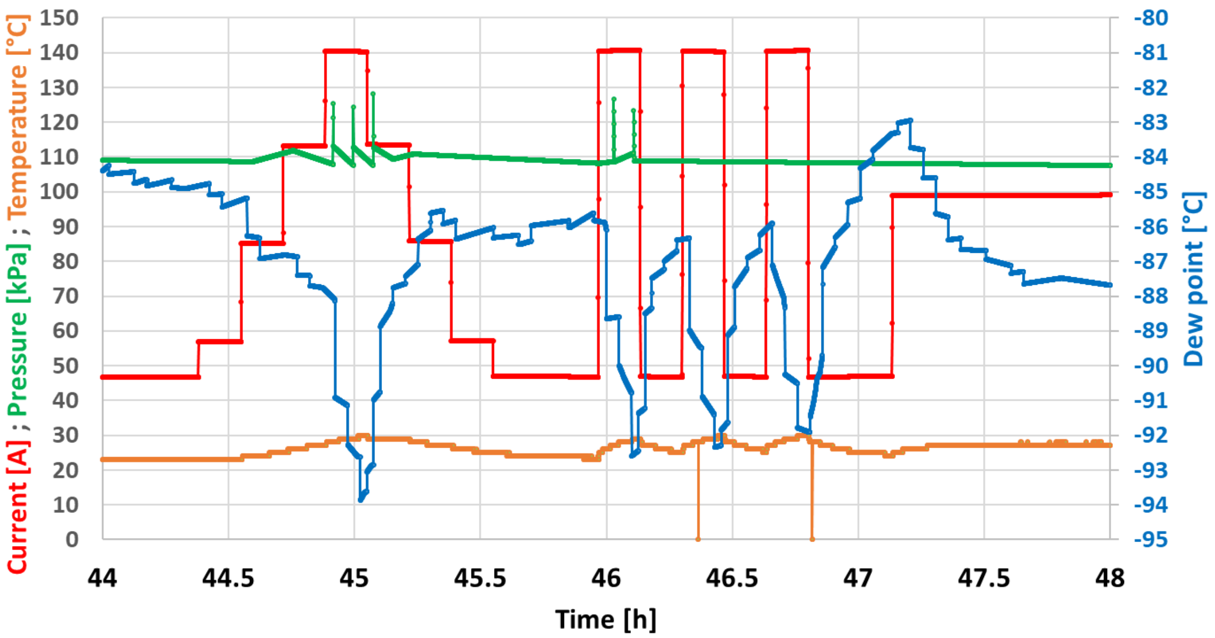

Figure 9 : Zoom on the humidity measurement test on SENEPY platform during variable current cycles. Main operating parameters are detailed: Stack current, Pressure and Temperature (close to RH sensor) (left axis) and dew point (right axis)

Overall the water content measurements performed on the SENEPY platform at CEA confirmed that the hydrogen quality from the HOGEN electrolyser meets its specified water content level of < 5 µmol mol^{-1}.

4 Conclusions

The suitability of the novel ITEX-DHS-GC-MS technique for the determination of halogenated VOCs has been proved. Up to 39 compounds can be quantified with the methodology developed and validated by UDC. In addition, a protocol for sampling both air and also H_2 with ATD tubes has been prepared. Finally, the whole methodology was applied to real samples obtained at the demonstration H_2 platform at CEA called “SENEPY”, in different gas lines and ambient air. The results show that only a few halogenated VOCs are present, and at very low levels that probably do not affect the PEMFC performance or durability. Thus, the implemented purification systems for air and hydrogen are enough to remove these organic halogenated impurities. Still, further studies must be carried out to confirm these results.

In association with WP1 in Mefhysto project, humidity measurements have been carried in the H_2 platform at the outlet of the commercial electrolyzer. The response of a commercial humidity sensor has been characterized and compared to other humidity measurement methods (see D1 and D2 deliverables for detailed information). The values obtained are in the same range compared to the NPL measurements on an equivalent electrolyzer. The specifications for water content in hydrogen is respected (< 5 µmol mol^{-1}) at all operating points tested.

5 References

[1] Smith, G. et al. HYDRAITE D2.2 A summary report of FC measurements for the first half of the project. (2019).

[2] Air Quality e-Reporting (AQ e-Reporting) — European Environment Agency. https://www.eea.europa.eu/data-and-maps/data/aqereporting-8.

[3] Bigazzi, A. Y., Figliozzi, M. A., Luo, W. & Pankow, J. F. Breath Biomarkers to Measure Uptake of Volatile Organic Compounds by Bicyclists. Environ. Sci. Technol. 50, 5357−5363 (2016).

[4] Healy, J. et al. Aspects of the chemical degradation of PFSA ionomers used in PEM fuel cellsx. Fuel Cells 5, 302–308 (2005).

[5] Kinumoto, T. et al. Durability of perfluorinated ionomer membrane against hydrogen peroxide. J. Power Sources 158, 1222–1228 (2006).

[6] Zhou, C., Guerra, M. A., Qiu, Z. M., Zawodzinski, T. A. & Schiraldi, D. A. Chemical durability studies of perfluorinated sulfonic acid polymers and model compounds under mimic fuel cell conditions. Macromolecules 40, 8695–8707 (2007).

[7] Ishimoto, T. & Koyama, M. A review of molecular-level mechanism of membrane degradation in the polymer electrolyte fuel cell. Membranes (Basel). 2, 395–414 (2012).

[8] Zatoń, M., Rozière, J. & Jones, D. J. Current understanding of chemical degradation mechanisms of perfluorosulfonic acid membranes and their mitigation strategies: A review. Sustain. Energy Fuels 1, 409–438 (2017).

[9] El Kaddouri, A., Flandin, L. & Bas, C. Chemical degradation of PFSA ionomer binder in PEMFC's catalyst layer. Int. J. Hydrogen Energy 43, 15386–15397 (2018).

[10] Frühwirt, P., Kregar, A., Törring, J. T., Katrašnik, T. & Gescheidt, G. Holistic approach to chemical degradation of Nafion membranes in fuel cells: Modelling and predictions. Phys. Chem. Chem. Phys. 22, 5647–5666 (2020).

[11] Robert, M., El Kaddouri, A., Perrin, J. C., Raya, J. & Lottin, O. Time-resolved monitoring of composite NafionTM XL membrane degradation induced by Fenton's reaction. J. Memb. Sci. 621, (2021).

[12] Arrhenius, K. et al. METROHYVE D8 A4.4.5: Good practice on the suitability of vessels and gas cylinders for sampling hydrogen as required by ISO14687

[13] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

ANNEX - Sampling protocol to measure halo-genated volatile organic compounds (VOCs) in air and in H_2

MEFHYSTO

Metrology for Advanced Hydrogen Storage Solutions

Partner: UDC

TASKS: A3.1.4 & A3.4.1

Sampling protocol to measure halogenated volatile organic compounds (VOCs) in air and in H_2.

1.- Preparation of the sorbent tubes before submission (to be done at UDC)

For ambient air sampling, stainless steel sorbent tubes (¼” outer diameter, 3½” length) were selected, filled with 200 mg of Tenax® TA (60/80 mesh) as sorbent. Commercially packed tubes are available, but they can be prepared in the laboratory as well using silanised glass wool to plug the sorbent at both sides of the tube. That is the case for the sorbent tubes employed here.

Before use, the packed sorbent tubes must be conditioned and cleaned, at 300 ºC during 4 h under a Nitrogen or Helium gas stream (60 mL/min) or at 330 ºC during 4 h followed by 1 h of Nitrogen gas stream (60 mL/min) at room temperature. After that, they are sealed with proper caps (metallic long term storage caps), placed into Pyrex® tubes and then in an airtight container, like a zipped bag (**Figure 1**). The bag is then stored in a container with charcoal.

These steps will be carried out at UDC and the containers with the adsorption tubes –ready for use– will be sent to the other partners.

2.- General precautions

1.- During storage and transport, materials emitting VOCs like wood or certain new plastics shall be avoided.

2.- The sorbent tubes will be enclosed in Pyrex glass tubes which in turn will be inside a zipped bag. The bag has to be placed into a container with charcoal to avoid any possible contamination of the tubes with VOCs.

Please, do not let the container with charcoal open for a long time so that it can still protect the samples during transport back to UDC.

3.- Once received from UDC, keep the box at a fridge or freezer until ca. 30 min before use. This time is required to temperate the sorbent material of the tubes before aspirating the sample gas.

After sampling it is recommended to keep the box again in a freezer or, at the very least, refrigerated.

4.- Avoid direct sunlight and/or heat sources, mostly after sampling.

3.- Sampling at the site (to be done by MefHySto partners at their points-of-interest)

There are 2 different kind of samples to be collected, with some differences in the sampling protocol:

3a. Active sampling
For active sampling, a pump and a manifold (pressure reduction device and a flow meter) to get the required flows are needed. These will not be included in the container with the sorbent tubes.

1.- Open the plastic container sent by UDC only before use. There you will find a plastic bag with the sorbent tubes, each protected by a Pyrex glass tube and caped with two caps. The surrounding charcoal in the plastic container is still needed and, accordingly, close the container as soon as possible.

2.- Extract one sorbent tube from its Pyrex glass tube and remove the caps only immediately before using the sorbent tube for sampling.

3.- Connect one extreme of the metallic sorbent tube to either the pump itself or to an auxiliary tube that links the sorbent tube to the pump. Let the other extreme of the sorbent tube free and ready to aspirate gas (**Figure 2**).

4.- Set an **aspiration flow of 50 mL/min (for air sampling) or 40 mL/min (for H_2 sampling)** and adjust the **sampling time to 1 h**.

Before the pump starts aspirating the sample, remember to get ready the "field blank" close to you (see section 5 below).

3b. Sampling from a gas supply system
To sample air or hydrogen from a gas supply system (e.g. a compressor, a tank or a hydrogen line) a pump will not be required as the pressure of the system itself makes the gas flow. In this case, the ¼" O.D. sampling tube shall be connected to the line to be sampled and a 40-50 mL/min flow has to be set. Ad-hoc ferrules (i.e., adaptors and connections) would be needed, including a flow meter to control the gas flow (its range must include 40-50 mL/min), as well as the connections for the sampling tube. None of these will beincluded in the container with the sorbent tubes.

1.- Set an **outflow of 50 mL/min (for air sampling) or 40 mL/min (for H_2 sampling)** from the gas supply system to be sampled.

Get the connection ferrules ready to connect the ¼" O.D. sampling tube to the gas supply (see point 4 below).

2.- Open the plastic container sent by UDC only before use. There you will find a plastic bag with the sorbent tubes, each protected by a Pyrex glass tube and caped with two caps. The surrounding charcoal in the plastic container is still needed and, accordingly, close the container as soon as possible.

3.- Extract one sorbent tube from its Pyrex glass tube and remove the caps only immediately before using the sorbent tube for sampling.

4.- Using the proper ferrules, connect an extreme of the metallic sorbent tube to the exit of the gas pipeline (previously adjust flow to 40 (H_2 sampling) or 50 (air sampling) mL/min). Let the other extreme of the sorbent tube free.

5.- The **sampling time is 1 h.** Then, the sorbent tube must be disconnected and capped (see section 4).

Before sampling starts remember to get the "field blank" ready, close to you (see section 5 below).

4.- After sampling: storage, identification and preservation

1.- Disconnect the sorbent tube from the pump or the gas supply system and recap it with the two metallic caps. Squeeze the caps with a wrench or a similar tool.

2.- Store it within its glass Pyrex tube, close it and set an identification label. Labelling can be done manually with a permanent pen on the glass or with an adhesive tape.

Sample identification can be as simple as a number or a letter, as long as more information is provided in a Data Sheet. It is also very important to notify any problem during sampling (e.g., less time or less flow, etc.).

Then, introduce the glass tubes into a zipped bag.

3.- **Sample preservation:** To avoid losing volatile compounds after sampling it is required to keep the sorbent tubes refrigerated. The recommended option is to freeze them once they are in the zipped bag.

Due to physical dilations and contractions it is recommended to re-tight the caps of the sorbent tubes once they got frozen (approx. 1 h after they were introduced into the freezer).

Place again each sorbent tube in its corresponding Pyrex glass tube. Close the glass tube and put all glass tubes in the zipped bag. The bag is stored in the container with charcoal (that from UDC should be fine).

4.- Finally, before submission introduce the zipped bag into the container with charcoal and close the container tightly.

Keep it cold during storage, transport and submission to UDC.

5.- Quality control tasks

1.- For quality control at least one “background” or “transport blank” will be included (this is a sorbent tube identical to those for sampling that is transported and stored with them). That quality control tube will be labeled externally as “background control” and should NOT be used at all.

2.- However, a “procedural” or “field blank” is required during sampling. The tube for this task will be found in its corresponding glass protection tube (label = “field blank”).

This is a sorbent tube to be handled exactly as the tubes where samples are taken BUT without passing neither air/hydrogen nor connecting it to the pump or the gas supply system.

To obtain the field blank, extract the sorbent tube from the glass tube, remove its two caps and let it open at your side while aspirating a true sample. When the sampling is finished, recap the blank tube and proceed as for the true sample tubes.

6.- Submission of the samples back to UDC

Send the sorbent tubes prepared as detailed in section 4 (stored in a zipped bag, and placed in a container with charcoal), along with two or three cold accumulators to UDC by urgent post because the analysis should be accomplished as soon as possible after sample collection.

Please, do not send the samples by the end of the week (Friday) because there is a real risk that they are delivered only after the weekend.

Send the boxes to	INSTITUTO UNIVERSITARIO DE MEDIO AMBIENTE. UNIVERSIDADE DA CORUÑA PAZO DE LÓNGORA R/ Casares Quiroga, 29 15179 Liáns, Oleiros, A Coruña, España

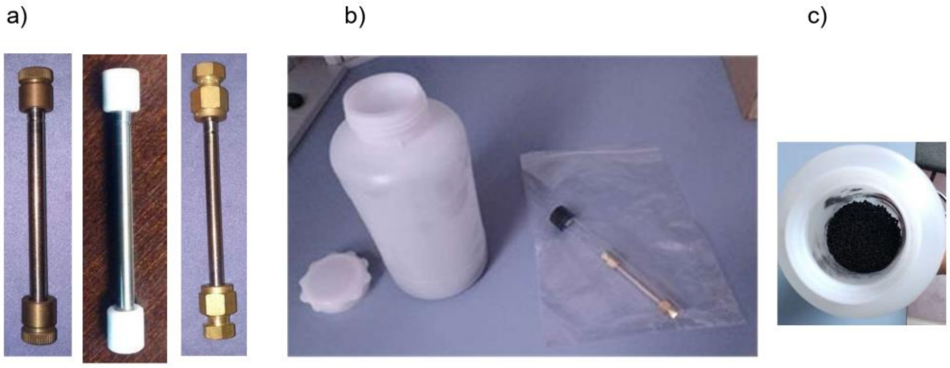

Figure 1: (a) Stainless steel sorbent tubes with different caps (from left to right: brass, PTFE and long term storage caps). (b) an example of a sorbent tube inside a Pyrex glass tube and a zipped bag ready for storage. (c) upper view of the plastic container with charcoal

Figure 2: Example of a sorbent tube connected to a portable pump ready for sampling.