21GRD05 Met4H2

D6: Good practice guide on metrologically traceable quality monitoring in the hydrogen supply chain, including offline measurements and onsite calibration, and recommendations for future improvements of ISO 19880-8 and ISO 21087

Organisation name of the lead participant for the deliverable: INRIM

Due date of the deliverable: 30 September 2025

Actual submission date of the deliverable: 28 November 2025

Confidentiality Status: PU - Public, fully open (remember to deposit public deliverables in a trusted repository)

Deliverable Cover Sheet

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

Task	Activity	Reporting date
3.3	3.3.8	30.09.2025

Title

Good practice guide on metrologically traceable quality monitoring in the hydrogen supply chain, including offline measurements and onsite calibration, and recommendations for future improvements of ISO 19880-8 and ISO 21087

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INRIM, BAM, CEM, DFM, PTB, VSL, VTT, DTU, ENVIPARK, Nippon Gases, POLITO, NPL

Key words
Traceable quality monitoring, hydrogen, hydrogen supply chain, offline measurements, onsite calibration, technical standards

Acknowledgement

The project Met4H2 21GRD05 has received funding from the European Partnership on Metrology, co-financed from the European Union’s Horizon Europe Research and Innovation Programme and by the Participating States.

Feedback

The consortium welcomes feedback. Please send your comments, suggestions or other feedback to the project coordinator, Dr. Adriaan van der Veen (VSL), avdveen@vsl.nl.

Glossary

AEM	Alkaline exchange membrane
ALWE	Alkaline water electrolysis
ATEX	Regulations 2014/34/EU and 1999/92/EG for working safely in explosive environments
BB-CEAS	Broadband cavity-enhanced absorption spectroscopy
CRM	Certified reference material
DEDS	Diethyl disulphide
DMDS	Dimethyl disulphide
DOI	Digital object identifier
DVGW	Deutsche Verein des Gas- und Wasserfaches / German Association for Gas and Water
EN	European norm
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
IR	Infrared
ISO	International organization for standardization
LED	Light emitting diode
LoD	Limit of detection
LoQ	Limit of quantification
MEDS	Methyl ethyl disulphide
MFC	Mass flow controller
OFCEAS	Optical feedback cavity enhanced absorption spectroscopy
OGS	Optical gas standard
PEM	Proton-exchange membrane
PRMs	Primary reference materials
PSA	Pressure swing adsorption
PTR/MS	Proton transfer reaction mass spectrometry
QCM	Quartz crystal microbalance
SCD	Sulphur chemiluminescence detector
SMR	Steam methane reforming
TD	Thermal desorption
TD-GC-SCD	Thermal desorption gas chromatography with sulphur chemiluminescence detector
TDLS	Tunable diode laser spectroscopy
UV	Ultraviolet
VIS	Visible
TULIPS	Demonstrating lower polluting solutions for sustainable airports across Europe
16ENV01	MercOx (Metrology for oxidised mercury)
16ENG05	Biomethane (Metrology for biomethane)
21GRD06	MetCCUS (Metrology support for carbon capture and utilisation)
21GRD10	quantiAGREMI (On farm quantification of ammonia and greenhouse gas emissions from livestock production)

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Foreword

This good practice guide was developed as part of the project 21GRD05 Met4H2 "Metrology for the hydrogen supply chain" project. This project is a response to the urgent need to mitigate climate change and to limit greenhouse gas emissions is driving actions to reduce the use of fossil fuels. However, to meet existing and future energy needs necessitates the increased use of alternative energy sources such as, for example, hydrogen. To achieve this goal, the metrological infrastructure for hydrogen needs to address all parts of the supply lines.

This guide was developed as part of the activities related to the further development of measurement standards and methods to enable traceable validation and performance evaluation of gas quality measurement methods for hydrogen, to thus improve on the current lack of equivalence for impurities, e.g., oxygen, hydrogen sulfide, moisture content, and for reactive components such as hydrogen chloride and chlorine, as well as the development and improvement of analysers for critical impurities for online monitoring of changes in gas quality, through the supply chain and processing equipment, to ensure the gas quality meets the required specifications as described in, e.g., ISO 14687. For more details about this project, please visit https://met4h2.eu/.

Specifically, this good practice guide focuses on online analysis, on-site calibration and validation using reference standards and offline measurements relevant to the hydrogen supply chain. Based on experience of quality monitoring at two different industrial sites and on the results obtained online and offline, this document also includes recommendations for future improvements to ISO 19880-8 and ISO 21087.

Introduction

Hydrogen gas quality is a critical parameter in an emerging supply chain with a large scope of applications (i.e., home boiler, industry heat, power to electricity, or transport). It must be monitored over the whole supply chain from production to distribution.

Metrological tools ensure reliable and traceable measurements necessary to apply appropriate quality control on hydrogen throughout the supply chain.

To show the industry how metrological activities can bridge the gap between laboratory-based measurement research and real-life situations, improving and ensuring the quality of hydrogen gas, under the Met4H2 project demonstrations of on-site monitoring, calibration and sampling were carried out at two real-life sites.

The chosen demonstration sites are a hydrogen production facility and an alkaline electrolyser production location. Indeed, although significant attention has recently been focused on proton exchange membrane electrolysers, alkaline electrolysers currently represent the majority of "green" hydrogen production systems. The experience gained and results obtained in the field are summarised in this document. The aim of this redacted document is to support the quality infrastructure for the distribution of hydrogen, and it is intended to serve as a practical guide to metrologically traceable quality monitoring in the hydrogen supply chain (below 200 bar).

1 Scope

This document provides guidelines for ensuring metrologically traceable quality monitoring of the gaseous hydrogen along its supply chain.

Based on experimental findings, it provides advice to carry out on-line measurements and gas sampling for off-line analysis (i.e., laboratory measurements) and gives specific recommendations for improvements of ISO 19880-8 and ISO 21087.

2 Findings on traceable quality monitoring in alkaline electrolyser

For a traceable monitoring of the gas quality, it is important to select suitable sensors and analysers, to use the correct sampling procedure to collect samples, to apply uniform standardised quality control tools (e.g. reference materials, gas calibrant). In addition, the knowledge of the expected contaminants in the gas being monitored helps define the necessary instrumentation.

A comprehensive literature review was conducted within Met4H2 to identify the main contaminants and impurities that are most likely present in a gas stream produced by an alkaline electrolyser (for more details see MET4H2 – Task 3.3.1 report).
Based on the findings of the literature review, few research activities have been performed for hydrogen fuel quality from alkaline water electrolysis (ALWE). A scarcity of studies related to the presence of contaminants in hydrogen gas sampled from alkaline electrolysers and to the sampling methodology has been observed.
The results of the few contaminant analyses of hydrogen produced by alkaline electrolysis found in literature indicate mostly the presence of N_2, O_2, CO_2 and H_2O. The threshold allowed by the normative ISO 14687 and maximum values observed in the literature for these components are detailed in **Error! Reference source not found.**:

Table 1. List of the contaminants for hydrogen produced by alkaline electrolyzer [1] compared to classification of hydrogen purity grades [2] according to ISO 14687:2025 [3] and DVGW [4]. MOP: maximum operating pressure.

Parameters	**H_2 Grade A ISO 14687**	**H_2 Grade A DVGW**	**H_2 Grade D ISO 14687**	**Literature research**
H_2	≥ 98 mol %	≥ 98 mol %	≥ 99.97 mol %	≥ 99.97 mol %
N_2	∑ O_2, N_2, Ar ≥ 1.9 mol %	-	300 µmol/mol	6.06 µmol/mol
O_2		0.001 mol % /1 mol %	5 µmol/mol	< 0.24 µmol/mol
H_2O	Non-condensing at all ambient conditions	200 mg/ m^3 (MOP ≤ 10 bar) 50 mg/m^3(MOP ≥ 10 bar)	5 µmol/mol	2.97 µmol/mol
CO_2	∑ CO, CO_2 ≤1 µmol/mol	4 mol% (MOP<16 bar) 2.5 mol % (MOP≤16 bar)	2 µmol/mol	0.24 µmol/mol
Total halogenated compounds	-	-	0.05	< 0.032
Maximum particulate concentration	-	-	1 mg/kg	1.75 mg/kg

According to Table 1 and assigning probabilities based on the concentrations (in µmol/mol) at which contaminants are typically detected, N_2 appears to have the highest probability of presence, H_2O a high probability, and O_2 and CO_2 comparatively lower probabilities.

For other kinds of contaminants (e.g. HCl, Cl_2), it may be hypothesized that they are less likely to be observed, since few scientific articles dealing with them have been found in the literature. However, nothing certain on them can be affirmed without more experimental data. Their absence among the contaminants detected reflects indeed only a lack of articles searching for them and not effective evidence of detection of no-traces of these compounds.

2.1 Reference standards to provide traceability to offline measurements

In general, the quality of a gas can be monitored online or offline. If the quality control is carried out offline, some gas samples are collected and then analysed in the laboratory.

The labs where the gas composition is analysed must apply clear procedures and protocols for the measurement and use traceable analysers, that implies the existence of a reference standard. Within Met4H2 project, standard and analytical methods were developed for a traceable detection of Cl-compounds in gas mixture, specifically for the measurement of Cl_2 and HCl in hydrogen.

2.1.1 Preparation of reference gas mixtures of Cl_2 and analytical method development at VSL

Chlorine is a poisonous gas with a 15-minute exposure limit of 1.5 mg/m^3 (~0.52 µmol/mol) in the Netherlands. The odour threshold in most people is about 0.2 µmol/mol.

Due to the safety issues when working with pure chlorine, a 104.1 µmol/mol chlorine in nitrogen gas standard (50 L, 150 bar) was purchased from a specialty gas supplier and used to prepare the 10 µmol/mol gas standards in a nitrogen or hydrogen matrix.

The mixture has a stated accuracy of 3 % and a stability period of 36 months. Using this gas standard, four gas standards at 10 µmol/mol (2× N_2 matrix and 2× H_2 matrix) were gravimetrically prepared in 10 L cylinders with an Aculife IV treatment (see Table 2) in accordance with ISO 6142-1. For the preparation, high purity nitrogen and hydrogen (BIP$^+$ quality, Air Products) were used as a matrix gas. The gas standards with the H_2 matrix also contain about 10 % of N_2 (from the parent gas mixture containing the Cl_2).

The chlorine in hydrogen gas standard VSL110732 (see Table 2) was later sent to the project partner DTU for further analysis using their UV spectrometer. The far-UV in-flow measurements on the standard prepared by VSL have shown the presence of about 2 µmol mol^{-1} of HCl and 9 % of N_2. A reduced amount fraction of Cl_2 and appearance of HCl in H_2 matrix were expected because of the slow reaction between H_2 and Cl_2 in the cylinder at elevated pressures.

*Table 2. Overview of the prepared static chlorine gas standards. The mother mixture was a 104.1 µmol/mol Cl_2 in N_2 gas standard. *Cylinder sent to DTU for analysis using far-UV spectrometer.*

Filling name	Preparation date	Filling pressure (bar)	Gravimetric amount fraction (µmol/mol)	Matrix
VSL110726	2023-08-18	120	10.03	90.4% H_2 9.6% N_2
VSL110732*	2023-08-18	120	9.98	90.4% H_2 9.6% N_2
VSL109774	2023-08-11	120	9.99	100% N_2
VSL1A9787	2023-08-11	120	9.98	100% N_2

Chlorine has a strong absorption band in the UV-VIS region (see Figure 1). However, chlorine with hydrogen can react violently upon exposure by UV light. Therefore, for safety issues, the visible range was used for detection. Specifically, a homebuilt instrument based on broadband cavity-enhanced absorption spectroscopy (BB-CEAS) was utilised. BB-CEAS method typically uses a LED light source and a high-finesse cavity to achieve sensitive measurements over a relative broad wavelength range. The system operates in the visible wavelength region between 430-460 nm. Albeit there the absorption by Cl_2 is about 40 times lower than at the peak value around 330 nm, the sensitivity using BB-CEAS is still sufficient to detect chlorine at µmol/mol levels.

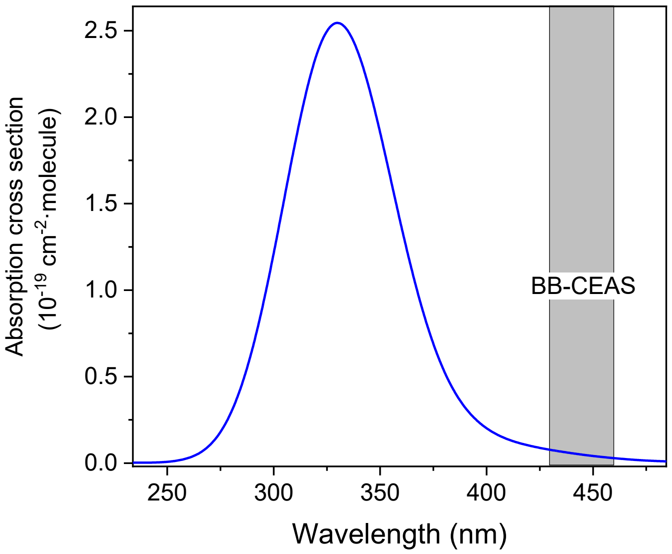


Figure 1. Absorption cross-sections of chlorine at a 1 nm resolution as obtained by Tellinghuisen [5]. The grey area indicates the wavelength region of the BB-CEAS spectrometer.

To test the measurement method, the 104.1 µmol/mol Cl_2 in N_2 standard was dynamically diluted with N_2 using thermal mass flow controllers. The spectra as recorded by the BB-CEAS spectrometer are shown in

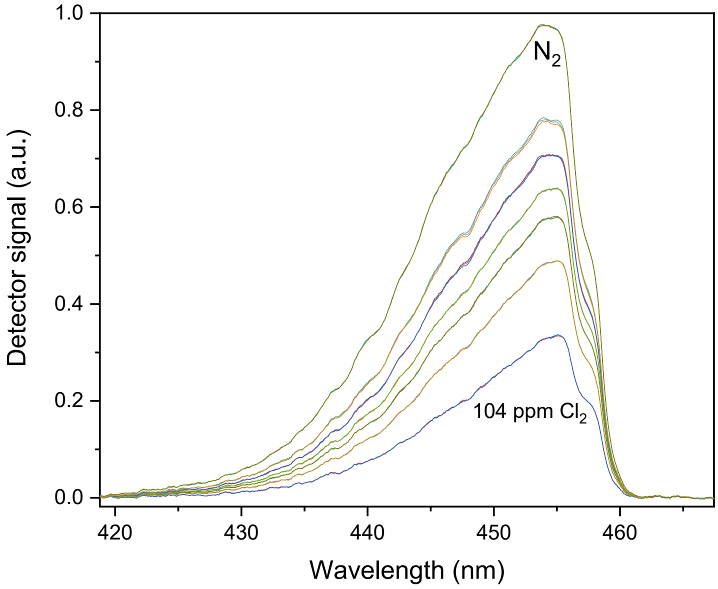


Figure 2.

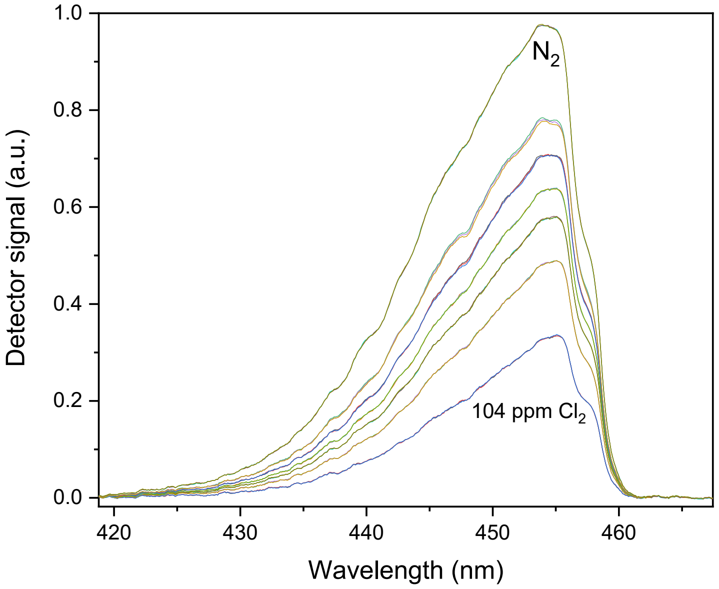
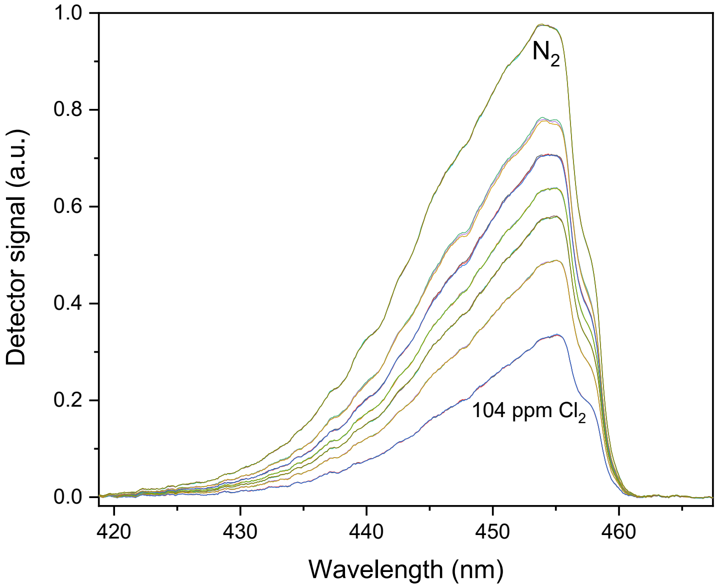


Figure 2. Spectra measured for the dynamic dilution of the 104.1 µmol/mol Cl_2 in N_2 standard. For each Cl_2 concentration, three measurements were performed. Higher Cl_2 concentrations, lead to more absorption in the measurement cell and hence less light falling on the detector.



From the recorded spectra as shown in Figure 2, an absorbance signal is obtained. The results are shown in Figure 3. A good linearity is observed over the range under test.

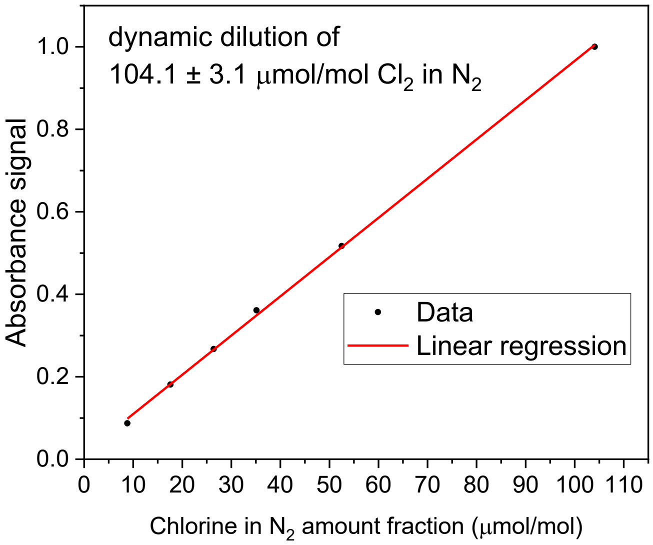


Figure 3. Measured absorbance when dynamically diluting the 104.1 µmol/mol Cl_2 in N_2 standard.

The chlorine standards were measured several times to assess the stability of these mixtures. After M4, both N_2 mixtures showed (within the measurement uncertainty) no sign of instability while the mixtures in hydrogen had lost nearly 40 %. At M10, again both N_2 mixtures showed no sign of instability while the mixtures in hydrogen had lost nearly 30 %.

As in the mixtures in a H_2 matrix it was observed that the Cl_2 amount fraction decreased in time, it was tested if a reaction product was formed. Most likely this is HCl, due to the following reaction in the gas phase:

$$H_2 + Cl_2 \rightarrow 2\,HCl$$

Measurements were done using two different analytical methods. Both a TDLS spectrometer equipped with a 76 m multi-pass cell specific and using a Interband cascade laser (probing the strong 1-0, P6-line HCl absorption line centred at 2752.04 cm^{-1}) and a FTIR spectrometer (Bruker Vertex 70 V, equipped with a SilcoNert 2000 coated absorption cell with a path length of 10 m) that can analyse, next to HCl, numerous other infrared absorbing gases. Figure 4 shows some of the results of the FTIR measurements. The distinctive HCl signature ($H^{37}Cl$ and $H^{35}Cl$ peaks with 1:3 intensity ratio) is seen in both Cl_2 in N_2 and Cl_2 in H_2 mixtures where the latter contains about 5 times more HCl. The TDLS measurements confirmed the presence of HCl in the gas mixtures.

The FTIR measurements showed that no CO_2, CO, or N_2O was present in both Cl_2 mixtures but interestingly, about 0.1 µmol/mol formaldehyde was also present in the analysed Cl_2 in H_2 mixture.

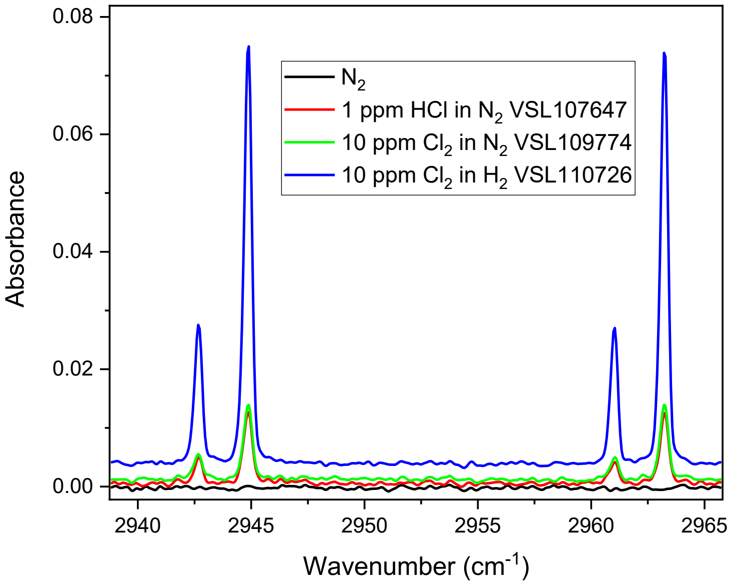


Figure 4: FTIR measurement of a 10 µmol/mol Cl_2 in N_2 standard and a 10 µmol/mol Cl_2 in H_2. For comparison a measurement of high purity N_2 and a 1 µmol/mol HCl in N_2 standard. Measurements were performed in May 2025 (M19) when the Cl_2 mixtures were 21 months old. The Cl_2 in N_2 standard contains about 1.1 µmol/mol HCl while the Cl_2 in H_2 standard contains even around 5.2 µmol/mol HCl, i.e. about 25 % of the original Cl_2 amount fraction should be converted (in reasonable agreement with the 30 % loss observed at M10).

2.1.2 Preparation of reference gas mixtures of HCl at CEM and VTT

Reference gas mixture of HCl where prepared gravimetrically at CEM and using a trace gas generator at VTT.

Concerning the gravimetrical preparation of reference gas mixtures of HCl, as a preliminary step, an exhaustive study of cylinder passivation techniques was conducted at CEM, leading to the selection of ACULIFE® IV from Air Liquide wall treatment cylinders for the process. The pure gases, including H_2, N_2 and HCl, are stored in an outdoor gas shed, where the pure HCl gas is connected to a control panel, while the dry nitrogen is used as a purge gas. The HCl filling station is installed indoors, where nitrogen purging is performed before each filling to eliminate moisture traces.

Before use, the cylinders are subjected to a vacuum of 10^{-2} mbar. Lower pressures are not reached to protect the internal treatment of the cylinders, as higher vacuum could potentially damage it.

Standard gas mixtures are gravimetrically prepared at high pressure (140 bar to 160 bar) in 5 L aluminium alloy cylinders with appropriate passivation (ACULIFE® IV). To obtain low-concentration mixtures (µmol·mol^{-1}), a four-step dilution process is carried out, starting with pure hydrogen chloride (Linde, quality 3.0) and pure hydrogen (Praxair, quality 5.5; Linde, quality 6.0).

The analytical measurement of the prepared mixtures is then performed with a ProCeas® analyser from AP2E/DURAG. This instrument is an infrared spectrometer, equipped with two lasers: laser 1 for HCl concentrations below 10 µmol·mol^{-1} and H_2O between 0 µmol·mol^{-1} and 50 µmol·mol^{-1} and laser 2 for HCl concentrations above 10 µmol·mol^{-1} (up to 1000 µmol·mol^{-1}). After preparation and analysis, the gravimetric and analytical values of HCl mole fractions in the mixtures are compared.

Two cylinders of these standard gas mixtures of HCl in H_2 were prepared and sent to DTU and Nippon Gasses, respectively, to be used for the calibration of the DTU far-UV analyser in laboratory and on site during the online monitoring of the hydrogen quality at the Nippon Gases industrial plant. In Table 3 the characteristics of the two cylinders are summarised.

Table 3. Characteristics of the two samples of standard gas mixture of HCl in H_2 sent to DTU and Nippon Gases.

Cylinder code	Preparation pressure /bar	[HCl] gravimetry /µmol·mol^{-1}	[HCl]PROCEAS /µmol·mol^{-1}	Sending pressure /bar	Destination laboratory
MRP204451	160	16.08	9.23	95	DTU
MRP304438	150	9.71	4.03	> 80	Nippon Gases

At low mole fraction levels, notable discrepancies were observed between the gravimetric and the analytical values. These differences suggest that the current preparation process may be subject to losses—most likely due to adsorption effects—during the final dilution steps. Optimizing this stage of the preparation process is essential to improve the reliability and accuracy of HCl measurements at trace levels.

A key challenge in OFCEAS (Optical Feedback Cavity Enhanced Absorption Spectroscopy) analysis is the high gas consumption during measurement. A minimum of 50 bar of the mixture is required to achieve stable measurements, which makes it challenging to undertake long-term stability studies of the mixtures. In the final phase of the project and after receiving valuable information from VSL, the analytical process was improved. A stability study was conducted using two mixtures of HCl in H_2: 5-month stability test for MRP204430 (13.89 ± 0.76) µmol·mol^{-1} and 2-month stability test for MRP104444 (1.24 ± 0.38) µmol·mol^{-1}. The initial electropolished steel sampling line was modified to use SilicoTek® tubes and on this occasion, a Sulfinert®-coated pressure regulator was used instead of an untreated one. The results showed good stability over 5 months for the mixture with the higher HCl mole fraction, while a poorer stability for mixtures with the lower HCl concentration was found.

At VTT a trace gas generator, based on liquid evaporation technique, was developed. It can be used for generating reference gases of water-soluble chemical compounds in a wide mole fraction range from µmol mol^{-1} down to nmol mol^{-1} levels. It is especially well suited for compounds which easily stick to surfaces and for which it's challenging to produce traceable, long lived and stable static reference gas mixtures. It is also possible to make these systems portable, enabling their use both in laboratory and field conditions.

A schematic of the VTT trace gas generator is given in **Error! Reference source not found.**5.

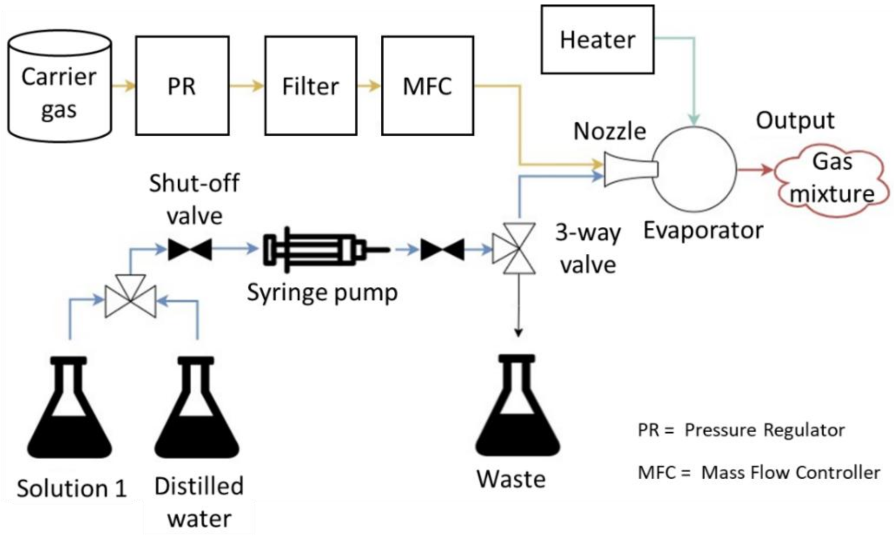


Figure 5. Schematic of operating principle of VTT trace gas generator.

The operating principle is based on injecting a solution with known concentration into a carrier gas stream using an automatic syringe. Proper mixing and evaporation are ensured by applying a nozzle and evaporation heater. In this study hydrogen was used as a carrier gas and the flow rate was controlled using a mass flow controller with a nominal flow up to 10 L/min. Ammonium hydroxide (NH_4OH) or Hydrochloric acid (HCl(aq)) was used as the solution for generating trace amounts of Ammonia (NH_3) and Hydrogen Chloride (HCl), respectively, into the carrier gas. Distilled water is used to flush the system between measurement runs.

Traceability to the SI system of units is achieved by calibrating the mass flow controller and the syringe pump traceably to international standards and using certified solutions. To achieve the desired concentration, diluting the solution is in many cases necessary. This can be done using a calibrated weighing balance and a micropipette to dispense a known amount of the solution into water weighed by the balance.

The VTT portable trace gas generator (Figure 6) can be applied for calibrating gas analyzers in the field.

Figure 6. VTT portable trace gas generator.

Any water-soluble chemical can be generated with the device, but it is especially well suited for generating ppm to ppb concentrations of reactive gases, e.g. NH_3, HCl, HF and Hg, which are difficult to realize, although gas cylinder standards exist for NH_3 and HCl. Moreover, any carrier gas can be used, as long as it is chemically compatible with the injected solution and the inner surfaces of the generator. This makes the generator a versatile tool for flexible generation of a multitude of gas mixtures. In past and ongoing research projects the device has been successfully demonstrated for the following gas mixtures: Hg in air (16ENV01 MercOx [6]), HF and HCl in biomethane (16ENG05 Biomethane [7]), NH_3 in carbon dioxide (21GRD06 MetCCUS [8]) and NH_3 in air (21GRD10 quantiAGREMI [9]). In this project (21GRD05 Met4H2 [10]) the generator was further developed for generating µmol mol^{-1}-levels of HCl and NH_3 in hydrogen. More detailed specifications are given in Table 4.

Table 4. Specification of VTT trace gas generator.

Generator output flow rate	up to 10 L/min
Generated gas concentration	ppm to ppb levels
Generated trace gases	water-soluble chemical (e.g. NH_3, HCl, HF, Hg)*
Carrier gas	Air, N_2, CH_4, H_2, CO_2*
Typical water concentration of generated gas	0.1 - 1.5 vol-%
Typical uncertainty of generated gas concentration	1.9 %

* As long as chemical compatibility with carrier and trace gas, and generator inner surfaces is ensured.

The uncertainty of generated mole fraction in the matrix gas was determined based on the measurement model (Equation 1) and the operation parameters (Table 5).

$$x_x = \frac{n_x}{n_{\mathrm{gas}} + n_{\mathrm{H_2O}}} = \frac{c_x \cdot \frac{q_{m,\mathrm{H2O}}}{\rho_{\mathrm{H2O}}}}{\frac{q_{v,\mathrm{gas}}}{V_m} + \frac{q_{m,\mathrm{H2O}}}{M_{\mathrm{H2O}}}} + \delta_{\mathrm{ev}} + \delta_{\mathrm{rep}} \qquad (1)$$

The uncertainty of mole fraction of gas mixture is given in Table 5 for the nominal concentration of 10 ppm. From the table it can be seen that the largest source of uncertainty is the concentration of the solution, which is mainly caused by the uncertainty of the micropipette used for preparing the solution. The uncertainty of pipetting is estimated as the maximum permissible error (mpe) as stated in the ISO8655 standard. Combining all the uncertainty components results in an expanded uncertainty (*k* = 2) of 1.9 %. In the typical operational range of the generator, the relative values of the uncertainty components are considered constant, therefore the expanded uncertainty of 1.9 % can be applied in the whole operational concentration range.

Table 5. Uncertainty budget for generated trace concentration of reactive gas.

Quantity	**Unit**	**Value**	**Uncertainty**	**Sensitivity coefficient**	**Uncertainty / mol · mol^{-1}**	**Type**	**PDF**	**Divisor**	**Contribution to standard uncertainty/ mol · mol^{-1}**
Concentration of solution of target compound, c_x	mol·l^{-1}	$6.96 \cdot 10^{-3}$	$4.62 \cdot 10^{-5}$	$2.87 \cdot 10^{-4}$	$1.33 \cdot 10^{-8}$	B	Norm.	1	$1.33 \cdot 10^{-8}$
Liquid mass flow of syringe, $q_{m,\mathrm{H2O}}$	g·min^{-1}	$8.41 \cdot 10^{-2}$	$5.05 \cdot 10^{-4}$	$8.11 \cdot 10^{-8}$	$4.09 \cdot 10^{-11}$	B	Norm.	2	$2.04 \cdot 10^{-11}$
Volume flow at standard temperature (23 °C), $q_{v,\mathrm{gas}}$	l·min^{-1}	7.01	$7.01 \cdot 10^{-2}$	$-2.81 \cdot 10^{-7}$	$-1.97 \cdot 10^{-8}$	B	Norm.	2	$-9.85 \cdot 10^{-9}$
Evaporation losses, δn_{ev}	mol·mol^{-1}	0	$1.20 \cdot 10^{-8}$	1	$1.20 \cdot 10^{-8}$	B	Rect.	1.73	$6.93 \cdot 10^{-9}$
Repeatability, δn_{rep}	mol·mol^{-1}	0	$1.20 \cdot 10^{-8}$	1	$1.20 \cdot 10^{-8}$	B	Rect.	1.73	$6.93 \cdot 10^{-9}$
Mole fraction of NH$_3$, $x_{\mathrm{mol\_NH3}}$	mol·mol^{-1}	$2.00 \cdot 10^{-6}$			**Combined standard uncertainty**				$1.92 \cdot 10^{-8}$
	ppm	2			**Expanded uncertainty (*k*=2)**				$3.84 \cdot 10^{-8}$
					Percent relative standard uncertainty				1.9 %

The complete evaporation of the gas-liquid mixture is critical to ensure reliable performance of the trace gas generator. The evaporation has to be complete and adsorption of the mixture to the generator surfaces needs to be minimized. Evaporative losses were thoroughly investigated in previous research by Sari S. et al. [11] for oxidized mercury. This value can be used as a worst-case estimate of generation losses for hydrogen chloride (HCl) and ammonia (NH_3), because the relative influence of evaporative losses is minimal.

2.1.3 Validation of the far-UV method

A far-UV based multi-component analyser has been developed by DTU and validated using VSL's and NPL's gas standards. The analyser includes a SilcoNert2000 coated variable length Ø3 mm SS-interface which can be used for the analyser connection to a high-pressure H_2 source (e.g. a storage tank or a pipeline). All the analyser components in contact with the gas are SilcoNert2000 coated. The analyser working pressure is up to 40 bar at variable H_2 flow rates, typically between 1 l/min and 10 l/min.

Figure 7 shows the measurement of the VSL's gas standard (VSL110732) composition carried out with the far-UV analyser. The far-UV spectrum shows clear absorption features of Cl_2, N_2 and HCl which are the main gas components in the mixture.

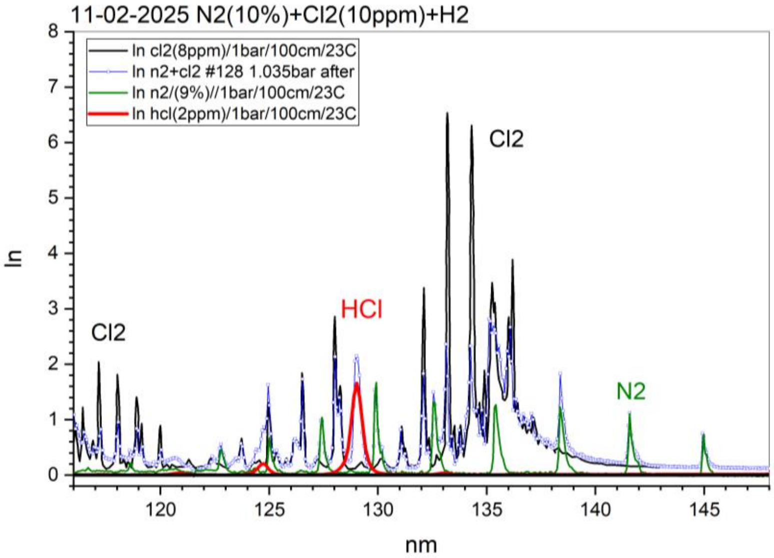


Figure 7. Far-UV absorption spectra measured with VSL's VSL110732 gas standard at about 1 bar and 23 °C, blue. Modelled partial spectra: HCl (2 ppm, red), N_2 (9 %, olive) and Cl_2 (8 ppm, black).

The measured spectrum in Figure 7 is dominated by many strong Cl_2 narrow bands and a broad, dome-like pedestal at around 135 nm. This Cl_2 absorption spectrum is in a sharp contrast compared to the Cl_2 spectrum shown in Figure 1. The reference Cl_2 absorption cross-sections used in the spectra fit are obtained elsewhere from high-spectral resolution measurements. Therefore, the modelled Cl_2 bands are narrow and have higher intensities compared to the measured ones. The pedestal, however, as the broadband structure is not affected by the difference in the spectral resolutions, can be used for the Cl_2 spectra fit which gives Cl_2 (8 ppm) concentration in the mixture which is in agreement with VSL's measurements.

The N_2 has well-defined absorption bands in 116-146 nm spectral range which can be used for N_2 identification and quantification in complex data sets with multiple spectral interferences. The fit of the measured spectrum in the Figure 7 by reference N_2 data gives N_2 (9 %) in the mixture. This value is close to the reported N_2 concentration in the mixture.

The HCl absorption band with maximum at around 129 nm has a minimum interference with Cl_2 and no interference with N_2. Calculated HCl concentration in the mixture with use of HCl reference data is 2 ppm.

Possible interferences with broad O_2 and H_2O absorption bands which are most prominent contaminants in H_2 don't affect analysis of Cl_2, HCl or N_2 because of the differences in their spectral band shapes. Indeed Cl_2, HCl and N_2 have discrete-like absorption features while the O_2 and H_2O have broad-band continuum-like features.

The analysis for e.g. N_2 or Cl_2 is done in the entire spectral range, e.g. in 116-148 nm, and all their absorption features are used in overall spectra fit over the entire spectral range. This is in a sharp contrast to many laser-based approaches which rely on typically single absorption line analysis.

Figure 8 shows the absorption spectra measured with the far-UV analyser on NPL's 2744 standard. The spectrum is dominated by N_2 and H_2S absorption features.

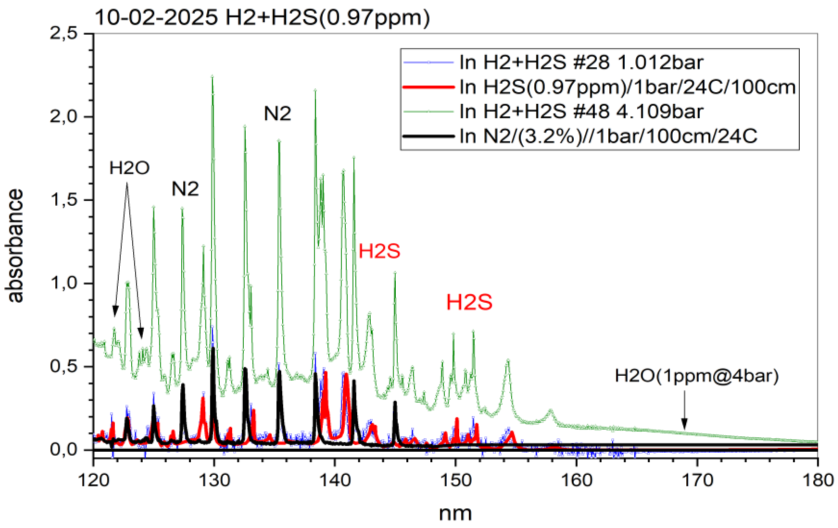


Figure 8: Far-UV absorption spectrum at 1 bar (blue) and 4 bar (olive) (24 °C) measured on NPL's 2744 standard. Modelled partial H_2S (0.97 ppm, red) and N_2 (3.2 %, black) at 1 bar spectra. Positions of H_2O lines and band are given by arrows.

A spectrum fit gives an amount fraction of H_2S of about 0.97 µmol mol^{-1} which is in a very good agreement with the H_2S amount fraction in the mixture. Calculated N_2 amount fraction from the spectrum fit was found to be 3.2 %. Weak spectral absorbances can further be enhanced by increasing the gas pressure in the analyser. In Figure 8 a far-UV absorption spectrum in the same mixture at around 4 bar is shown for a comparison. As one can see, the H_2S and N_2 bands are much better pronounced at 4 bar than at 1 bar (i.e. have higher absorption values). In addition, H_2O (1 µmol mol^{-1}) and O_2 (1.3 µmol mol^{-1}) absorptions become visible in the spectrum at 4 bar.

As mentioned above, O_2, H_2O, CO and CO_2 are the most probable contaminants in H_2 streams, especially when H_2 is industrially produced from e.g. SMR process. Therefore, the far-UV measurement method and the analyser have been evaluated on NPL's D089839 gas standard which in H_2 balance contains traces of H_2O, N_2, O_2 and C_3H_8 in addition to CO (0.212 µmol mol^{-1}) and CO_2 (2.331 µmol mol^{-1}). A representative far-UV spectrum measured on that gas standard is shown in Figure 9.

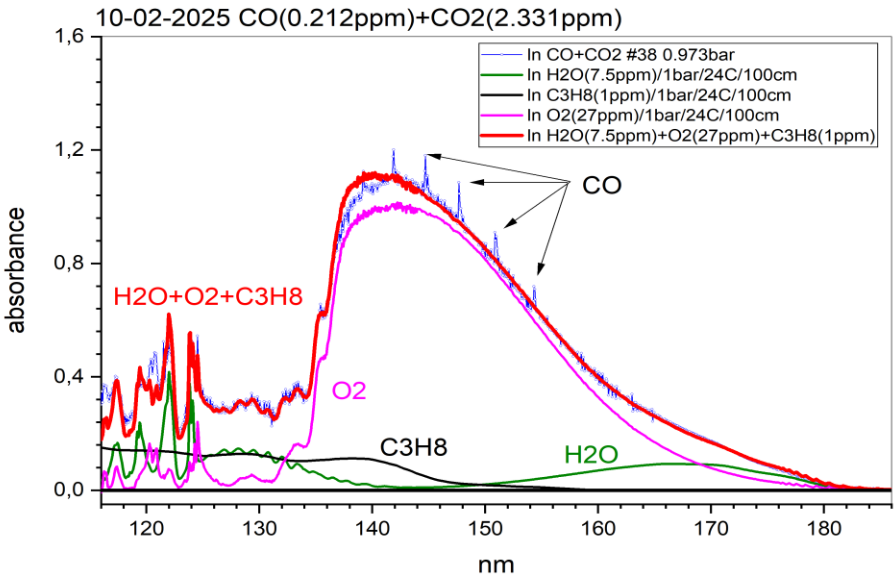


Figure 9: Far-UV absorption spectrum at around 1 bar and 24 °C (blue) measured on NPL's D089839 gas standard. Modelled H_2O+O_2+C_3H_8 spectrum (red) and partial contributions to the modelled spectrum: O_2 (27 ppm, magenta), H_2O (7.5 ppm, olive), C_3H_8 (1ppm, black). Positions of CO bands are given by arrows.

The far-UV spectrum analysis shows clear presence of CO, H_2O (7.5 µmol mol^{-1}), O_2 (27 µmol mol^{-1}) and C_3H_8 (1 µmol mol^{-1}). CO has very distinguished band structure with well-defined positions (similar to N_2) that simplify the data analysis of complex experimental data with many spectral interferences.

The CO_2 (2.331 µmol mol^{-1}) has very weak absorption which is difficult to measure at around 1 bar. However, the CO_2 can be measured by an IR-based system coupled to the far-UV one as it was demonstrated in the MetCCUS project. The N_2 (319 µmol mol^{-1}) cannot be measured at 1 bar pressure, but it can be done at e.g. 10 bar pressure in the analyser. This pressure is a common pressure for pipes and medium size storage tanks.

As can be seen from the Figures 7 to 9, the developed far-UV method and the analyser are sensitive to a vast number of impurities in H_2 matrixes and can be used for on-line process measurements in H_2 gas streams up to 40 bar. Reference data for the far-UV spectral range are normally limited and the results on the high-quality gas standards obtained in the project will be used as a part of the database in future applications of the far-UV analyser.

2.2 Onsite measurements

Within Met4H2 project, onsite measurements were also carried out at two different sites: i) a hydrogen production location at the Torino Airport and ii) a hydrogen industrial production plant at Nippon Gases in San Salvo, Italy. At both sites, gas sampling as well as online measurements were carried out. Online measurements concerned the content of oxygen and water vapour in the hydrogen stream. At the Nippon Gases hydrogen production plant, a far-UV based analyser was also used to detect the presence of H_2O, CO, N_2, O_2 and potentially all other contaminants in the H_2, if they are present.

Concerning the electrolyser production location, an Alkaline Exchange Membrane (AEM) electrolyser was made available by the Airport Authority (SAGAT) who is a project collaborator. The electrolyser is part of a demonstration plant (see Figure 10) developed within the Horizon 2020 Project TULIPS[1] to demonstrate an integration of renewable energy and hydrogen production to provide electricity and heat through some high temperature fuel cells, according to the scheme illustrated in Figure 11. The system is installed at the Torino Airport airside within the Fire Brigade's precinct as it serves their buildings.

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[1] TULIPS - DemonsTrating lower pollUting soLutions for sustaInable airPorts acrosS Europe is an Horizon 2020 project (Grant agreement ID: 101036996). It aims to accelerate the implementation of innovative and sustainable technologies targeting reduced greenhouse gas emissions at airports. The project will roll out 17 demonstrations of green airport technological, non-technological and social innovations at Amsterdam Airport Schiphol and at the Oslo, Turin and Larnaca airports. TULIPS will measure and quantify the benefits of these technologies and concepts and forecast their impact on EU climate goals. The project will consider economic, geographical and political scenarios to deliver a robust roadmap presenting the way of implementation from international hubs to the regional level. https://tulips-greenairports.eu/

Figure 10: Alkaline electrolyser demonstration plant at the Torino Airport.

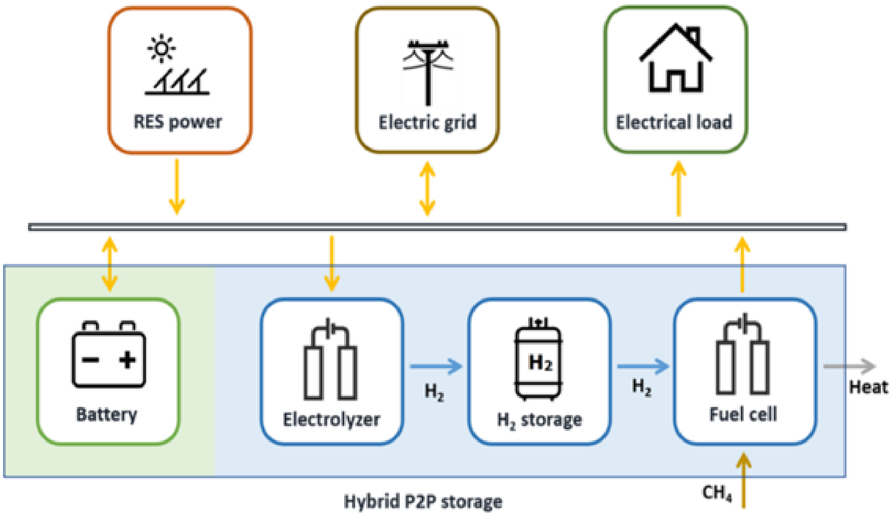

Figure 11: Power to power scheme of the demonstrator installed at SAGAT facilities.

The electrolyser is made of two modules based on the Enapter EL2.1 AEM[2] and it produces around 1 m^3/hr of > 99.9 % hydrogen with water impurities around 1000 μmol mol^{-1}, suitable for fuelling a 3-kW high temperature fuel cell installed on site. The hydrogen is produced at 30 bar and can be mixed with methane from the grid for use in the fuel cells. A 0.4-m^3 hydrogen storage tank (at 30 bar) is also installed there. The installation had undergone PED certification and safety assessment and was fully authorised by the local Fire Brigade Authority.

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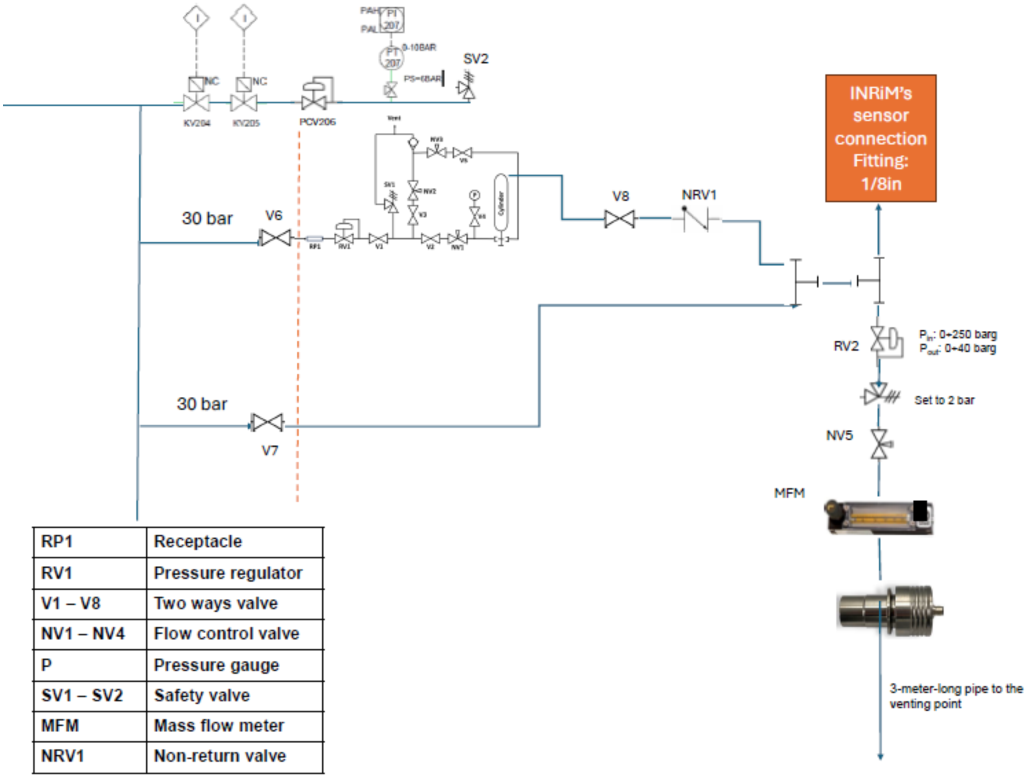
[2] https://handbook.enapter.com/electrolyser/el21/downloads/Enapter_Datasheet_EL21_EN.pdf

To meet the requirements of the present activity, an Enapter pressure-swing dryer was installed by the plant integrator SimplyfHy. This increased the quality (dryness) of the hydrogen 99.999 % purity ($H_2O < 5$ µmol mol^{-1}, $O_2 < 5$ µmol mol^{-1}).

With the support of the plant integrator, the team composed by Envipark, INRIM and NPL identified the best sampling points in the section of tubing just before the mixing skid and receiving hydrogen from either the storage or directly from the electrolyser. This to ensure that sufficient hydrogen could be provided for the sampling operation, including the venting procedure, but also that the required operational parameters of the samplers and analysers could be satisfied. The additional sampling line is shown in the section of the P&DI below (Figure 12), while the following operational details were taken into account:

- Sampling rig and connected cylinders: two 10-L hydrogen samples for off-site lab analysis were required; the device was connected to one of the 30 bar outlets of the testing line. A procedure for the flushing of the rig and the cylinders was to be followed before the start of the sample collection. The venting stack is described in section 2.2.1 to ensure the safe release of hydrogen as a vent create an ATEX zone.
- Minox i Galvanic Fuel Cell Oxygen Transmitter (oxygen analyser): this device was connected to the hydrogen source using a pressure reducer (inlet: 0-to-30 barg; outlet: 0-to-2 barg). The flow was controlled by using a flowmeter and needle valve.
- Humidity sensor system: this INRIM custom setup was connected to both 30 bar system outlet and at NPL's sampling rig outlet. A flow of 1-to-3 l$_n$/min was provided.

Each device was connected to the testing line via compression-type (Swagelok) fittings. The levels of water and oxygen impurities in hydrogen were monitored for three days.



RP1	Receptacle
RV1	Pressure regulator
V1 – V8	Two ways valve
NV1 – NV4	Flow control valve
P	Pressure gauge
SV1 – SV2	Safety valve
MFM	Mass flow meter
NRV1	Non-return valve

Figure 12: P&DI scheme of the testing connection inclusive of the sampling device and, cascading, the humidity and oxygen analysers

The additional installations (dryer and sampling taps) were subject to an integration by the plant integrator of the safety assessment documents prepared for the original installation.

Similarly, an ATEX assessment was produced to define the zones and the safety issues linked to the venting of the hydrogen from the sampling and analysing devices. Each device was individually connected to their own venting lines, more specifically:

- Sampling rig: proprietary venting piping, set up on site with venting point set at 3-m or higher above the floor. The vent was mounted on a tripod and secured to the structure covering the installation and to the concrete safety wall surrounding the storage.
- Humidity sensors system: venting line of around 4.5 meters set at 3-m or higher above the floor and secured to the cover structure of the electrolyser and the storage containment.
- Oxygen analyser: venting line of around 4.5 meters set at 3-m or higher above the floor and secured to the cover structure of the electrolyser/ the storage containment.

The whole system operation was then assessed for risks with the production of a supporting document compiled and agreed upon by the whole team.

2.2.1 Sampling procedure

NPL succeeded in sampling hydrogen gas produced from an alkaline electrolyser at Turin Airport with the support of SAGAT, Envipark and POLITO. The sampling point was chosen after the storage tank. The pressure was approximately 30 bar. The area for sampling system was identified with site operators considering risk assessment using results of ATEX evaluation and requirement of the portable vent stack.

The sampling procedure started from sampling kit installation. Figure 13 shows the setups from NPL DirSam sampling kit [12] at Turin Airport. The sampling kit contains a receptacle with high pressure quick connect, a sampling panel, two flexible hoses for connection with a sampling cylinder and a vent stack with a flexible hose. It can be used to collect samples under the pressure of 10 to 875 bar. All the piping on the sampling panel is sulfinert-coated. There is also a venting line installed on the sampling panel. It helps to remove the purging gas before the sample collection and vent the excess gas after the sample collection. To ensure the safe release of hydrogen as a vent create an ATEX zone, the venting stack can reach a height of more than 3 meters with a T-shape outlet. Two flexible hoses are utilised to connect the panel with the inlet and outlet of the sampling cylinder. They are made of high-pressure wire polyamide hoses (product 2440N, Parker, Coventry, United Kingdom). Two 10 L aluminium Luxfer SGS™ with double-ended DIN 477 no. 1 valve were selected as sampling cylinders. They were vented and evacuated for at least 12 hours and reach the pressure less than 1×10^{-6} mbar at NPL prior to sampling. The inlet of the cylinder is connected with the sampling kit while the outlet of the cylinder is connected to two sensors for online measurement.

After the installation, the purging process is required to remove air and moisture from the sampling kit and cylinder. In the usual manner, the sampling kit and cylinder requires to be properly purged with 500 g of hydrogen gas, i.e. 7-10 times purging with around 100 bar hydrogen sample. Due to the limited hydrogen gas and operational time at Turin airport, the sampling kit was purged 50 times and the cylinder was purged 11 times at around 30 bar. In total, about 300 g of hydrogen gas was used during the purging process which is less than the required 500 g hydrogen for this sampling kit.

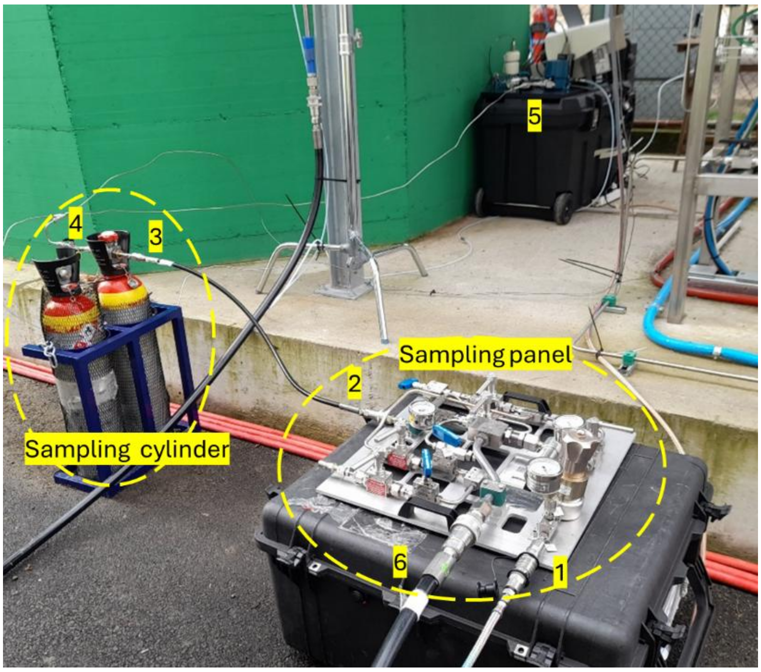


Figure 13: NPL sampling kit setup at Turin airport (1: sampling inlet, 2: outlet connection to cylinder, 3: sampling cylinder inlet, 4: sampling cylinder outlet, 5: sensor monitoring setups, 6: vent line of sampling kit).

Two samples (D923897 and D923893) were collected on Day 2 and 3. The transport of the pressurised hydrogen gas sample was realised using an authorised dangerous goods transport company (TheCourierCompany, UK) following appropriate packaging and labelling by NPL trained staff. The safe transportation of flammable and pressurised dangerous goods should be done according to local and international regulations to ensure the safety of the samples, human and environment between sampling site and analytical laboratory location.

The two samples arrived at the NPL in an acceptable condition. Their pressure was 28.8 and 26.7 barg respectively on arrival. The samples were stored upon analysis at (20 ± 3) °C.

2.2.1.1 Offline measurement results at NPL

The offline analysis according to ISO 14687 excluding HCl and Cl_2 was conducted at NPL's hydrogen purity laboratory. Laboratory analyses were performed using ISO-17025 accredited NPL internal methods for the measurement of N_2, O_2, Ar, CO, CO_2, CH_4, total non-methane hydrocarbons, total sulphur and H_2O. The details can be found in Annex 1.

Table 6 illustrates the analytical instrument used and results of the hydrogen samples (D923897 and D923893) collected from alkaline electrolysers at Turin airport. The results were applied with expanded uncertainty (*k*=2).

Table 6. Offline measurement results of hydrogen samples from alkaline electrolyser at Turin airport.

Compound	**Alkaline electrolyser sample 1 (D923897)**	**Alkaline electrolyser sample 2 (D923893)**	**ISO 14687:2025 Grade D**
	Measured amount fraction and uncertainty (k = 2) [µmol/mol]		Maximum amount fraction [µmol/mol]

Total non-methane hydrocarbons	0.0166 ± 0.0036	0.041 ± 0.007	2
CH_4	<0.005	<0.005	100
CO_2	0.060 ± 0.006	0.0192 ± 0.0025	2
He	<3.5	<3.5	300
H_2O	23.8 ± 1.4	11.5 ± 0.7	5
NH_3	<0.010	<0.010	0.1
HCOOH	0.0212 ± 0.0022	0.0084 ± 0.0019	0.2
HCHO	< 0.010	< 0.010	0.2
Total sulphur compounds	< 0.0010	< 0.0010	0.004
CO	<0.015	<0.015	0.2
N_2	10.42 ± 0.55	2.38 ± 0.23	300
Ar	0.096 ± 0.020	0.049 ± 0.010	300
O_2	11.2 ± 0.7	7.07 ± 0.44	5
Total halogenated compounds	< 0.017	< 0.016	0.05

2.2.1.2 Results comparison with ISO 14687:2025 Grade D

The actual compliance of the hydrogen produced from alkaline electrolyser at Turin airport with ISO 14687:2025 Grade D was not considered critical to this study. Table 6 shows that the levels of key contaminants in the hydrogen fuel samples were mostly consistent with the stringent limits set forth by ISO 14687:2025 Grade D, except water and oxygen.

In this case, the hydrogen application was stationary fuel cell and therefore would better comply with ISO 14687 grade E category 2. For such application, water should be non-condensing at any ambient conditions and oxygen should be below 50 µmol/mol. For this application, the hydrogen from the alkaline electrolyser at Turin airport is fully compliant. Assessing fuel quality should always be in line with the expected applications.

2.2.1.3 Impact of purging prior to sampling

It is observed that the amount fractions of water in hydrogen for both samples are significantly higher than ISO 14687:2025 grade D threshold (5 µmol/mol). This may be related to sampling system purges challenges in presence of low pressure and low volume available. The results also shows difference between the 1st and 2nd sample for oxygen, nitrogen and water which are often related to air contamination. The readings of nitrogen and oxygen in the sample 1st sample taken (D923897) were much higher than those in the 2nd sample taken (D923893).

In this case, the effect of air contamination due to insufficient purging should be considered prior to reporting final results. In the usual manner, the NPL DirSam sampling kit requires to be properly purged with 500 g hydrogen gas. Due to time constrain and low pressure of the system for the alkaline electrolyser of Turin Airport, NPL DirSam purges represented about 300 g hydrogen gas purged which is less than the required purges level for the NPL DirSam system (approximately 500 g hydrogen).

The fit-for-purpose of the sampling system is essential for the reliability of the results. Therefore, in the case of the NPL DirSam sampling kit, following the appropriate purging requirement is essential. Due to the low pressure and challenging volume of the system, the NPL DirSam may not be optimum for such small system. In such case, it is important to understand the limitation and strength of sampling system and consider changes if necessary *i.e.,* consider feasibility of using a portable ATEX pump for the sampling kit onsite to remove trace of air or reducing pipe diameter and dead-volume to ease the purging process.

2.2.1.4 Offline measurement results at VSL

VSL also analysed the 2 hydrogen samples which were both very low in pressure (just a few bar) when they arrived at VSL. The mixtures contained no HCl (<1 nmol/mol) but H_2O levels were above the ISO threshold (D923893: (13.6 ± 2) µmol/mol and D923897: (26.5 ± 2) µmol/mol. The VSL results for H_2O and HCl are both in line with the NPL measurements and the online H_2O measurements (see section 2.2.2).

2.2.2 Online humidity measurement

The amount of water vapour in hydrogen was measured online using the setup showed in Figure 14, where two impedance-based humidity sensors were connected in series along with gas pressure and flow rate meters by means of stainless steel 316 L fittings and tubing.

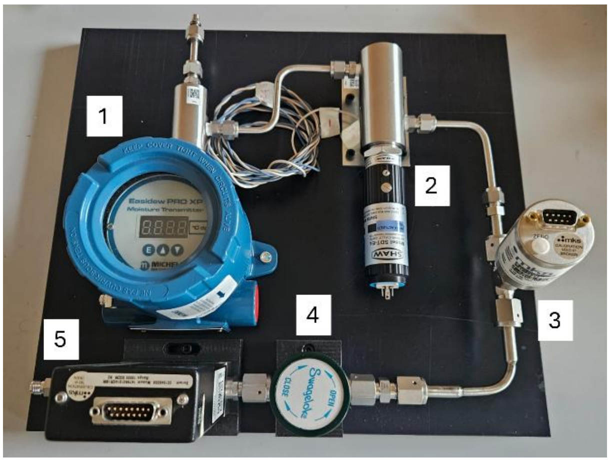


Figure 14. INRIM Humidity measurement system: 1) Michell – Easidew PRO XP humidity sensor; 2) SHAW - Model SDT – Ex Silver humidity sensor; 3) MKS 750C pressure gauge; 4) pressure reducing valve; 5) MKS 1179 thermal mass flow meter/controller.

Two commercially available aluminium oxide impedance sensors were used for humidity measurement in moist hydrogen (see Figure 15). Specifically, one model produced by SHAW (model SDT – Ex Silver) with dew point measuring range from -100 °C to -20 °C and pressure rating from 0.01 bar up to 350 bar, while the other produced by Michell (model Easidew PRO XP) with a dew point measuring range from -100 °C to 20 °C and pressure rating up to 450 bar. The sensors were calibrated before and after the field measurements with both moist nitrogen and hydrogen in the water vapor amount fraction range 1 µmol mol^{-1} to 120 µmol mol^{-1} at several working pressures between 0.2 MPa and 3 MPa against the INRIM t-PHG standard generator.

The pressure was measured using a MKS 750C capacitance pressure transducer with a full-scale range of 6.8 MPa while the flow rate was measured by a MKS 1179 thermal mass flow meter/controller with a full scale of 10 l_n/min. As the mass flow meter/controller can operate at up to 10 bar, a pressure reducing valve has been installed between the pressure gauge and the mass flow meter/controller.

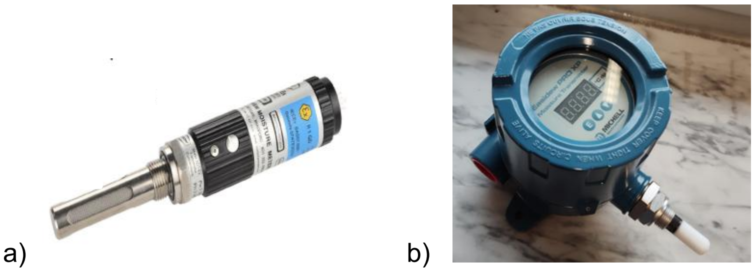


Figure 15. Aluminium oxide humidity sensors: a) SHAW - Model SDT – Ex Silver; b) Michell – Easidew PRO XP.

Only one sensor was required for humidity measurements. However, it was decided to use two sensors in series to assess both the agreement in readings from the same sample and to minimise the risk of unsuccessful measurements in the field should one of the sensors fails.

During the campaign at the Turin Airport (see the setup installation in Figure 16), the humidity measurement system was initially placed downstream the NPL's sampling systems and later on was switched to an independent gas line directly connected to the electrolyser.

Figure 16: INRIM humidity sensor setup at Turin Airport.

Figure 17 shows as an example the frost point temperature in hydrogen measured downstream the NPL's sampling systems during the sampling of the second cylinder until minute 325 when it was switched to the independent gas line (from minute 345 until the end).

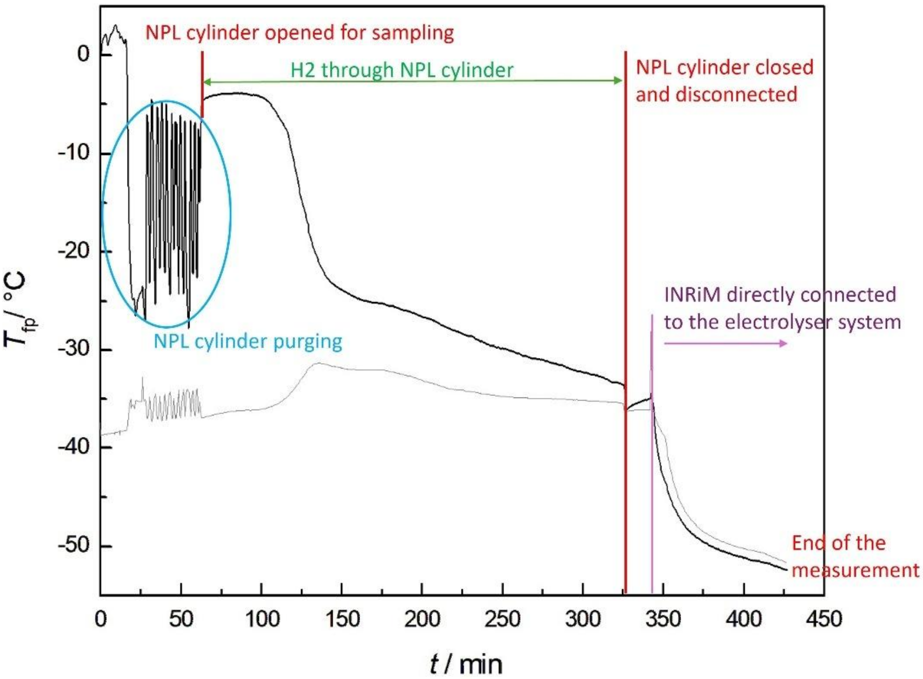


Figure 17. Measurement of hydrogen frost point temperature measured downstream the NPL's sampling systems during the sampling of the second cylinder and then switched to an independent gas line. ▬ Michell sensor ▬ SHAW sensor.

The dark line refers to the frost point measurement (T_{fp}) recorded by the Michell humidity sensor, while the grey line refers to the T_{fp} measured by the SHAW humidity sensor. Both sensors show the same trend and the frost point temperatures agreed to within the measurement uncertainty when the measurement system was directly connected to the hydrogen sampling point. When the humidity sensors were connected to downstream the NPL's sampling system, the SHAW sensor (grey line) went out of scale and only the Michell sensor was capable of taking humidity measurements.

As the plot shows, the amount of water vapour in the gas is greatly affected by the presence of the sampling system. In fact, the release of water vapour during purging operations on the NPL cylinder was clearly observed, as well as the degassing of the NPL sampling system (panel and cylinder) during filling operations. It is speculated that if the cylinder had been left to flush and fill for a longer time, the water content measured at the cylinder outlet would have been closer to the actual amount as measured on the gas directly coming from the production plant.

Tables 7 and 8 report the gas pressure, p, and the frost point temperature, T_{fp}, as measured with sensors placed downstream the NPL's sampling systems. The measurement standard uncertainties, $u(p)$ and $u(T_{fp})$ are also reported. The reported data correspond to those measured at the time the valve cylinder was closed (e.g. referring to Figure 14, the frost point temperature and pressure measured at minute 345). Specifically, Table 7 refers to the collection of the first hydrogen sample (D923897) on the second day of the campaign, while Table 8 refers to the collection of the second hydrogen sample (D923893) on the third day of the campaign. Table 7 and 8 also report the water vapour amount fraction, x_w, and its measurement standard uncertainty, $u(x_w)$. The latter quantity was determined from the measured values of T_{fp} and p and by the water vapour saturation pressure and enhancement factor calculated using the Sonntag and Greenspan equations, respectively.

Table 7: Online humidity monitoring during collection of the sample D923897.

p = 28.7 bar $u(p)$ = 0.1 bar				
Sensor	T_{fp} / °C	$u(T_{fp})$ / °C	x_w/ µmol·mol^{-1}	$u(x_w)$ / µmol·mol^{-1}
Michell – Easidew PRO XP	-25.41	1.75	24.08	4.17
SHAW - Model SDT – Ex Silver	Out of range	-	-	-

Table 8: Online humidity monitoring during collection of the sample D923893.

p = 26.5 bar $u(p)$ = 0.1 bar				
Sensor	T_{fp} / °C	$u(T_{fp})$ / °C	x_w/ µmol·mol^{-1}	$u(x_w)$ / µmol·mol^{-1}
Michell – Easidew PRO XP	-33.25	1.09	11.58	1.33
SHAW - Model SDT – Ex Silver	-35.35	1.01	9.26	1.01

Table 9 reports the values of p, T_{fp} and x_w with the respective measurement standard uncertainty when the measurements were carried out by connecting the humidity sensor system directly to the sampling outlet tap of the electrolyser by means of the independent gas line. The reported values refer to the average of the last half-hour of measurements. The amount of water vapour measured in this condition corresponds to approximately 1 µmol·mol^{-1}. It is speculated that if monitoring had continued for a longer period of time, thanks to the purging effect due to a continuous dry-gas flushing, the sensor readings would have been even lower than the values reported here.

Table 9: Online humidity monitoring of the hydrogen line using an independent line.

p = 28.1 bar $u(p)$ = 0.1 bar				
Sensor	T_{fp} / °C	$u(T_{fp})$ / °C	x_w/ µmol·mol^{-1}	$u(x_w)$ / µmol·mol^{-1}
Michell – Easidew PRO XP	-52.26	1.01	1.25	0.16
SHAW - Model SDT – Ex Silver	-53.83	1.00	1.03	0.13

It is worth noting that the amount fractions reported in Table 7 and 8 are consistent with the water vapour amount fractions as measured during the offline analysis of the samples collected by NPL. This points out that by positioning the sensors downstream the NPL sampling cylinders, it is likely that the cylinders outgassing was measured.

Considering the experience gained at the Torino Airport, it should be emphasised that, if multiple samplings are taking place simultaneously, to obtain reliable humidity measurements it is crucial to position the humidity sensors on an independent gas line rather than downstream of any sampling systems. In fact, the latter could release an unknown amount of water into the gas stream, causing an incorrect humidity measurement. For low water vapour amount fraction measurements (at ppm level or lower), it is highly advisable to purge the line and the sensors with a drier gas before any measurements. Purging may help to reduce the overall measurement time, whereas if agas line is not purged, care should be taken to wait enough time for the sensor to reach a stable reading. E. g. in the present experiments, measurements with impedance sensors at sub-ppm level required more than 10 hours to reach a stable, consistent, reading.

2.2.3 Online oxygen measurement

The sensor chosen by NPL for this experiment was the Minox i oxygen transmitter, which consists of an electrochemical (EC) oxygen sensor and inbuilt microprocessor. It is encased in stainless steel, with a process connection on the removable housing and an electrical signal connector on the main housing. The sensor is replaceable, accessed via the removable housing and is configured for 0 – 20 ppmv (4 - 20mA) oxygen concentration measurement within pressure range of 0.9 to 1.1 bar(a). The EC sensor is a galvanic fuel cell and is designed to be unaffected by the presence of other background gases. This sensor required calibration prior to its installation following the manufacturer's instruction. This was done using NPL's validated CRM with an oxygen mole fraction of (8.80 ± 0.54) μmol/mol (k =2) in hydrogen matrix.

The calibration was not feasible onsite due to health and safety challenges at the monitoring site related to handling high pressure cylinders. It was realised the day before the experiment, at INRIM laboratory (few kilometres away from the site) and the sensor was then transported by road to the site.

The set up presented in Figure 18 was used to calibrate the sensor. The pressure delivered to the sensor was regulated by using a pressure regulator with input pressure of 250 barg and output of 0 to 2 barg, to ensure that required pressure is delivered to the sensor manifold. The flow is regulated by using a needle valve and monitored by using a mass flow meter (MV-394-H2 mass flow regulator, Bronkhorst, NL) to ensure a constant and stable flow.

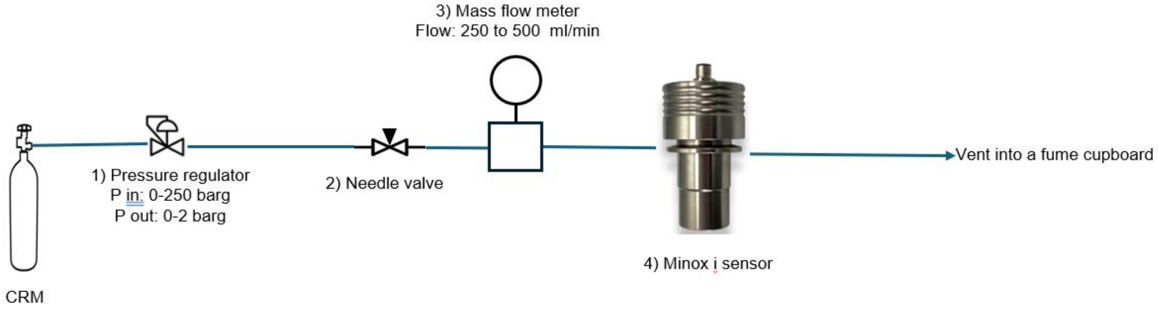


Figure 18. NPL online oxygen monitoring setup: 1) pressure regulator with input pressure of 0 to 250 barg and output of 0 to 2 barg; 2) Needle valve; 3) Mass flow meter; 4) Minox i sensor.

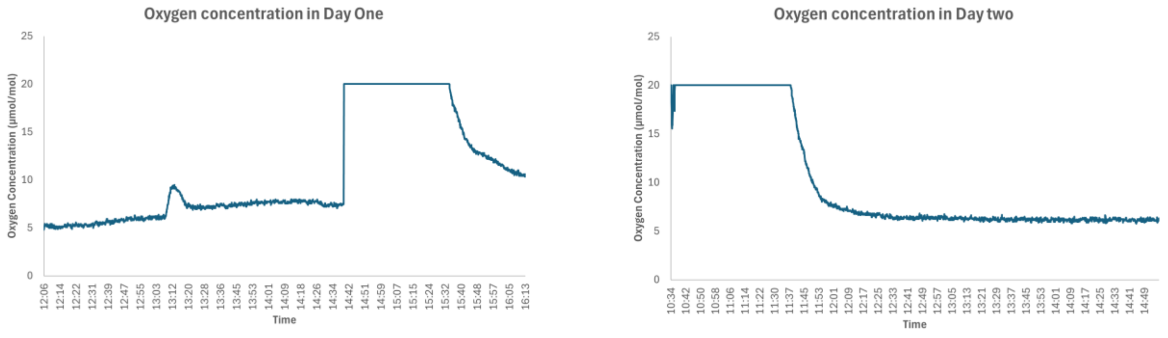
The calibration was carried out at a pressure of 0 – 0.1 bar(g) and a flow rate of 350 ml/min until sensor reading reached stability and were within the target range.

Figure 19 shows the setup installation at the alkaline electrolyser in Torino airport.

Figure 19: NPL oxygen sensor setup at Turin Airport.

2.2.3.1 Online measurement results

During the two-day exercise at the alkaline electrolyser, the oxygen sensor provided continuous real-time monitoring that revealed key process behaviour. On Day One (see Figure 20a), a spike in oxygen concentration was observed shortly after the start-up; while the reason for this is not clear, the event represents the sensor's ability to detect rapid and short-lived transients. This was then followed by a period of saturation, during which the flow was temporarily increased to support purging and then readjusted to the calibrated flow rate for the sensor. The concentration gradually decreased and approached stable levels. On Day Two (see Figure 20b), the oxygen concentration again started at elevated values but decreased smoothly with purging and then remained stable over time, confirming that the line was properly conditioned, and the sensor delivered consistent measurements under calibrated flow. These observations demonstrate how online monitoring captures the evolution of oxygen concentration in real time, including transient effects and stabilisation behaviour, thereby providing a more representative picture of the process than offline.



(a) (b)

Figure 20. Oxygen sensor readings of (a) Day one and (b) Day two of online measurements during pipeline purging and stabilization.

2.2.3.2 Comparison of online and offline laboratory analysis

A comparison between offline analysis and online analysis was realised to determine the accuracy of the online analysis and confirm the representativity of the offline sample. The oxygen sensor measurements gave results of (10.41 ± 0.06) µmol/mol for Sample 1 (D923897) and (7.620 ± 0.035) µmol/mol for Sample 2 (D923893). The offline laboratory analysis reported (11.2 ± 0.7) µmol/mol for Sample 1 and (7.07 ± 0.44) µmol/mol for Sample 2. The close agreement between the two sets of measurements (see Table 10) confirms the reliability of the online monitoring and demonstrates its capability to capture both transient changes and stable process conditions.

Table 10. Online measurement results of oxygen amount fractions in hydrogen samples from alkaline electrolyser at Turin airport.

	Online sensor measured amount fraction (µmol/mol) and uncertainty (*k*=2)	**NPL analysis from sampling cylinder - measured amount fraction (µmol/mol) and uncertainty (*k*=2)**
Alkaline electrolyser sample 1 (D923897)	10.41 ± 0.06	11.2 ± 0.7
Alkaline electrolyser sample 2 (D923893)	7.620 ± 0.035	7.07 ± 0.44

2.3 Summary of contaminants probability of presence for hydrogen produced by

alkaline electrolyser

Based on the online and offline measurement results from the samples collected from Turin airport, the key contaminants were compared with the findings in report A3.3.1. Table 11shows the summary.

Table 11. Summary of contaminants for hydrogen produced by alkaline electrolyser.

Probability of presence	Impurity from alkaline electrolyser from report A3.3.1	Impurity from measurement made at alkaline electrolyser at Turin airport according to ISO 14687 grade D application	Impurity from measurement made at alkaline electrolyser at Turin airport according to ISO 14687 grade E category 2 application
Possible	N_2, H_2O, O_2, CO_2	O_2	-
Unlikely	HCl, Cl_2	H_2O, N_2, CO_2, total non-methane hydrocarbons, HCOOH, Ar, Total halogenated compounds, He, NH3, HCHO, Total sulphur compounds, CO, CH_4	H_2O, O_2, N_2, CO_2, total non-methane hydrocarbons, HCOOH, Ar, Total halogenated compounds, He, NH3, HCHO, Total sulphur compounds, CO, CH_4

When considering the actual application of the hydrogen for ISO 14687 grade E category 2, none of the contaminants were found close to the threshold. Therefore, it is unlikely to find any contaminants in hydrogen for this application at the alkaline electrolyse of Turin airport. It may be recommended to monitor oxygen amount fraction as it may be possible in case of electrolyser purification system failure. The online analysis realised by NPL didn't show any significant variation of oxygen amount fraction over couple of days of operation Therefore this impurity may be relevant to monitor online over longer period of time to clarify the frequency of control required.

3 Findings on traceable quality monitoring in hydrogen distribution

The probability of occurrence of the contaminants in hydrogen distribution including production methods as steam methane reforming (SMR), distribution through pipeline or hydrogen carrier as ammonia have been defined in the report A3.4.1. A summary can be found in Table12.

Table 12. Summary of probability of occurrence of the contaminants in hydrogen distribution.

Impurities potentially present in H2 produced by SMR	**Possibility of impurity over ISO 14687:2025 grade D threshold**	**Impurity**
	Potentially present	N_2, CH_4, CO, H_2O, total hydrocarbons (except methane), He, O_2
	Very unlikely	CO_2, Total sulphur compounds, NH_3, HCHO, HCOOH, halogenated compounds
Impurities potentially introduced during repurposed network transportation	**Possibility of impurity over ISO 14687:2025 grade D threshold**	**Impurity**
	Potentially present	N_2, O_2, total hydrocarbons (except methane), total sulphur compounds, halogenated compounds (NH_3, HCHO and HCOOH until demonstrated very unlikely)
	Very unlikely	Ar, CO_2, H_2O, CO, CH_4, He

Impurities potentially introduced during dedicated H2 pipeline transportation	**Possibility of impurity over ISO 14687:2025 grade D threshold**	**Impurity**
	Potentially present	N_2, O_2, H_2O, halogenated compounds
	Very unlikely	Ar, CO_2, CO, CH_4, He, NH_3, HCHO, HCOOH, total sulphur compounds, total hydrocarbon (expect methane)

Impurities potentially introduced using ammonia as transportation medium	**Possibility of impurity over ISO 14687:2025 grade D threshold**	**Impurity**
	Potentially present	N_2, O_2, H_2O, NH_3
	Very unlikely	Ar, CO_2, CO, CH_4, He, HCHO, HCOOH, total sulphur compounds, total hydrocarbon (expect methane), halogenated compounds

Nitrogen, oxygen and water are the most probable contaminants present in the three scenarios. The potential amount fraction of these three impurities is expected to be above 300 µmol/mol, 5 µmol/mol and 5 µmol/mol, respectively. Suitable sensors capable to perform online measurement of oxygen, water and nitrogen were selected for evaluation by 21GRD05 Met4H2 consortium.
In addition, contaminants such as total sulphur compounds, halogenated compounds and ammonia are expected to be present in hydrogen distribution. It is critical to gather real data (analysis) to improve the probability of presence of these contaminants. It would support better hydrogen gas monitoring plan.

To tackle the challenge, several measurement solutions of these compounds are proposed in Task 3.3 and 3.4 in Met4H2 project. It includes prepare new primary reference materials of sulphur compounds and chlorine, development of a traceable method for ammonia analysis or a novel portable reference gas generator for ammonia.

3.1 Reference standard to provide traceability to offline measurements

3.1.1 Reference materials and analytical methods for the determination of sulphur impurities in hydrogen

Gaseous gravimetric and dynamic primary reference materials containing sulphur compounds were prepared and suitable analytical methods for its measurement were developed and validated. Sulphur compounds have a high potential to cause damage to proton exchange membrane (PEM) fuel cells.

3.1.1.1 Preparation of gravimetric primary reference gas standards

BAM and VSL independently prepared primary sulphur reference gas standards with amount fractions of 1000 and 100 nmol/mol following ISO 6142-1 [13]. Hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (MeSH), ethyl mercaptan (EtSH), dimethyl sulfide (DMS), diethyl sulfide (DES), and tetrahydrothiophene (THT) were selected as target components. For reasons of comparison, the gas mixtures were prepared in 100 % hydrogen (VSL) and 100 % argon (BAM). The use of argon can be beneficial since fewer dilution steps are required due to the higher density of argon. The cross-validation between both mixtures has confirmed that both balance gases can principally be used. However, when mass flow controllers (MFC) are used, measures need to be taken to ensure that they are properly calibrated for the matrix gas.

Preparation was carried out in aluminium gas cylinders of 5-10 L volume with a targeted end pressure of 120 bar. To avoid adsorption of molecules on the cylinder wall as well as catalytically induced chemical reactions with the cylinder material, it is recommended to treat/coat the inner wall surface. The gas cylinders used in this project have been specially treated with a proprietary procedure by Air Liquide. Based on the work of Benesch et al. (2004) [14], but also from own experience, this surface treatment has proven to be effective for sulphur components.

3.1.1.2 Preparation of dynamic reference gas standards

ISO 14687 [3] defines, among others, the hydrogen quality specifications for PEM fuel cell road vehicles application with a threshold level for total sulphurs of 4 nmol/mol. For the validation work, an amount fraction range of 0.5-100 nmol/mol was targeted. For this purpose, the gravimetrically produced gas standards must be dynamically diluted. Each partner set up their own dilution system based on dynamic dilution with mass flow controllers (MFC, Bronkhorst/NL) according to ISO 6145-7 [15]. To avoid adsorption on contact surfaces (e.g. walls) and potential chemical reactions, it is recommended that all tubing, pressure regulators and connectors are made from stainless steel and are specially coated. Very good experience was made with SilcoNert2000® coating from SilcoTek®. For the same reason, all parts of the MFC that come into contact with the sample should also be coated, if possible.

Another aspect concerns the accuracy of the MFC when using gases or gas mixtures. Due to the different gas properties, in this case hydrogen and argon matrices, the devices should be calibrated with the respective gases. If this is not possible, conversion factors can be used, which can be obtained from the manufacturer. In this case, it should be noted that these factors are usually based on calculations, which lead to a greater uncertainty than real gas calibrations and to lack of metrological traceability.

3.1.1.3 Development and validation of analytical methods

Both BAM and VSL have used thermal desorption gas chromatography with sulphur chemiluminescence detector (TD-GC/SCD) to analyse the single sulphur compounds. VSL tested also the feasibility of measuring the total sulphurs using a special GC column included in the TD-GC-SCD system. In addition, BAM tested an online measurement method using proton transfer reaction mass spectrometry (PTR/MS).

Thermal desorption is a sampling technique that consists of adsorbing sulphur molecules on a sorbent trap at low temperature, thereby concentrating the sample followed by a rapid desorption at high temperature and injection in the gas chromatograph where they are separated per species or analysed as total. With this technique, large “known” volumes of trace amount fractions of sulphurs can be sampled on the trap allowing to obtain a concentrated sample. The sampling of the sulphurs was carried out by means of an MFC that controlled the flow of gas streaming through the sorbent trap. As for the dynamic dilution system, the MFC should be properly calibrated for the matrix gas used. The SCD detector has the advantage of being selective towards molecules that contain at least one sulphur atom. It burns the sulphur compounds under a reducing atmosphere (with hydrogen). A chemiluminescent reaction between the combustion products and ozone follows, and the resulting emission is measured by a photomultiplier tube. PTR/MS is an online analytical method based on chemical ionisation of the analyte and gives a direct signal making it a time-efficient solution. The methods were validated according to a previously agreed protocol, which was based on ISO 21087 [16]. The validation parameters involved selectivity, the limits of detection and quantification, linearity of calibration, trueness and precision.

Gas chromatographs from two different manufacturers [BAM: Perkin Elmer®, VSL: Agilent Technologies /USA (GC) and Markes™/UK (TD)] equipped with SCDs from the same manufacturer (PAC L. P./NL) were used. In both cases, the complete flow path getting into contact with the target compounds was equipped with SilcoNert2000® coated material. Samples of amount fractions of up to 100 nmol/mol were either taken directly from the gas cylinder or from a dynamically dilution system onto the sorbent trap. The trap was specially designed for the sampling of sulphurs (proprietary multi-bed sorbent combinations from Markes™ and Antelia). Samples of amount fractions between 100 and 1000 nmol/mol were sampled via the GC’s sample loop (e.g. 250 µL) and directly injected into the GC/SCD system (bypassing the TD system).

An Ionicon 6000 X2 PTR-MS was used for the online analysis of sulphur impurities in hydrogen. The inlet of the Ionicon device was modified to enable analysis of hydrogen (and other gases, e.g. nitrogen or argon) from gas cylinders. A system of mass flow controllers is used to generate a controlled flow of 1 to 20 ml/min from the gas cylinder, which is further diluted with nitrogen to get a total flow of 200 ml/min. PTR-MS was operated in the H_3O^+ mode, which was suitable for all compounds but COS.

Selectivity

Analytical selectivity is the extent to which the method can be used to determine analytes in mixtures or matrices without interferences from other components of similar behaviour. The SCD detector is sensitive to components containing one or more sulphur atoms, therefore other sulphurs present in hydrogen could be interfering the analysis. The retention time during analysis of these interferents should be tested and the possible impact on the speciated sulphurs considered. Typically, the interferent should be tested at one amount fraction alone (identified through literature research) and in presence of a sulphur mixture at 4-10 nmol/mol. During the investigations with GC/SCD, one important possible interference to take into account is SO_2, since it overlaps with the COS peak, as shown in Figure 21. It is therefore important to check the GC carrier gas, the dilution gas for the preparation of the dynamic standards as well as the balance gas that was used for the preparation of the gravimetric standard in advance if possible.

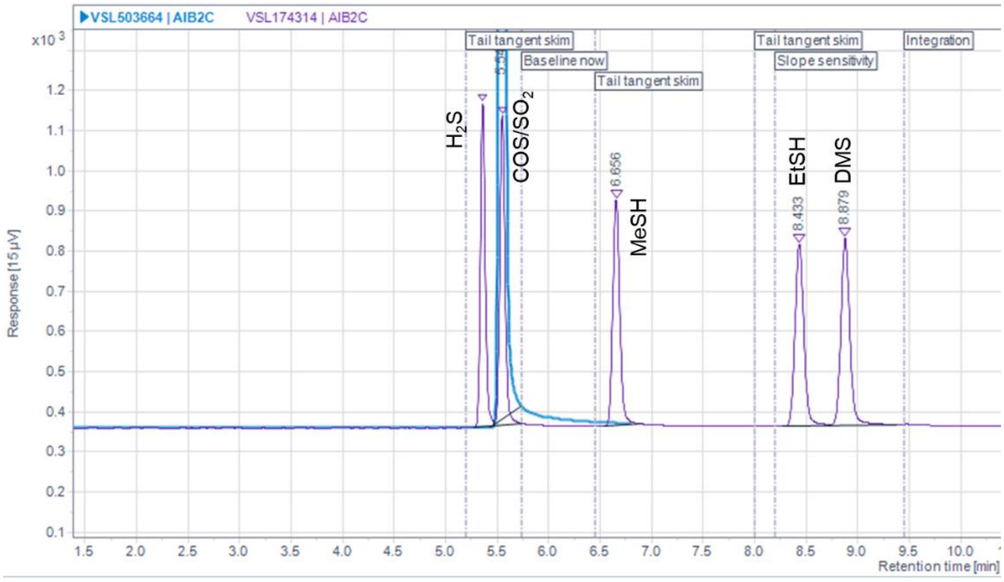


Figure 21. Overlay of two chromatograms showing peaks of some of the target compounds (purple) and the peak of an SO_2 analysis (blue).

In Figure 22, the chromatogram of the complete multi-component reference gas standard mixture is shown. Three peaks in the chromatogram can be assigned to artefacts/impurities of the pure sulphur substances that were used for the preparation (highlighted in red). They could be found in both independently prepared multi-component gas mixtures of BAM and VSL. It is assumed that these artefacts are dimethyl disulfide (DMDS), methyl ethyl disulfide (MEDS), and diethyl disulfide (DEDS). The pure substances used to produce the gas standards must therefore be of the highest possible purity. Here, these artefacts/impurities are not affecting the analysis because the target compounds are known. That is why particular attention must be paid in the case of samples of unknown composition.

It can be also assumed from the investigations that artefacts are formed catalytically on partially uncoated surfaces in the tubing, pressure reducers or valves. This could be observed when the dynamic dilution system was not used for a longer period. With increasing flushing time the peak size decreased again. The lines should therefore always be flushed with sample gas before measurement/calibration.

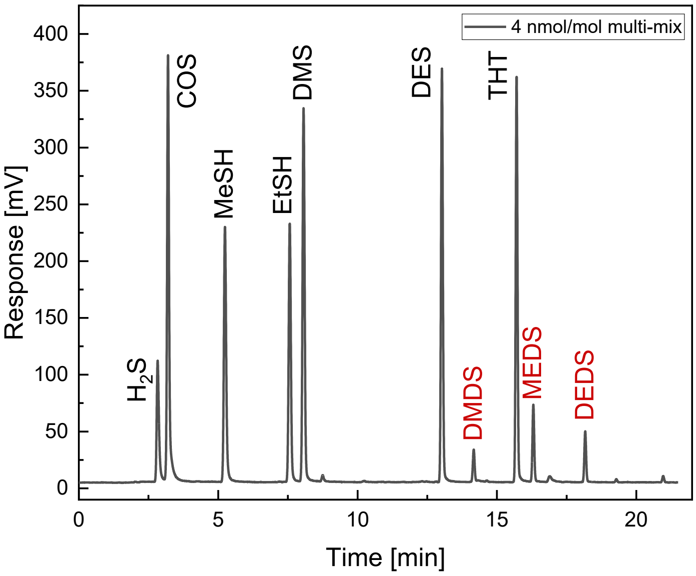


Figure 22. Chromatogram of 4 nmol/mol multi-mixture in argon. Artefacts/impurities are highlighted in red.

PTR/MS cannot separate DMS and EtSH because both compounds have the same molecular mass. Another problem is the formation of H_2S from EtSH due to the ionisation process. Therefore, the quantification of H_2S is falsified.

Matrix effect

This effect is relevant in case the calibration standards used are in a (partially) different matrix than the sample to be analysed. The effect could be seen in terms of response and/or retention time during analysis by TD-GC/SCD. During the sampling phase, to preconcentrate the sample into the trap (thermal desorber), the flow controller may be sensitive to the matrix (e.g., thermal mass flow controller). The GC carrier gas and the type of column stationary phase could also interact with the matrix and influence the response, shape of the peaks and retention time.

For investigating the matrix effect, the gas mixture in argon was diluted with different ratios of hydrogen or vice versa. No effect, e.g. in terms of a peak shift, was observed on both TD-GC/SCD systems. However, different use of matrix (hydrogen and argon) could be noted on direct measurement of sulphurs (bypassing the TD) and specifically in a shift of the retention time.

Working range and linearity

Target working range of the measurement method for the analysis of single sulphurs in hydrogen was set to 0.5-100 nmol/mol. The measurement at the lowest and highest fraction as well as at 4 nmol/mol and at intermediate fractions was demonstrated for each sulphur component. A six-point calibration over the target working range was analysed 4 times. The analysis of residuals according to ISO 6143 [17] has been used to get information on the goodness-of-fit of the calibrations.

Because of the linearity of the detector, a 1st order linear regression was expected to be used for the linearity tests. However, for the complete range, a quadratic function (2nd order) fits best with both investigated analytical systems. A function of 1st order could be obtained for the range 0.5-10 nmol/mol (4 points) indicating linearity of the detector in the lower amount fraction range which is the most relevant for the measurement of the hydrogen quality.

Limit of Detection (LoD) and Limit of Quantification (LoQ)

The calculation of the limit of detection (LoD) of the method is based on the analysis of samples after application of the entire measurement procedure (including sample preparation or preconcentration in case of TD-GC) and calculated using the same equation as for the test samples. The limit of quantification (LoQ) is the smallest amount of substance of the analyte in a sample that can be quantitatively determined under specified experimental conditions with a specified acceptable precision and accuracy.

Experimentally, the dynamically generated sulphur gas standard with the lowest amount fraction (0.5 nmol/mol) was measured at least 10 times (repeated measurements). Data treatment was carried out as described in ISO 21087. The following ranges depending on the compound were obtained:

	LoD (nmol/mol)	**LoQ (nmol/mol)**
BAM (TD-GC/SCD)	0.02–0.04	0.03–0.06
BAM (PTR/MS)	0.05–0.20	0.08–0.33
VSL (TD-GC/SCD)	0.01–0.03	0.02–0.05

Precision (repeatability and reproducibility)

Repeatability is a measure of result variability when a measurement is conducted by a single analyst using the same equipment over a short period. For this, repeated measurements of the 4-10 nmol/mol standards with at least 6 runs have been carried out. The measurement results have been checked for outliers so that at least 5 repeated measurement data could be used for the calculation.

Reproducibility measures the variability of results and has been carried out by measuring the same standards in the range 4-10 nmol/mol on three different days with at least one day between the measurement days. To prevent a possible drift of the detector, an external standard has been used as a corrective measure. Therefore, two concentrations have been measured repeatedly each time, and the reproducibility has been evaluated by calculating the ratio of the responses. For the evaluation of the repeatability and reproducibility of the measurement method, an analysis of variance (one-way ANOVA) in accordance with ISO 5725-2 [18] has been carried out.

With the TD-GC/SCD system at VSL, the repeatability ranged from 0.9 % to 1.8 % depending on the compound and the reproducibility from 1.8 % to 3.3 %. With BAM's system the values varied stronger, particularly for the more volatile compounds (H_2S, MeSH, EtSH: repeatability 3.1 %-4.2 %, reproducibility 5.6 %-6.5 %; DMS, DES, THT: repeatability 1.1 %-1.6 %, reproducibility 1.2 %-2.3 %). A reason was not obvious.

With PTR-MS the repeatability ranged from 1.4 %-2.7 % (BAM cylinder, Ar) and from 2.0-3.3 % (VSL cylinder, H_2), reproducibility ranged from 6.2 %-9.7 % (BAM cylinder, Ar) and from 5.3 %-9.1 % (VSL cylinder, H_2).

Trueness

The 'Trueness' of a measurement result is an expression of how close the mean value of a large number of measurements (generated by the procedure) is to a reference value. Trueness can be experimentally determined by repeated measurements of a reference material. The measure of trueness is typically quantitatively expressed as 'bias'. In this work, the assessment of accuracy is the bias between the dynamically diluted and gravimetrically prepared standards at 100 nmol/mol. The calculation was carried out following ISO 21087.

With BAM's dilution and analytical system, the deviations for all compounds were systematically below the reference value and ranged from -3 % to -12 %. VSL obtained values ranging from -0.2 % to +7.7 %.

3.1.1.4 Cross-validation between BAM and VSL reference gas standards

This part of work aimed to compare the gravimetric gas standards prepared at BAM and VSL. For this purpose, the gas mixtures have been divided after preparation and one part has been sent to the other partner for measurement.

The cross validation involved three parts:

1. Comparison of the high fraction gas mixtures at 1000 nmol/mol directly using GC/SCD (no thermal desorption)
2. Comparison of the 100 nmol/mol gas mixtures directly using GC/SCD and/or TD-GC/SCD

3. Dynamic dilution of the 100 nmol/mol and/or 1000 nmol/mol gas mixtures down to 4 nmol/mol and analysis by TD-GC/SCD.

In general, the differences between the analyses of the gas standards are within 5 %, with only a few exceptions at 100 nmol/mol and 4 nmol/mol level. This confirms the good agreement between both independently prepared primary reference gas mixtures, especially when taking the different matrices into account. The results also show the usability of argon as a balance gas for the preparation of gas standards. However, this statement can only be made here for the TD-GC/SCD analysis, as there are no matrix effects.

Different use of matrix (hydrogen and argon) could in VSL's case be noted on direct measurement of sulphurs (bypassing the TD) and specifically in a shift of the retention time.

As already mentioned above, matrix effects must be checked for the measurement principle used in each case.

Nevertheless, the use of different matrix gases posed a difficulty for the comparison at 4 nmol/mol level with BAM's TD-system. The thermal desorber is equipped with an MFC for sample dosing, which is calibrated to air by default, and which could not be calibrated to the relevant gases argon and hydrogen used in the standard gas mixtures. This led to the case that no comparable dosing was possible (identical sampling flow settings led to different sampling volumes of argon and hydrogen sample due to the different densities). This again underpins the importance of gas-specific calibration of the MFCs used.

3.1.2 Reference materials and analytical methods for the determination of ammonia in hydrogen

PTB has developed a laser spectroscopic method for ammonia, targeting the amount fraction range between 50 nmol/mol to 1000 nmol/mol. The method is based on Optical-feedback cavity enhanced absorption spectroscopy (OF-CEAS). The instrument has been metrologically characterized to achieve gas "calibration free" measurements and to be operated as an Optical Gas Standard (OGS). An OGS is a laser spectrometer that can provide gas species amount fraction results that are directly traceable to the international system of units (SI). The instrument has been tested in Nitrogen and Hydrogen matrices demonstration good results.

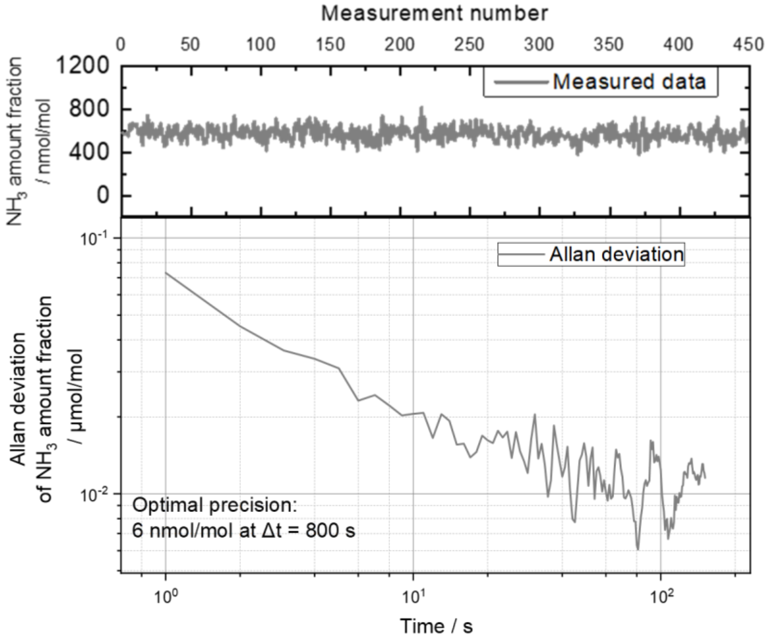


Figure 23: Top panel; OF-CEAS NH3 amount fraction results. Bottom panel; Allan deviation of the NH3 amount fraction results

Figure 23 (top panel) shows amount fraction results of NH_3 in H_2 at about 600 nmol/mol. Figure 23 (bottom panel) show an Allan deviation of the results in Figure 23 (top panel), depicting an optimal precision of 6 nmol/mol for the OF-CEAS instrument at a time resolution (Δ*t*) of 800 s. The relative combined uncertainty of the NH_3 amount fraction results delivered by the instrument currently stands at 5 %.

Also, the DTU's far-UV analyser was developed to be used with ammonia. The analyser validation in ammonia was carried out by using the NPL's gas standard mixture of methane and ammonia (CH_4+NH_3 (19.6 μmol/mol)). Values measured on NPL's gas standard by using the analyser are reported in Figure 24 where it is possible to observe the fast response time of the far-UV analyser in respect to NH_3.

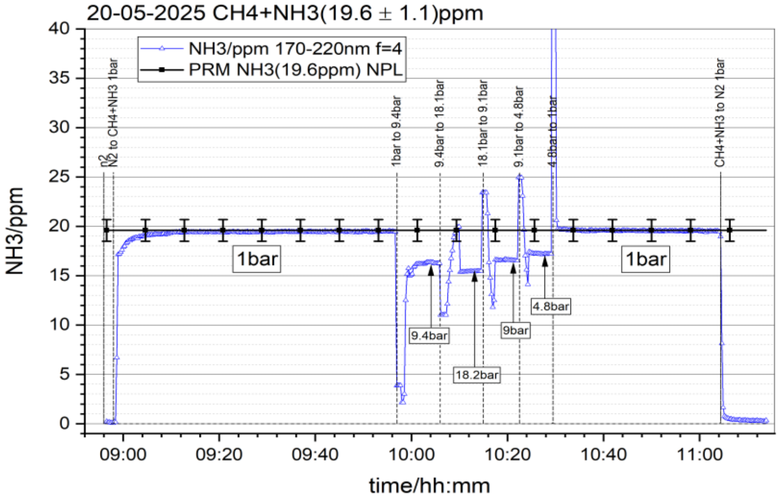


Figure 24: Validation of DTU's far-UV analyser with NPL's gas standard (CH_4+NH_3(19.6ppm)). The pressure in the analyser ranges from 1 bar to about 18 bar and back to 1 bar. Error bars show NH_3 concentration uncertainties at 1 bar.

DTU's far-UV analyser was also used to validate the VTT generator described in paragraph 2.1.2 in ammonia. Actually, it should have been used to validate the VTT trace gas generator in HCl too, but as HCl is a very reactive molecule and reacts with almost all materials in the generator, analyzer and interface line connecting the generator and the analyzer, the measured HCl value could have been lower than expected. Therefore, performance evaluation of the VTT generator was made on NH_3, which is less reactive gas than the HCl in terms of possible reactions in the generator-analyzer chain. As a carrier gas, methane with a purity of 99.998 % was used. Results of validation of the VTT generator are shown in Figure 25.

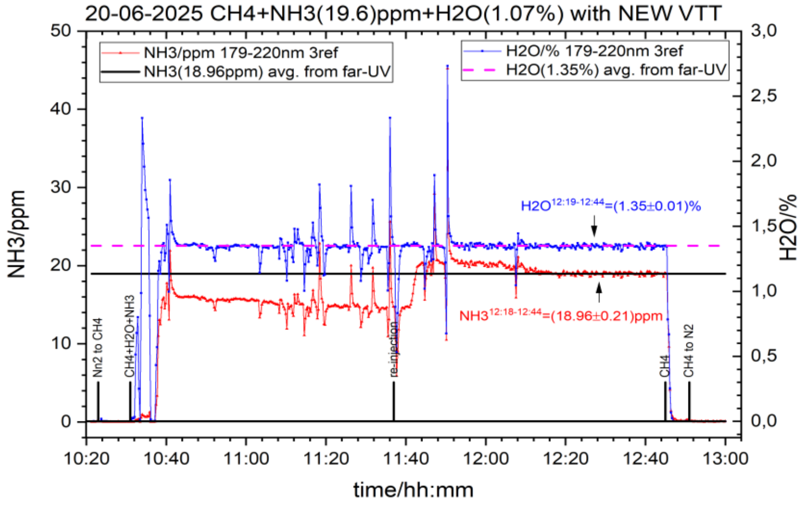


Figure 25: Measurements of NH3 in a CH4+NH3+H2O mixture using the DTU's far-UV analyser.

As it is possible to observe in Figure 25, while H_2O amount fraction reaches quite fast a steady state value of about 1.35 %, it takes around 90 min from the NH_4OH injection start (at 10:40) to reach a stable NH_3 amount fraction (from 12:10 and onwards). The achieved NH_3 amount fraction is about 18.96 µmol mol^{-1} which is a bit below the NH_3 set point of 19.6 µmol mol^{-1}. Ammonia as well as HCl are highly soluble molecules and very prompt to surface adsorption, so that using the VTT generator at high H_2O and low NH_3 concentrations and unheated interface/analyzer measurement section (even well below the H_2O dew point), a stable steady-state concentration is reached after a substantial waiting time.

3.2 Onsite measurements

Onsite measurements were carried out at the hydrogen industrial production facility of Nippon Gases in San Salvo. Both sampling and online measurements were performed. Online measurements entailed the amount of oxygen and water vapour in the hydrogen stream. At this site, online measurements of impurities in H_2 such as CO, H_2O and O_2 were also carried out using the far-UV based multi-component analyser developed by DTU.

The San Salvo hydrogen production plant is designed to produce ultra-high purity hydrogen from natural gas by SMR.

Figure 26. Nippon Gases steam methane reforming plant for the hydrogen production in San Salvo.

Hydrogen is generated through a catalytic reforming reaction of natural gas and steam at high temperature in the vertical cylindrical reformer furnace. Additional hydrogen is also produced via the reaction of carbon monoxide and steam in the "Shift Converter". Impurities such as carbon monoxide, methane, carbon dioxide, nitrogen, and water vapor are removed by a single absorption system, thus producing ultra-pure hydrogen. The fuel gas for the Reformer furnace is a combination of Vent Gas from the PSA and natural gas supplied by the Italian provider. The steam required for the process is generated by recovering excess heat at various points in the hydrogen production plant. The produced hydrogen is purified through the PSA system and sent to the distribution network (pipelines), as well as to storage and backup tanks. From the tanks, the hydrogen is drawn by two compressors and compressed to 200 bar into mobile containers. The plant is completed by the analysis section, which ensures that the product meets quality specifications and purity levels.

Similar to the experimental activity carried out at the Torino Airport, site information and sampling location were collected between NPL, INRIM, DTU and Nippon Gases and suitable sampling points at the tank line and pipeline were selected to evaluate the gas quality at the hydrogen distribution point.

Impedance-based humidity sensors selected by INRIM, oxygen sensor selected by NPL and the multi-compound analyser developed by DTU were used to monitor the hydrogen gas quality from the very same sampling point exploited by the NPL's sampling kit. Following the lesson learnt in the first test rig at Turin Airport, it was decided to run a separate sampling line for humidity measurements. Of course, such an independent branch line was derived from the common hydrogen pipeline where the NPL sampling systems were connected.
Figures 27 and 28 illustrate the setups from INRIM humidity sensor and DTU multi-compound analyser installed at Nippon Gases facility. The most likely impurities in hydrogen from this site were identified to be water, oxygen, nitrogen, ammonia and total sulphur. The gas lines were monitored over three days.

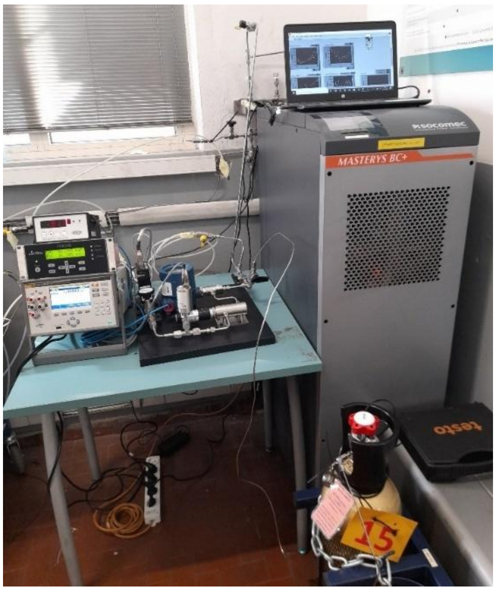


Figure 27. INRIM humidity measurement setup at Nippon Gases.

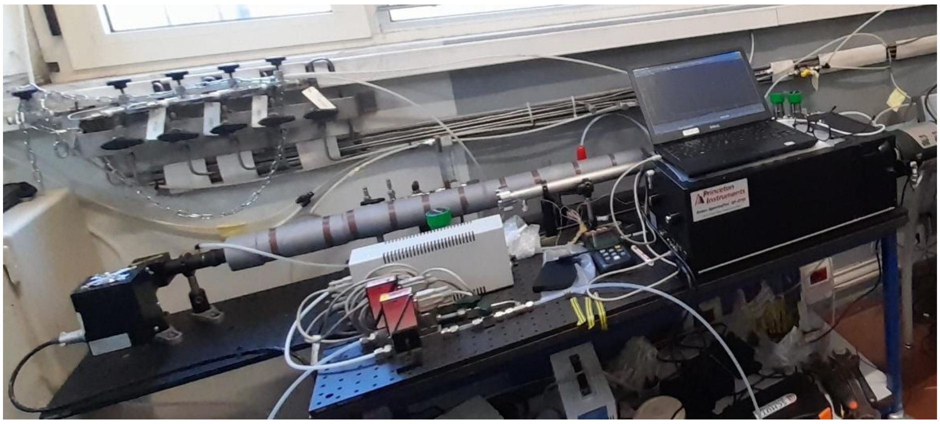


Figure 28. DTU multi-compound analyser setup at Nippon Gases.

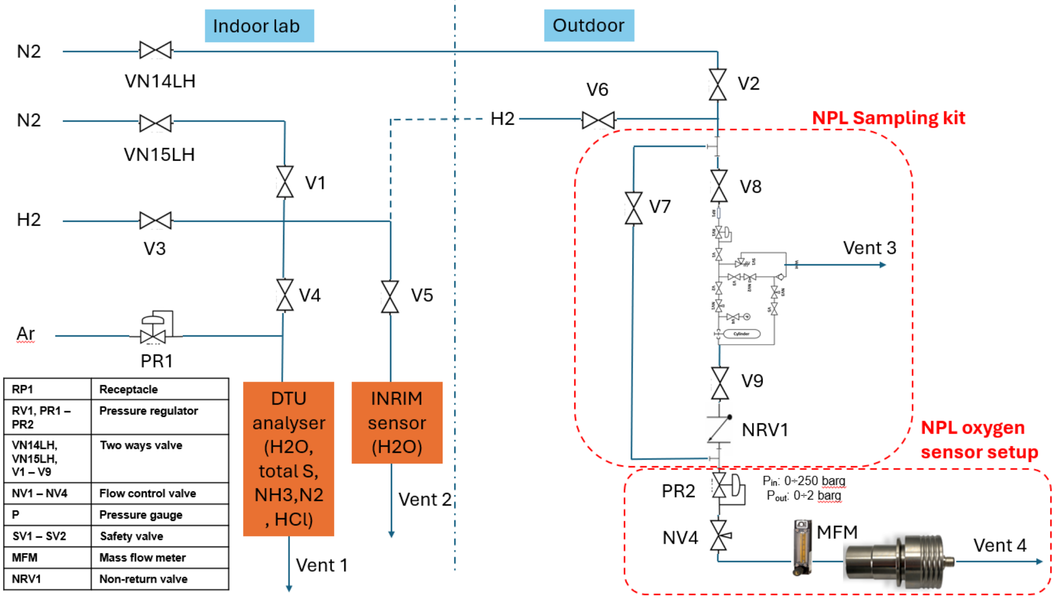
3.2.1 Sampling procedure

Hydrogen gas sampling was successfully conducted by NPL at Nippon Gases (San Salvo, IT). The hydrogen is produced using steam methane reforming reaction (SMR) and distributed to local customers using a dedicated pipeline. Two distinct sampling points were identified on this network: the hydrogen production by

SMR which was sampled from the storage tank and the distribution of hydrogen through pipeline with a sampling point directly in the pipeline between Nippon Gases and their customers.

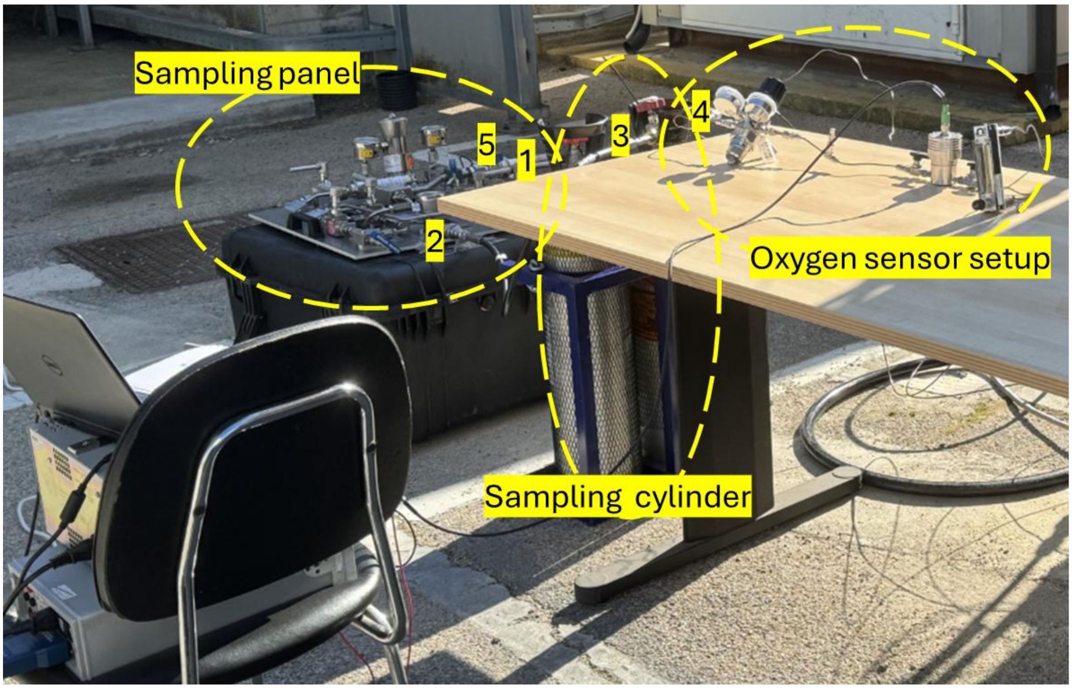
The area for sampling system was identified with site operators considering risk assessment using results of ATEX evaluation and requirement of the portable vent stack. The sampling was realised using NPL DirSam sampling kit as described in section 2.2.1. Ten litres aluminium Luxfer SGS™ with double-ended DIN 477 no. 1 valve were selected as sampling cylinders. They were cleaned, prepared and evacuated at least 12 hours to reach less than 1 × 10^{-6} mbar according to NPL procedure at NPL prior to sampling. Pressure was around 16 bar for both sampling points. However, the hydrogen gas was circulated to 3 outlets for several instrument connections, resulting in 8-10 bar pressure for purging the system. The sampling kit was purged 55 times, and the cylinder was purged for 11 times. In total, about 100 g hydrogen was used during the purging process and it is much less than the required amount (500 g hydrogen) for purging the sampling system.

Figure 29 illustrates the setups from NPL sampling kit and oxygen sensor at Nippon Gases. The inlet of sampling cylinder is connected to sampling kit while the outlet is connected to the oxygen sensor setup.



RP1	Receptacle
RV1, PR1 – PR2	Pressure regulator
VN14LH, VN15LH, V1 – V9	Two ways valve
NV1 – NV4	Flow control valve
P	Pressure gauge
SV1 – SV2	Safety valve
MFM	Mass flow meter
NRV1	Non-return valve

(a)



(b)

Figure 29. (a) Schematic diagram and (b) photo of NPL sampling kit and oxygen sensor setup at Nippon Gases (1: sampling inlet, 2: outlet connection to cylinder, 3: sampling cylinder inlet, 4: sampling cylinder outlet, 5: vent line of sampling kit).

Two samples (D923901 and D923900) were collected from pipeline sampling point. Two samples (D819918 and D819919) were collected from storage tank sampling point representing the SMR production.

The transport of the pressurised hydrogen gas sample was realised using an authorised dangerous goods transport company (TheCourierCompany, UK) following appropriate packaging and labelling by NPL trained staff. The safe transportation of flammable and pressurised dangerous goods should be done according to local and international regulations to ensure the safety of the samples, human and environment between sampling site and analytical laboratory location.

The four samples arrived at the NPL in an acceptable condition. The pressure in the samples was approximately 10-12 barg on arrival.

The offline analysis according to ISO 14687 excluding HCl and Cl_2 was conducted at NPL's hydrogen purity laboratory. The detailed analytical methods can be found in Annex 1. Laboratory analyses were performed using ISO-17025 accredited NPL internal methods for the measurement of N_2, O_2, Ar, CO, CO_2, CH_4, total non-methane hydrocarbons, total sulphur and H_2O.

3.2.1.1 Offline measurement results at NPL

NPL offline measurements are presented in Table 13 with the analytical instrument used and results of the samples from pipeline (D923901 and D923900) and the samples from SMR (D819918 and D819919) at Nippon Gases site (San Salvo). The results are presented with expanded uncertainty (*k*=2).

Table 13. Offline measurement results of samples from hydrogen distribution at Nippon Gases.

Compound	**Pipeline sample 1 (D923901)**	**Pipeline sample 2 (D923900)**	**SMR sample 1 (D819918)**	**SMR sample 2 (D819919)**	**ISO 14687:2025 Grade D**

	Measured amount fraction and uncertainty (*k* = 2) [µmol/mol]				**Maximum amount fraction [µmol/mol]**
Total non methane hydrocarbons	<0.021	<0.021	<0.021	<0.021	2
CH_4	<0.006	<0.006	<0.006	<0.006	100
CO_2	0.0254 ± 0.0027	0.0308 ± 0.0033	<0.008	<0.008	2
CO	<0.009	<0.009	<0.009	<0.009	0.2
He	101 ± 6	96.8 ± 4.9	100 ± 6	100 ± 6	300
H_2O	44.9 ± 2.7	21.7 ± 1.3	13.4 ± 0.8	7.57 ± 0.45	5
NH_3	< 0.005	< 0.005	< 0.005	< 0.005	0.1
HCOOH	0.0084 ± 0.0020	0.0084 ± 0.0021	<0.008	<0.008	0.2
HCHO	< 0.010	< 0.010	< 0.010	< 0.010	0.2
Total sulphur compounds	<0.0007	<0.0007	<0.0007	<0.0007	0.004
N_2	1.63 ± 0.09	3.32 ± 0.18	0.40 ± 0.08	2.20 ± 0.12	300
Ar	0.169 ± 0.017	0.159 ± 0.020	0.163 ± 0.018	0.166 ± 0.017	300
O_2	0.451 ± 0.040	0.181 ± 0.042	0.185 ± 0.042	0.173 ± 0.042	5
Total halogenated compounds	<0.017	<0.018	<0.025	<0.019	0.05

3.2.1.2 Results comparison with ISO 14687:2025 Grade D

The hydrogen produced from SMR and distributed by dedicated pipeline was used in industrial processes and was defined under technical specification between producer and end user. The actual compliance of the hydrogen produced and distributed from Nippon Gases with ISO 14687:2025 grade D was not considered critical to this study. In Table 13, it shows the levels of key contaminants in the hydrogen fuel samples were mostly consistent with the stringent limits set forth by ISO 14687:2025 Grade D except water. Similar to section 2.2.1.3, the NPL DirSam purging procedure was not completed according to requirement due to time and pressure available. Insufficient purges affected significantly the water measurement with decreasing amount fraction in function of the sampling order.

3.2.1.3 Offline measurement results at BAM

BAM analysed the samples D923901 and D819918 using the TD-GC/SCD method. From each cylinder two different volumes (0.6 and 1.2 L) were sampled. The analyses were carried out in duplicate. The chromatograms are shown in Figure 30.

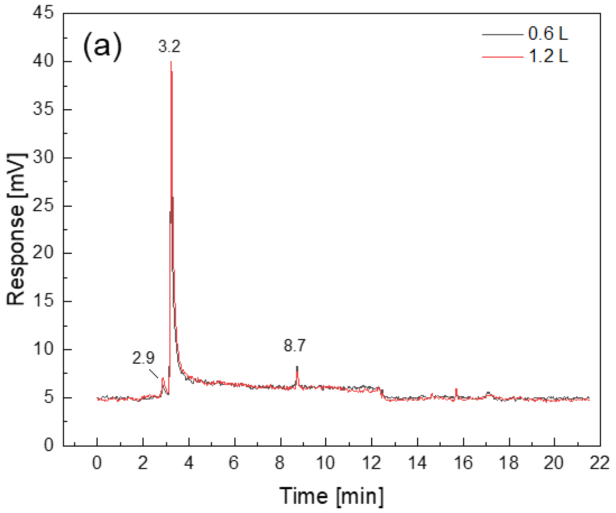
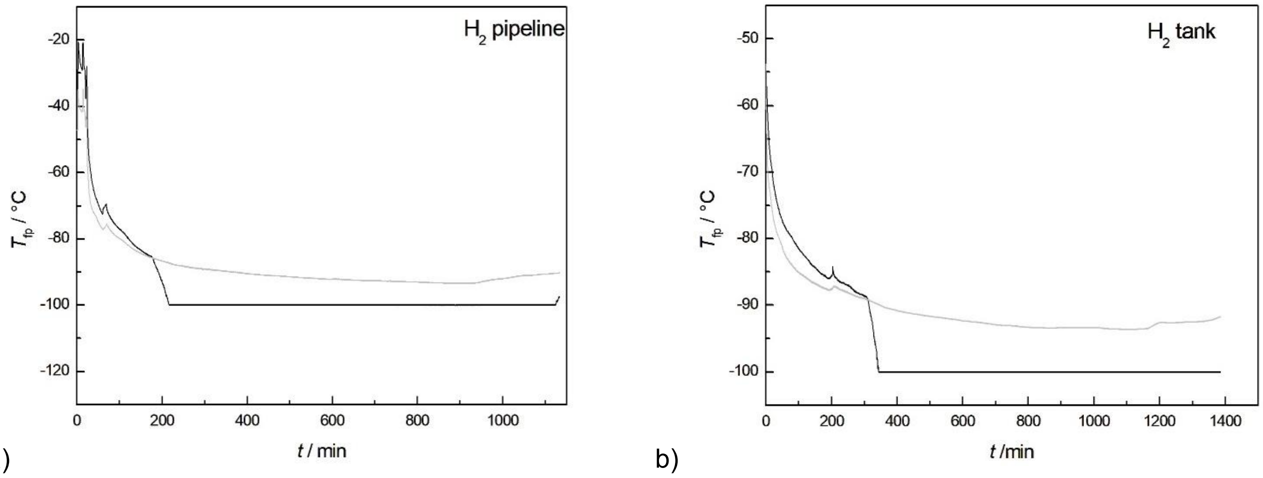


Figure 30. Chromatograms of the analyses of samples D923901 (a) and D 819918 (b) using TD-GC/SCD. The overlays of the sampling volumes of 0.6 and 1.2 L are shown.

Three significant peaks were detected. Due to their proportionality at the different sampling volumes, the peaks at 2.9 and 8.7 minutes are very likely blanks that cannot be assigned to the sample. The peak at 3.2 minutes is a known system blank that unfortunately cannot be eliminated. It retains at the retention time of COS and SO_2. However, since the peak area usually varies within this range, the presence of these substances in the sample is unlikely. It can therefore be concluded that both samples from pipeline and storage tank are most probably free of sulphurous compounds.

3.2.2 Online humidity measurement

At the Nippon Gases facility in San Salvo, humidity measurements were taken by connecting the humidity measurement setup and sensors to an independent branch line from the main hydrogen pipeline, that was the same line were the other sampling systems were connected. This enabled the amount of water vapour in the gas from both the pipeline and the storage tank to be continuously recorded over two days without any interference while the cylinders were being filled.
Figures 31 shows the frost point temperature trend in hydrogen when (a) the gas comes from the pipeline and (b) from the storage tank.



a) b)

Figure 31. Measurement of hydrogen frost point temperature at Nippon Gases in hydrogen coming from a) pipeline and b) tank.

▬ Michell sensor ▬ SHAW sensor

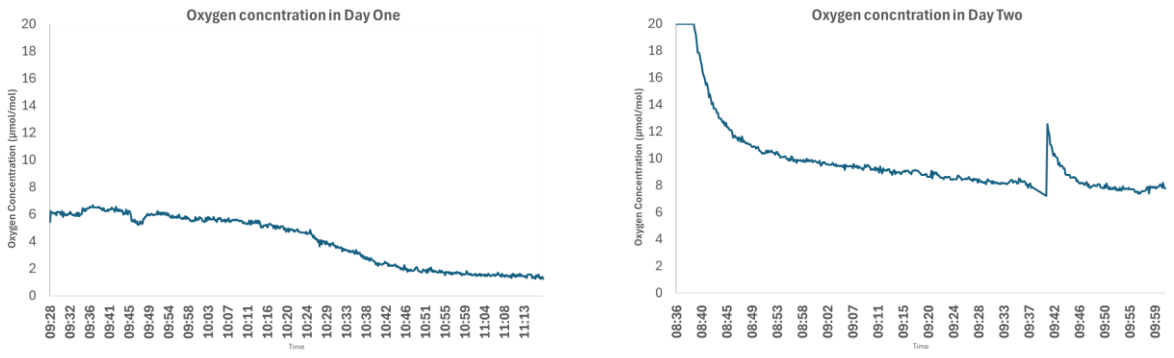
As shown in Figure 31, a continuous real-time online monitoring revealed that, after an initial transient, the amount of water in both the pipeline gas and the storage tank was well below the detection limit of both humidity sensors. Consequently, it can only be concluded that the water vapour amount fraction in the hydrogen lines was below 50 nmol·mol^{-1} (parts per billion). This figure has been calculated from the measured line pressure (1382 ± 5) mbar and the measured frost point temperature of about -100 °C (i.e., the lower limit of the sensor measurement range). This is a case where instrumentation with a higher sensitivity than capacitive sensors must be used (such as spectroscopic analysers, QCM or chilled-mirror hygrometer).

3.2.3 Online oxygen measurement

The calibration of the sensor was done on Nippon gases site. The calibration was done on the day of installation, using the exact same procedure and set up described in section 2.2.3.

3.2.3.1 Online measurement results

The oxygen concentration over time for two pipeline samples highlights the performance of the oxygen sensor for its purging and stabilization. As illustrated in Figure 32, the sensor readings for both days are initially high and unstable, reflecting the need to purge the sensor line upon its first installation. The concentration gradually decreases until it reaches a stable, low level. this purging, the readings remain consistently stable with no spikes detected in day one and a short-lived spike in day 2, indicating effective process control. Once the sensor line is properly conditioned and purged, the oxygen sensor delivers continuous, reliable measurements that accurately represent true process conditions. As reported in Report A.1.3.4, this stable behaviour, combined with its validated performance, demonstrates the advantages of online monitoring over offline methods by enabling immediate observation of transient fluctuations and robust, real-time process control.



(a) (b)

Figure 32. Oxygen sensor readings for (a) Day One and (b) Day 2 during pipeline purging and stabilization.

3.2.3.2 Comparison of online and offline laboratory analysis

The oxygen sensor measurements for the four samples are presented in Table 14. A noticeable variation between samples was observed with results ranging from (1.76 ± 0.36) µmol/mol, (1.33 ± 0.34) µmol/mol, (9.31 ± 0.67) µmol/mol, to (4.95 ± 0.38) µmol/mol, particularly the third sample, which recorded a significantly higher concentration. The online results were therefore consistently higher than the offline measurements as offline laboratory analysis reported all results below 1 µmol/mol (see Table 14).

Table 14. Online measurement results of oxygen amount fractions in hydrogen samples from Nippon Gases.

	Online sensor measured amount fraction (µmol/mol) and uncertainty (*k*=2)	NPL analysis from sampling cylinder - measured amount

		fraction (µmol/mol) and uncertainty (*k*=2)
Pipeline sample 1 (D923901)	1.76 ± 0.36	0.451 ± 0.040
Pipeline sample 2 (D923900)	1.33 ± 0.34	0.181 ± 0.042
SMR sample 1 (D819918)	9.31 ± 0.67	0.185 ± 0.042
SMR sample 2 (D819919)	4.95 ± 0.67	0.173 ± 0.042

This discrepancy can partly be explained by the following points:

- the detection capability of the online sensor: as established in MET4H2 A1.3.4 (in accordance with Test Protocol A1.3.2), its limit of quantification (LOQ) was determined to be 1.1 µmol/mol, and three of the offline results fell below this threshold. Therefore, the results close to the limit of quantification may not be so accurate in real life condition compared to laboratory validation.
- Possible decay of oxygen in offline sample due to long delay between sampling and analysis: the cylinders were analysed in the lab ten weeks after sampling. During this period oxygen present in hydrogen can decay, leading to the formation of water, which reduces the measured oxygen content [19]. This interpretation is supported by the elevated concentrations observed in the offline laboratory analysis compared with the online measurements performed by INRIM.
- Leak in the gas line supplying the online sensor: for the third sample specifically, a leak was detected in the downstream section of the sampling kit supplying hydrogen to the oxygen sensor. Although it was fixed once realised, the leak affected the stabilization period, preventing the sensor from reaching equilibrium before offline sampling, and likely accounts for the anomalously high oxygen concentration recorded in the online measurement. This highlights the importance of ensuring full stabilization time before performing offline validation.

Overall, the discrepancy between online and offline results highlights the importance of continues online monitoring, as offline analysis represents only a snapshot of the process in time and may not fully representative on evolution of the contaminants overtime. At the same time, offline analysis and online analysis are sensible to compounds evolution over time in cylinder or leak in the gas line supplying the sensor, it is critical to ensure timeline and suitable leak detection are applied not only for safety reason but to keep the sample integrity and representativity.

3.2.4 Online far-UV analyser measurement

The far-UV analyser used in the San Salvo campaign was essentially the same as for the laboratory measurements with the gas standards. The analyser consists of a far-UV broad band light source, far-UV full spectral range spectrometer and around 100 cm gas cell with pressure regulators. The analyser has two gas inlets: one for a reference gas e.g. Ar and one for the process gas. Argon (5.0) gas was used for optical components purge (spectrometer, light source, optics). The analyser is connected to a gas intake point with a variable length Ø3 mm stainless steel tubing interface. All analyser and interface elements and the measurement volume (gas cell) are coated by SilcoNert2000 coatings to ensure minimum surface effects onto the measurements. Working pressure of the analyser is up to 40 bar which is defined by recommendations from Swagelok. Hydrogen flow through the analyser is variable and typically is between 1 and 10 l/min. The analyser is leak-proofed and can be used for 24/7 in-flow or static (no-flow) measurements.
The far-UV measurements in San Salvo have shown that the H_2 gas was very clean, similar to H_2 (6.0) specifications. The major impurities found in the gas from all sampling locations are H_2O, O_2, CO_2, CH_4 and CO. Water contents varied from one sampling point to another, and the measured H_2O concentrations was typically biased by trace H_2O in the gas panel (analyser connection point) and in overall piping system of the plant.
It was found variations in CO (< 1 µmol/mol) and O_2 (< 5 µmol/mol) amount fractions. CO_2 and CH_4 was indirectly measured in the analyser's static operation mode. Further data analysis is still ongoing.

3.2.5 Summary of contaminants for hydrogen distributed by pipeline

In Table 15, the key contaminants over ISO 14687:2025 grade D threshold based on the measurement results from dedicated pipeline were compared with the findings in report A3.4.1. Their amount fractions were all consistent with the stringent limits set forth by ISO 14687:2025 Grade D. Although the offline measurement of water is over the ISO 14687:2025 Grade D threshold, it was likely due to the insufficient purging prior to sampling as explained in section 3.2.1.2. Thus, the online measurement results of water amount fraction from INRIM and DTU are considered (<50 nmol·mol^{-1}), which is under the threshold set forth by ISO 14687:2025 Grade D.

Table 15. Summary of contaminants for hydrogen distributed using dedicated pipeline.

Probability of impurity over ISO 14687:2025 grade D threshold	Impurity from literature report	Impurity from measurement results
Potentially	N_2, O_2, H_2O, halogenated compounds	-
Very unlikely	Ar, CO_2, CO, CH_4, He, NH_3, HCHO, HCOOH, total sulphur compounds, total non-methane hydrocarbon	N_2, CH_4, CO, CO_2, H_2O, total non-methane hydrocarbons, O_2, Total sulphur compounds, NH_3, HCHO, HCOOH, halogenated compounds, Ar, He, H_2O

It should be noted that nitrogen is related to the purging of infrastructure after maintenance. In this study, no measurement was done close to a maintenance event. Therefore, nitrogen is considered relevant as potential contaminant.

3.2.6 Summary of contaminants for hydrogen produced by SMR

In Table 16, the key contaminants over ISO 14687:2025 grade D threshold based on the measurement results from SMR were compared with the findings in report A3.4.1. Their amount fractions were all consistent with the stringent limits set forth by ISO 14687:2025 Grade D. Although the offline measurement of water is over the threshold, it was likely due to the insufficient purging prior to sampling as explained in section 3.2.1.2. Thus, the online measurement results of water amount fraction from INRIM and DTU are considered (<50 nmol·mol^{-1}), which is under the threshold set forth by ISO 14687:2025 Grade D. For oxygen amount fraction, the online measurement showed higher results potentially link to a leak on the gas path to the sensor, therefore the offline measurements were considered more reliable and used for Table 16 assessment of probability of presence.

Table 16. Summary of contaminants for hydrogen produced using SMR method.

Probability of impurity over ISO 14687:2025 grade D threshold	Impurity based on process knowledge from the pilot plant experts	Impurity from measurement results
Potentially	N_2, CH_4, CO, H_2O, total non-methane hydrocarbons, He, O_2	-
Very unlikely	CO_2, Total sulphur compounds, NH_3, HCHO, HCOOH, halogenated compounds	N_2, CH_4, CO, CO_2, H_2O, total non-methane hydrocarbons, O_2, Total sulphur compounds, NH_3, HCHO, HCOOH, halogenated compounds, Ar, He, H_2O

It should be noted that nitrogen is related to the purging of infrastructure after maintenance. In this study, no measurement was done close to a maintenance event. Therefore, nitrogen is considered relevant as potential contaminant.

4 Guidelines and recommendations

4.1 Reference materials and analytical methods for the determination of sulphur impurities in hydrogen – Summary of recommendations for potential users.

a. Preparation of gravimetric and dynamic primary reference gas standards

- All pure substances and matrix/balance gases must be of the highest available purity.
- Hydrogen and argon can both be used as matrix gases for the preparation of gravimetric gas standards. Other gases might be suitable as well but were not tested in this project. However, it must be ensured that no matrix effects (peak shift, change in sensitivity, etc.) are to be expected with the analytical method used. The use of argon can be beneficial since fewer dilution steps are required during the standards preparation due to the higher density of argon.
- Inner surfaces of gas cylinders (aluminium, stainless steel) should be treated/coated to avoid adsorption of molecules on the cylinder wall as well as catalytically induced chemical reactions with the cylinder material.
- For the same reason, all tubing and connectors used in the dynamic dilution system should be made from stainless steel and passivated, e.g. with SilcoNert2000® coating from SilcoTek®. Additionally, all parts of the MFC that come into contact with the sample should also be coated if possible. Before analysis/calibration it is recommended to thoroughly flush all sample lines.
- The used MFC must be calibrated to the respective matrix gases.

b. Analysis

- For the analysis of sulphur impurities in hydrogen gas, a sulphur chemiluminescence detector (SCD) is recommended as it is selective towards molecules that contain at least one sulphur atom.
- All tubing that comes into contact with the sulphur sample should be made from stainless steel and coated as already described in 3.3.1a.
- GC carrier gas and the dilution gas for the preparation of the dynamic standards must be checked in advance for possible interferences. This is of particular importance when the sample is of unknown composition.
- If the Thermal desorber is equipped with a MFC, this must be calibrated to the respective matrix gases and possible mix.

4.2 Sampling procedure and online hydrogen quality monitoring – Summary of recommendations for potential users.

a. Sampling procedure

- Maintain good communication with site operators to plan the sampling operation including location for sampling system and hydrogen vent (height and direction) to allow hydrogen safe release
- the transport of sampling cylinders should be agreed with site operators, i.e. collection location, time and responsible person. If there is a delay in transport collection, then accessible storage location for sampling cylinders must be agreed upon with site operators.
- Connect the sampling point to the sampling kit last when installing the sampling kit.
- Check for leaks step by step by opening one valve at a time

- The sampling kit and its procedure should be validated, documented and properly applied.
- Trained staff to handle sample labelling and dangerous goods transport
- The effect of trapped air due to insufficient purging should be taken into account when calculating the final concentration in the sample.

b. Online humidity measurement

- Minimise the length of the sampling line to humidity sensor.
- Carefully check the absence of any leaks from any point upstream or downstream the humidity sampling system.
- Wait a sufficient time for the humidity sensors to reach a stable, consistent, reading (i.e., several hours for sub-ppm water vapour measurement).
- Install humidity sensors on an independent sampling line; if the sensors are placed after the sampling cylinder they are likely measuring the purging level of the sampling cylinder instead of the water vapour in the gas line.

5 Recommendations for improvements of ISO19880-8 and ISO 21087

5.1 Recommendations to ISO 19880-8

The online and offline measurement results are compared with the impurities potentially present in hydrogen produced by alkaline electrolysis and SMR reported in Annex C, ISO 19880-8:2024. Table 17 illustrates that hydrogen may contain impurities exceeding the threshold, including oxygen and water, which are present in hydrogen produced by alkaline electrolysis. This result is consistent with the example shown in ISO19880-8:2024. Table 17 also shows that no impurities were detected over the threshold in the hydrogen samples produced by SMR in Nippon Gases, although nitrogen, methane, carbon monoxide and helium were listed in the example from ISO19880-8:2024.

Table 17. Comparison of impurities for hydrogen produced by alkaline electrolysis and SMR with ISO 19880-8:2024.

Impurities potentially present in H2 produced by alkaline electrolysis	**Probability of impurity over ISO 14687 grade D threshold**	**Results from ISO 19880-8:2024**	**Results from this study**
	Possible	O_2, H_2O	O_2
	Improbable	CO_2, CO, CH_4, He, N_2, Ar, total sulphur compounds, NH_3, total non-methane hydrocarbons, HCHO, halogenated compounds	H_2O, CO_2, CO, CH_4, He, N_2, Ar, total sulphur compounds, NH_3, total non-methane hydrocarbons, HCHO, halogenated compounds
Impurities potentially present in H2 produced by SMR	**Probability of impurity over threshold**	**Rsults from ISO 19880-8:2024**	**Results from this study**
	Possible	N_2, CH_4, CO, He	-
	Improbable	Ar, O_2, CO_2, H_2O, total sulphur compounds, NH_3, total non-methane hydrocarbon, halogenated compounds, HCHO	N_2, CH_4, CO, CO_2, H_2O, total non-methane hydrocarbons, O_2, Total sulphur compounds, NH_3, HCHO, HCOOH, halogenated compounds, Ar, He, H_2O

It is recommended that:

- water and oxygen are the impurities that potentially over the threshold when hydrogen is produced by alkaline electrolysis. Installation of online devices to monitor water and oxygen level in hydrogen gas sourced from alkaline electrolysers is suggested to hydrogen refuelling stations.
- Validate the performance of the sensors and online analysers according to procedures outlined in A.1.3.2 protocol prior to their deployment on site to confirm their performance, accuracy and response time under controlled environment
- Conduct scheduled calibrations for sensors and online analysers against known standards to ensure accuracy, especially before critical measurements or any process changes.

5.2 Recommendations to ISO 21087

For on-site sampling, it is recommended to:

- maintain good communication with site operators to understand sampling procedure, the pressure from the sampling points, available amount of hydrogen for purging and sampling collection and define the length of operation. Otherwise, the sampling activity may need to be suspended if there is inadequate hydrogen available to meet purging requirements or to obtain samples for offline measurement.

In addition to the mentioned indication of the minimum purging requirement of the sampling device, the sampling operators should also determine whether the sampling kit is suitable for collecting hydrogen samples at given pressure range to allow sufficient purging can be done to remove moisture and air out of the sampling kit and cylinder and ensure operational safety. If necessary, the components of the sampling kit need to be modified appropriately to enable the sampling kit is fit for purpose. The modification must be evaluated to ensure they meet safety usage requirements.

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7 Annex 1 – Analytical methods used for the analysis of impurities in hydrogen at NPL

The analyses were performed by the NPL’s hydrogen laboratory using NPL internal methods that were ISO-17025-accredited for N_2, O_2, Ar, CO, CO_2, CH_4, total non-methane hydrocarbons, total sulphur and H_2O. All the listed analytical instruments in Table 18 and Table 19 were calibrated using the NPL PRMs in hydrogen matrix gas. The NPL gravimetric gas standards (NPL, Teddington, UK) and/or dynamic standards were used to generate calibration curves covering both the EN 17124 and the ISO 14687 amount fraction thresholds and the measured values from the samples. The dynamic standards were prepared by dilution of the NPL PRM with high-purity hydrogen (BIP+ quality, Air Products, Walton-on-Thames, UK) using calibrated mass flow controller systems (Bronkhorst, Veenendaal, the Netherlands). All the data were examined so that no results were discarded without a valid technical reason. The calibration curve, results of the analysis, and associated uncertainties were determined using the NPL software XLGENLINE version 2 [Reference A]. An expanded uncertainty using a *k* value of 2 was used for all the results. In some cases, a more conservative uncertainty was derived from an analytical expert’s knowledge.

Table 18. Analytical instruments used for the analysis of impurities in hydrogen and the limits of detection for samples from alkaline electrolyser at Turin airport.

Compound	Analytical instrument	Limit of detection [µmol/mol]

Total non-methane hydrocarbons	Gas chromatography with flame ionization detector and methaniser	0.020
CH_4		0.005
CO_2		0.008
He	Micro gas chromatography with thermal conductivity detector	3.5
H_2O	Optical feedback cavity-enhanced absorption spectroscopy	0.024
NH_3		0.010
HCOOH		0.008
HCHO		0.010
Total sulphur compounds	Gas chromatography with sulphur chemiluminescence detector	0.0010
CO	Gas chromatography with pulsed discharge helium ionization detector	0.015
N_2		0.23
Ar		0.1
O_2		0.15
Total halogenated compounds	Thermal desorption gas chromatography with mass spectrometry and flame ionization detector	0.016

Table 19. Analytical instruments used for the analysis of impurities in hydrogen and the limits of detection for samples from hydrogen distribution at Nippon Gases.

Compound	**Analytical instrument**	**Limit of detection [μmol/mol]**
Total non methane hydrocarbons	Gas chromatography with flame ionization detector and methaniser	0.021
CH_4		0.006
CO_2		0.008
CO		0.009
He	Micro gas chromatography with thermal conductivity detector	4.3
H_2O	Cavity ring-down spectroscopy	0.021

NH_3	Optical feedback cavity-enhanced absorption spectroscopy	0.005
HCOOH		0.008
HCHO		0.010
Total sulphur compounds	Gas chromatography with sulphur chemiluminescence detector	0.007
N_2	Gas chromatography with pulsed discharge helium ionization detector	0.14
Ar		0.12
O_2		0.17
Total halogenated compounds	Thermal desorption gas chromatography with mass spectrometry and flame ionization detector	0.019

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