

Development of a Cross-Contamination-Free Hydrogen Sampling Methodology and Analysis of Contaminants for Hydrogen Refueling Stations

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Abstract

Hydrogen used in proton exchange membrane-based fuel cell applications is subject to very high quality requirements. While the influences of contaminations in hydrogen on long-term stability have been intensively studied, the purity of hydrogen for mobile applications provided at hydrogen refueling stations (HRS) is rarely analyzed. Hence, in this study, we present sampling of hydrogen at HRS with a specially designed mobile tank for up to 70 MPa. These samples are precisely analyzed with a sophisticated ion molecule reaction mass spectrometer (IMR-MS), able to determine concentrations of contaminants down to the ppb-level. Sampling and analysis of hydrogen at an HRS supplied by electrolysis revealed a high purity, but likewise considerable contaminations above the threshold of the international standard ISO 14687:2019. In this study, a state-of-the-art analysis coupled with a developed methodology for fuel cell electric vehicle-independent sampling of hydrogen with a mobile tank system is demonstrated and applied for comprehensive studies of hydrogen purity.

Keywords

Hydrogen, Refueling Station, Sampling Methodology, Purity Analysis, Contamination, Quality

1. Introduction

Establishing sustainable and cost-optimized options for the energy supply is a key task during the energy transition process from a fossil to a renewable energy generation of the upcoming years. Particularly in the transportation sector, locally emission-free vehicles are gaining more relevance in urban areas [1, 2]. In addition to battery electric vehicles (BEV), fuel cell electric vehicles (FCEV) powered by hydrogen offer the option for zero emission driving with fast refueling capability even for long range travels [3]. The needed hydrogen can be synthesized by a variety of methods; up to now the majority of hydrogen is produced by steam reforming of natural gas [4]. For emission-free fuel cell mobility, however, the production of hydrogen e.g. via electrolysis plants using renewable energy sources is required [3]. For the provision of both, seasonal and inter-seasonal energy storage of green hydrogen, salt caverns can be used to store relevant amounts of energy and to address alternative energy pathways for sector integration with hydrogen [5-10]. Stationary fuel cells can consequently use the chemically stored energy by hydrogen to balance seasonal fluctuating power generation sources as needed.

It is known that contaminants or noxious gases in hydrogen are responsible for numerous degradation modes within the fuel cell [11, 12]. To avoid damage processes initiated by these compounds, international standards for the quality of hydrogen set precise limits for contaminations allowed in hydrogen. These are namely ISO 14687:2019 [12], SAE J2719:2020 [13] and DIN EN 17124:2019 [14]. While the individual effects of the noxious gases have been studied intensively [11, 12, 15-17], the simultaneous analysis of all contaminants in hydrogen is far from trivial due to the very small concentrations in the low ppm and ppb-range [18]. The wide range of different contamination species further renders the measurements with a single analytical method. Another issue involves the influences of the supply chain to the HRS including production processes (e.g. electrolysis and steam reforming), transport, and storage of hydrogen in salt caverns, which are little studied as an integral system [5, 18-22].

For validation of probing and subsequent analysis, it is essential that the hydrogen from approached hydrogen refueling stations (HRS) is sampled and analyzed by various laboratories with different sampling devices and analyzation instruments. Interlaboratory studies have barely been carried out to date, and if so, then usually only with respect to individual components [23, 24]. Standardized procedures for contamination-free sampling with predefined protocols do not exist or are not sufficiently detailed. Especially for sampling at HRS a method on a kilogram scale at 70 MPa

is needed. However, transport to the site of the analysis poses a challenge since no conventional gas cylinder can be used [25].

For the investigation of hydrogen in the ppb-range at HRS, only a couple of devices for sampling at 70 MPa exist [26]. Commercially available are in particular the H₂ Qualitizer from Linde and an alternative system from AirLiquide [23]. As in this study, self-designed sampling devices are often used, which are filled in three distinct ways. Firstly, the sampling device is evacuated in the laboratory for a defined time before sampling, followed by refueling at the HRS [27]. Alternatively, the device is used directly without prior cleaning at the HRS. Either the sampling takes place after initial purging with an open end using a vent hose or by sampling a reasonable large amount of hydrogen and then depleting it to the minimum pressure before refueling the sample to be analyzed [23, 28, 29].

Regarding the analytical instruments used, also different non-standardized methods are applied in general. Only a few instruments can cover the entire ISO 14687 and EN 17124 measurement range. Usually, a combination of different instruments is used to measure the entire standard [18, 19, 23, 30-32]. Common analytical methods are in particular those based on gas chromatography (e.g. coupled with mass spectrometry (GC-MS) or with flame ionization detector (GC-FID)) and infrared spectroscopy [19, 30]. Especially the latter is also applicable for reactive contaminants and therefore species, which are generally difficult to detect. In the end, cost and reliability usually determine which instruments are used in the laboratory. Particularly in the case of infrared spectroscopy, the high level of resolution possible in combination with the pre-calibrated instruments is obviously advantageous in terms of expenditure and follow-up costs. Common gas chromatographs likewise provide a high resolution for stable components such as hydrocarbons and nitrogen, but can only be used to a limited extent for reactive species such as ammonia, formaldehyde and halides [31].

In this study, a high-performance gas analysis is combined with a self-designed and FCEV-independent mobile sampling device and a specifically developed method for contamination-free sampling of hydrogen at HRS with 70 MPa. With the application of high-resolution mass spectrometry based on ion molecule reactions and use of suitable calibration gases, particularly low detection limits on the ppb-scale can be achieved. Thus, nearly the entire ISO 14687 and EN 17124 standard are covered. Sampling is performed with a customized mobile tank in relevant size, which is particularly needed for sampling on HRS due to its similarity to tanks installed in mass production FCEV and its mobile properties. Outstanding advantages of the mobile tank system used in this study, besides the highest

comparability of the contaminations in the tank due to the similarity with FCEV, are the realization of the FCEV-independent sampling of hydrogen at HRS on 70 MPa level. Particularly in the case of HRS that are still to be commissioned or after maintenance, however, sampling and analysis of the contaminations can be carried out before the first FCEV is refueled and the fuel cell is consequently exposed to potentially harmful contaminations.

For the sampling and subsequent analysis in the laboratory, the methodology for contamination-free sampling and analysis presented in this paper will be applied. Thus, an understanding of the complexity of the international standards with sampling and analysis will be generated and selected results of a hydrogen analysis will be presented. Finally, the results show the need for more standardized procedures for comparability between measurements of individual laboratories and more comprehensive analyses of hydrogen with respect to critical components. In particular, round-robin tests to determine the quality of analysis of the laboratories and the sampling procedures are necessary to establish a convincing hydrogen infrastructure for the future.

2. Materials and Methods

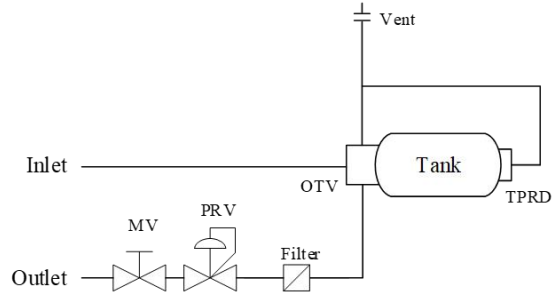
2.1 Mobile Tank for Sampling of Hydrogen

For the sampling of hydrogen at HRS, a self-designed composite type IV high-pressure hydrogen tank (Figure 1) similar to that in fuel cell vehicles is used. The tank has a polyethylene (PE) liner and a carbon woven wrapped structure. With a length of 840 mm and a diameter of 310 mm, the net volume for hydrogen storage is 37 liters. The maximum pressure for storing the hydrogen is 70 MPa, resulting in a maximum capacity of approx. 1.45 kg of hydrogen. The size of the tank was chosen that the tank, including all connections and couplings, can be transported in the trunk of a larger vehicle while complying with all necessary safety transport standards. The periphery surrounding the actual tank was designed to be as compact as possible. A flow diagram including the assembled parts is shown in Figure 1. Included directly on the tank are an on-tank-valve (OTV), the inlet pipe with a receptacle for the nozzle, an outlet pipe with filter element, pressure reducer valve (PRV) and manual shutoff valve (MV), and a thermal safety valve (thermal pressure relief device, TPRD) including a vent pipe. On the OTV, in addition to the electronically controlled valve unit, there is a manual valve common to the inlet and outlet, a pressure sensor and a temperature sensor for monitoring the temperature inside the tank. A programmable logic controller (PLC) with an HTML interface controls the outlet valve and allows for registering and recording pressure and temperature. The outlet pipe includes a quick connector for mounting a ¼" hose. At the inlet is the receptacle to mount the standardized nozzle to the HRS.

In this case, a WEH® TVR1 H2 70 MPa has been installed. The system can be used for sampling at 35 MPa and 70 MPa as the receptacle for 70 MPa is compatible for both. With all mentioned mounted components and attachments, the overall dimensions (length x width x height) of the mobile tank system are 1025 mm x 620 mm x 540 mm.

The tank and the used materials have a significant influence on the composition of the hydrogen to be analyzed. Studies have shown that especially the tank, valve and piping materials (e.g. aluminum, stainless steel, coatings such as SPECTRA-SEAL® and SilcoNert®) have an influence on the stability of individual contaminations and thus on the final analysis result [33, 34]. The transport properties, stability of contaminants and possible effects on the fuel cell of the hydrogen in the used mobile tank after refueling are similar to those of a fuel cell vehicle. Both, the mobile tank and the attached OTV with the couplings are identical or directly comparable to the parts installed in the Hyundai ix35 Fuel Cell. In both cases, a type IV tank [35, 36] with PE liner is used, so the materials (stainless steel 1.4404 and PE) that come into contact with hydrogen are largely similar.

A fuel cell vehicle is often required for hydrogen sampling [19, 23, 29]. In that case, the sampling device is bypassed between the HRS and the vehicle. This has several detrimental consequences. Firstly, a fuel cell vehicle to be refueled must be available and the vehicle's tank must be almost empty. Moreover, it is not possible to purge the sampling device on-site at the HRS, since the fuel cell vehicle can only be refueled once due to the size of the tank. In this study, the outstanding advantage of the design of the tank is that, compared to other sampling devices, no fuel cell vehicle is required. The mobile tank itself is suitable for refueling beyond the usage of the HRS's maintenance program. Normally, the HRS communicates with the tank or vehicle via an infrared interface. Here, information is shared regarding the current pressure and the pressure to be achieved, the temperature and the size of the tank. The exact specifications can be found in the refueling standard SAE J2601 [37]. In the case of the tank used in the study, there is no communication interface built in. As a consequence, a complete fast refueling according to the standard [37] cannot be performed. Instead, in normal mode, the HRS automatically selects the method for refueling without communication. The maximum pressure and the flow rate are limited. However, these limitations have no negative consequences other than the maximum pressure levels will not be reached.



(a)



(b)

Figure 1. (a) Scheme and (b) picture of the mobile 70 MPa type IV tank system for sampling hydrogen at hydrogen refueling stations for impurity analysis in the laboratory, with an directly on the tank mounted on-tank-valve (OTV), inlet pipe with a receptacle for the fueling nozzle, outlet pipe with filter element, pressure reducer valve (PRV) and manual shutoff valve (MV), and a thermal safety valve (thermal pressure relief device, TPRD) including a vent pipe.

Concerning safety issues, some precautions are taken on-site during refueling at the HRS and transportation. The OTV is designed normally-closed, so opening of the valve is only possible when electrical power is supplied via the PLC. The mobile tank is mounted on conductive wheels and a ground connection with appropriate cable length guarantees grounding during refueling and depressurization in the laboratory. The dimensions of the mobile tank are sufficiently compact to allow it to be transported in the trunk of a larger vehicle. During transport, several other safety precautions are maintained. The manual valve on the OTV is closed and residual hydrogen is released from the inlet and outlet pipes in a controlled manner using the MV. With the aid of a hydrogen sensor, the entire sampling device is checked for gas leakages and this is documented for later tests. During transport from the tank in the trunk, which is properly secured with belts, either a hand-held device with a hydrogen sensor is used or the sensors of a fuel cell vehicle are used to monitor the interior regarding released hydrogen.

The tank is labeled according to the safety regulations in Germany and the EU. According to the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) [38], transport does not fall fundamentally under this legislation. In order to use the exemption from the rules of carrying dangerous goods according ADR subsection 1.1.3.1 (c) [38], the transport of the tank must be related to the main activity of the company/enterprise.

For example, the transport of a container for a measurement task and/or surveying. It should be noted that no single container exceeds 450 liters and, according to ADR subsection 1.1.3.6 [38], the quantity to be transported does not exceed the maximum total quantity per transport unit. Hydrogen, compressed (UN 1049) belongs as a flammable gas to Class 2, Group F (section 2.2) according to ADR Table A, Dangerous Goods List [38]. Thus, a maximum total quantity per transport unit of 333 points is the threshold for using the exemption (ADR 1.1.3.1 (c) [38]). For compressed gases, the number of points corresponds to the nominal capacity (water capacity) of the container in liters. With a capacity in our case of 37 liters and the transport to perform a measurement task (sampling of hydrogen), the mobile tank used in this study is to the best of our knowledge exempted from all regulations listed in the ADR. However, it should still be noted that according to ADR subsection 1.1.3.1 (c) [38] measures are taken to prevent the contents from being released under normal transport conditions.

In case of an application outside research, for example if a service provider or HRS operator is not able to completely fulfill the exemptions of the ADR, from our point of view, according to the guideline, the driver still would not need an ADR license, nor the labeling of the vehicle due to the tank volume of 37 liters. However, the presence of a fire extinguisher with at least 2 kg of powder and the carrying of a transport document would be mandatory.

Shipping the mobile tank in accordance with European regulations via a forwarding agency is not readily possible, as the mobile tank used in this study is not tested and certified in accordance with the Transportable Pressure Equipment Directive (TPED) [39].

2.2 Mass Spectrometry for Analysis of Hydrogen Samples

For the analysis of impurities in hydrogen, the method of mass spectrometry (MS) is applied by using the device AirSense from the company V&F, Austria. The specific technique involves ion molecule reaction mass spectrometry (IMR-MS). With this ionization method, fragmentation of samples can be mostly eliminated because the positively charged ions undergo collisions with the molecules to be analyzed in the gas stream with particularly low energy of 10 to 14 eV. By using an octupole separator for focusing the primary ions (Xe, Hg and Kr) and filtering out interferences, the signal to noise ratio is further improved. After ionization, the molecules are separated using a quadrupole mass filter. For this device, the mass range is 7 – 519 amu with a resolution of < 1 amu. Every molecule is registered with a fast pulse counter. The described components of the instrument for the analysis of hydrogen are highlighted in form of a flow diagram in Figure 2.

This technique provides exceptionally reliable results (accuracy $< \pm 2\%$, reproducibility $< \pm 3\%$) with a fast response time ($T_{90} < 20$ ms for each fragment, depending on the measurement task) at remarkably low detection limits (generally parts per trillion level, for this measurement application see Table 1). Especially these limits are necessary for measurements according to ISO 14687 [12] and EN 17124 [14]. The instrument has 6 inputs for calibration gases and an input for the gas sample heated to 200 °C with pressure and temperature compensation.

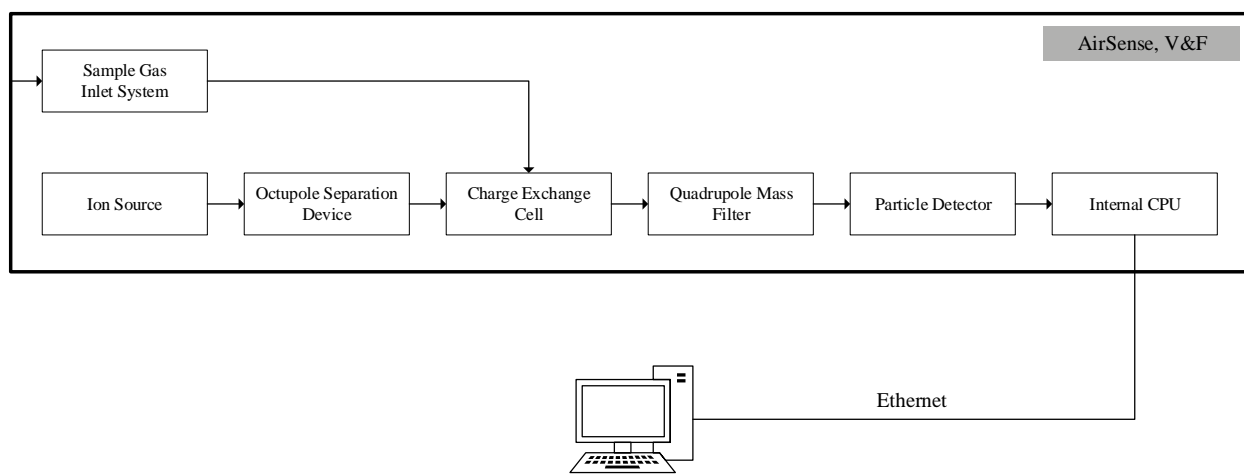


Figure 2. Scheme of the mass spectrometer AirSense, V&F based on ion molecule reaction (IMR-MS) for the analysis of hydrogen in the laboratory.

For each gas to be analyzed, a measurement procedure must be established and suitable calibration gases must be used. According to the manufacturer, the results obtained have an accuracy of $< \pm 2\%$ and a reproducibility of $< \pm 3\%$. To maintain low background noise, the instrument is continuously purged with H_2 in purity grade 5.0 ($> 99.999\% H_2$). In the standard setting, a flow rate of approx. 1 L/min is set, in stand-by operation even less. The maximum inlet pressure is limited to 0.2 MPa(a).

For the gases to be analyzed according to ISO 14687 and EN 17124, a measurement procedure was created which contains all substances from the standard that can be measured directly [12, 14]. Due to the low ionization energy of 10 to 14 eV mentioned earlier, it is not possible to analyze the gases helium and argon. Even though these gases have Severity Class 4 according to ISO 19880-8:2019 [40] and EN 17124 [14], the overall risk is assumed to be low. For helium, no clear source is known. For argon, the mixing of hydrogen with air is a source. Here, however, more than 3% air would have to be present in the hydrogen for the threshold of 300 ppm to be exceeded [14]. Due to the low

probability of occurrence and the resulting low risk, no further analysis is currently being carried out using alternative methods other than IMR-MS. The components summarized in the standards [12, 14] under hydrocarbons including oxygenated species have such a broad spectrum that the calibrated analysis is limited only to methane and further substances are only roughly considered due to the individually required calibration gases (Table 1). Water was calibrated only by the supplier of the analyzer due to the lack of availability of specific water contents in calibration gas standards and has thus not been calibrated again before each measurement in the laboratory. For the determination of the total sulfur content, carbon disulfide, hydrogen sulfide, methanethiol and sulfur dioxide were selected as representative sulfur-based contaminants, since these have a good volatility for calibration gases. The same applies to halogenated compounds. This includes all halogens and halogenated inorganic and organic compounds. Due to the occurrence probabilities of these components and the availability of calibration gases, the representative focus was laid on hydrogen chloride (HCl) [14, 40]. The sum of these individual contaminants is then used for comparison with the standards and estimation of the hydrogen purity.

Table 1. Contaminants and thresholds listed in the comprehensively convergent standards ISO 14687 [12] and EN 17124 [14] with corresponding limits of detection of the analyzer resulting from calibration with known gas standards.

Contaminants	ISO 14687 / EN 17124 thresholds [$\mu\text{mol/mol}$]	Limits of detection analyzer [$\mu\text{mol/mol}$]	Calibration gas standards
Water (H ₂ O)	5	0.58	None (pre-calibrated)
Methane (CH ₄)	100	0.02	O ₂ , CH ₄ , CO, CO ₂ in H ₂
Total hydrocarbons (except CH ₄)	2	0.002 (for single C ₂ – C ₈ hydrocarbons)	None (pre-calibrated)
Oxygen (O ₂)	5	0.14	O ₂ , CH ₄ , CO, CO ₂ in H ₂
Helium (He)	300	Not considered	None
Nitrogen (N ₂)	300	1.65	N ₂ in H ₂
Argon (Ar)	300	Not considered	None
Carbon dioxide (CO ₂)	2	0.02	O ₂ , CH ₄ , CO, CO ₂ in H ₂
Carbon monoxide (CO)	0.2	0.45	O ₂ , CH ₄ , CO, CO ₂ in H ₂
Total sulfur with Carbon disulfide (CS ₂) Hydrogen sulfide (H ₂ S) Methanethiol (CH ₃ SH)	0.004	0.0007 0.0009 0.0001	CS ₂ , H ₂ S, CH ₃ SH in H ₂

Sulfur dioxide (SO ₂)		0.003	SO ₂ in H ₂
Formaldehyde (HCHO)	0.2	0.007	HCHO in N ₂
Formic acid (HCOOH)	0.2	0.005	HCOOH in N ₂
Ammonia (NH ₃)	0.1	0.002	NH ₃ in H ₂
Total halogenated	0.05	HCl: 0.02	HCl in H ₂

All possible gases to be analyzed are shown in Table 1 along with the detection limits resulting from the calibration. This table also includes the thresholds depicted by the standards [12, 14] and the calibration gases used. H₂ 6.0 from Linde was used for the calculation of the background. H₂ 5.0 from Linde was used as purge gas during stand-by. The calibration gas standards are in all cases from AirLiquide with background gas H₂ N60 or N₂ N60 (purity grade 6.0). With this measuring procedure, reliable results are obtained after approx. 10 – 15 minutes at the flow rate mentioned. The decisive factors are the length of the pipes and hoses, the expected concentrations of the contaminants and the type of molecule. The latter will be discussed more specifically in the results and discussion section.

The ISO 21087:2019 [32] addresses the validation of equipment and methodology for the analysis of hydrogen in the laboratory. Here, fit for purpose criteria are defined for selectivity, limit of detection and limit of quantification, working range, trueness, precision, measurement uncertainty and ruggedness. The aim is to enable laboratories to demonstrate that the method used is suitable for the analysis of impurities in hydrogen. Due to the novelty of the application of the IMR-MS technology and the developed method of sampling and analysis, multiple influencing factors, and the fact that validation is not mandatory for research purposes, up to now no validation of the method presented here has been performed. However, the mass spectrometer based on IMR-MS used is remarkably suited for the contaminants to be analyzed due to the limit of detection and limit of quantification. In the context of future studies, validation based on a revised ISO 21087 is target-oriented and to be applied in the context of round robin tests.

3. Results and Discussion

3.1 Contamination-free Sampling of Hydrogen

3.1.1 Method of Sampling

For sampling hydrogen at HRS at 35 and 70 MPa, the mobile tank described in section 2.1 is used. For this purpose, the tank is placed on-site at the HRS near the fueling nozzle and secured via brakes. Grounding is usually ensured via the conductive wheels and the grounded base plate. A barricaded work area is set up for refueling, thus it is ensured

that no uninvolved third parties influence the sampling or put themselves in danger. For this purpose, traffic cones with barrier bands in signal colors are set up. Furthermore, the on-site requirements are analyzed concerning possible sources of ignition, traffic, contaminated and slippery ground, and any hazards are eliminated.

To fill the mobile tank with hydrogen, the additional manual valve on the OTV is first opened manually and the fueling nozzle of the HRS is connected to the receptacle. A power bank is used to supply power to the OTV and the temperature and pressure sensors, and the recording of the generated data with the PLC onto an SD card is started. Additional grounding during refueling is ensured via the fueling nozzle. In the optimal case, the HRS is operated in the maintenance mode, so that in case of any emergency a quick interruption of the refueling process is possible and monitoring of pressure rising, temperature, and flow rate can be arranged more flexibly. However, refueling also proceeds in the case of normal mode without error messages, but with the restrictions mentioned in section 2.1 concerning maximum pressure. Possibly, the pre-cooling [37] down up to $-40\text{ }^{\circ}\text{C}$ before refueling is only carried out to a limited extent, but, however, this does not influence following purity analyses.

Before the tank is filled at the HRS with the amount of hydrogen necessary for the analysis, it has to be properly purged. This is the only way to ensure that all determined contaminations are measured with respect to this specific sampling. The American standard ASTM D7606-17 [28] addresses the cleaning of sampling devices for hydrogen and describes specific guidelines. Following this standard practice, a similar procedure is also applied for the mobile tank used here. For this purpose, at least 1 kg of H_2 is first refueled in order to dilute or remove any existing contamination to a large extent. Sampling in flow-through with open end is not possible due to the tank design-related minimum pressure of approx. 1.8 MPa as described in section 2.1. Due to the tank size of 37 liters, the capacity at up to 70 MPa is approx. 1.45 kg. At 1.8 MPa there is approx. 0.05 kg in the mobile tank, so that the necessary amount of 1 kg is guaranteed for complete refueling from 1.8 MPa up to 70 MPa. If refueling is not performed in maintenance mode and therefore refueling to 70 MPa is not possible, refueling can also be divided into two or more independent refueling at lower possible pressure. After the tank has been refueled to the maximum pressure, it must be emptied. Before that, however, a waiting time of 5 minutes is maintained to set an equilibrium in the tank. It must be ensured that the HRS has depressurized the pipes and hoses including the fueling nozzle. The nozzle is then removed before the tank can be emptied by connecting a purge hose.

For this purpose, one end of a stainless-steel hose is connected to the sampling valve by using a quick coupling, the other end is placed at least 2.4 m above the ground with the help of a tripod. This ensures direct dilution of the released hydrogen at an appropriate distance from the HRS, potential ignition sources and third party influence, following ASTM D7606-17 [28]. A distance of 2 m is maintained from surrounding buildings and work is interrupted or not started in the event of strong winds and bad weather conditions. To empty the tank, the OTV is opened with the MV closed using the connected valve control via the HTML interface. The pressure reducer mounted between the OTV and MV has an outlet pressure of 2.0 MPa at a maximum inlet pressure of 70 MPa. Now the MV is opened carefully and a constant but small flow of hydrogen from the tank to the environment is set. After approx. 30 minutes reaching the minimum pressure of 1.8 MPa, the OTV is closed, and after that the MV. To maintain safety, the purge hose is removed several minutes after the released hydrogen has been diluted by the surrounding air. This is followed by either the second refueling, if 1 kg could not be refueled the first time, or the final sampling for analysis in the laboratory. After completion of the process, the manual valve near the OTV is closed, a detailed documented check is made for leakages with a hydrogen sensor, and the mobile tank is loaded into the vehicle.

With the help of the method described here for purging the sampling device, contaminations can be mostly excluded, in particular concerning water and sulfur components [28]. This applies not only to the tank itself but also to the surrounding pipes and valves. Normally, it would be recommended to heat out the pipes and the tank or to evacuate them. However, this is not possible with the tank used here due to its design, especially not directly at the HRS. However, compared to other sampling devices [23, 24, 27, 28] where open-end purging or evacuation is possible, the advantage here is clearly the independence from a fuel cell vehicle and the similarity to the tanks installed in these vehicles. The tank itself, the OTV and the couplings are similar to the parts installed in the Hyundai ix35 Fuel Cell. This means that contaminants measured after sampling can be compared directly with those to which the fuel cell would be exposed to in the car.

3.1.2 Sampling of Hydrogen at an Existing HRS in the Netherlands

In the following, the sampling with the mobile tank is explained based on an existing HRS in the Netherlands according to the previously described method. Prior to sampling, the tank was filled with high-purity hydrogen (H₂ 5.0) via a compressor at the manufacturer of the mobile tank to exclude any contamination before beginning the sampling campaign. On-site at the HRS, the sampling device was first connected to the 70 MPa nozzle

of the HRS (a 35 MPa nozzle is also available for heavy duty vehicles), the HRS was put into maintenance mode with trained personnel and refueled from 7.0 MPa to 15.0 MPa for initial test purposes and a first purge. Grounding was ensured. The tank was then depressurized to 2.0 MPa and subsequently refueled to 68.0 MPa. After 5 minutes an equilibrium in temperature is measured, the tank was depressurized to 2.0 MPa using the procedure described above and refueled to 7.5 MPa. This amount is sufficient to perform several analyses of hydrogen in the laboratory. Example photos of the sampling at the HRS and the setup of the purging with a tripod are shown in Figure 3.



Figure 3. Visualization of hydrogen sampling for contamination analysis using the mobile tank. Shown are the refueling at the HRS and the venting of the hydrogen for purging near the refueling station with the barricaded work area.

The hydrogen at the HRS had to comply with ISO 14687 [12] and EN 17124 [14], but it should be emphasized here that the sampled HRS is a non-public research HRS. Refueling takes place only in the context of individual fuel cell vehicles. In the case of a public HRS, it is stipulated by law [41] that there shall be compliance with currently valid fuel standards [12, 14]. Because the sampled HRS is a research object and since the hydrogen was produced via on-site electrolysis, compliance with the standards is of particular interest. However, the green hydrogen should reveal a high purity due to the production process of polymer electrolyte membrane (PEM) electrolysis [15, 16, 42].

3.2 Results and Challenges from Analysis of Hydrogen with Mass Spectrometry

3.2.1 Preparation of Gas Analysis

First, the mass spectrometer is prepared for the analysis of hydrogen. Our experience with this specific instrument has shown that at least 1 week before the planned analysis is carried out the instrument has to be in ultra-high vacuum and

purged with hydrogen (purity 5.0 or higher) at a flow rate of approx. 1 L/min. Especially the amounts of water and oxygen in the background can be minimized this way. We have learned from experience that it is highly recommended to purge the instrument 24/7 with H₂ 5.0 without switching off the instrument. Before the instrument can be calibrated, the background must be determined. For this, H₂ 6.0 is supplied for at least 15 minutes with the known flow rate and an automated correction of the background is carried out via the software of the device after determining the plausibility of the measured values.

3.2.2 Calibration of Gas Analysis and Determination of Interferences

On the day of the planned analysis, the instrument must be calibrated according to the contaminants mentioned in section 2.2. For this purpose, the calibration gases are fed to the instrument individually or in a defined mixture (Table 1) via the inputs for calibration gases and the concentrations specified from the calibration gas standards are entered at the corresponding measured value of the instrument (counts per second). Before the counts per second are set in relation to the entered concentration of the respective gas, a detailed plausibility check is performed. In this way, false positive and false negative results can be largely avoided. For each gas, the time required for purging was determined. This is the time required to achieve stable measured values. Particularly challenging in terms of general detection and duration of calibration are the gases hydrogen chloride (HCl), formic acid (HCOOH) and ammonia (NH₃). HCOOH and NH₃ are critical because of adhesion interactions within the pipes and hoses. As a consequence, particularly long purging times are required until equilibrium is reached. The same applies to HCl, but due to the intensity of similar masses, this gas also interferes with hydrogen sulfide (H₂S). A correction is possible by assuming that no HCl (0 ppm) is contained in the calibration gas for H₂S (CS₂, H₂S, CH₃SH in H₂, Table 1). Another interference detected during the experiments results from carbon monoxide (CO) and nitrogen (N₂). Due to the mentioned possible ionization energy of a maximum of 14 eV (Kr as ionization gas), normally no ionization of N₂ is possible (at least 15.6 eV are necessary). Here, an electron impact mass spectrometer (EI-MS) would have to be used. In the context of this and further investigations [43], it could be demonstrated that detection of N₂ in an H₂ atmosphere with appropriate CO concentrations is possible. N₂ is detected after ionization with the second ionization state at 16 eV (Kr) as N₂H⁺ at m/z 29. Due to the similar mass of CO at m/z 28, an exceedingly large interference results, which has a particularly large influence on the measurement according to ISO 14687 and EN 17124. The presence of a natural isotope overlapping the CO signal can be excluded based on the incorrect ratios. A correction of the interference to a limited extent is possible via the assumption that no CO is contained in the calibration gas for N₂. Further optimization of the

instrument was made concerning the resolution of CO. However, it was increased for better separation of m/z 28 and 29, which has a higher detection limit as a consequence.

Further challenges during the measurement result from the calibration gas standards. It must be considered that HCOOH and HCHO were calibrated with test gases containing N₂ instead of H₂ as residual gas. Thus, the density ratios of N₂ and H₂ result in different flow rates of the supplied test gases. These in turn influence the measured concentrations. Another influencing factor is concerning the particularly short shelf lives of the test gases. These are relatively short for the sulfur components with a maximum of 6 months. For H₂S, a 30 % too low concentration was detected by comparing an old gas cylinder (expiration date 9 months past) with a new gas cylinder.

3.2.3 Results of Hydrogen Analysis from HRS Sampling

In the following section, it will be shown how the analysis of an unknown hydrogen sample is realized in the laboratory using the mass spectrometer based on ion molecule reactions. For this purpose, the mobile tank is first grounded in the laboratory and the power supply to the OTV is provided. The manual valve is opened. A pressure reducer is attached to the outlet of the tank via a quick coupling. This pressure reducer is passivated with SilcoNert® [25, 44-47] via an inert non-reactive silicon coating process so that particularly sensitive components such as ammonia, hydrogen sulfide, formaldehyde and formic acid are not neglected due to false-negative results. A stainless-steel hose is now used to connect the mobile tank and the mass spectrometer at the heated inlet. The OTV is opened via the HTML interface, then the MV and finally the pressure reducer is opened and set to an outlet pressure of 0.2 MPa(a). A data file is created to record the analysis data. Now the sample to be analyzed is fed to the instrument. After about 15 minutes of feeding with a minimum flow rate of 1 L/min, the measurement is finished. The analysis of the sample shown in section 3.1.2 was carried out according to this procedure. The results are shown in Table 2.

Table 2. Results of the analysis of a hydrogen sample from an HRS in the Netherlands, referring to ISO 14687 and EN 17124. Shown are the concentrations measured after complete calibration and background correction with the device AirSense, V&F as well as associated valid thresholds from the international standards (LOD: limit of detection).

Contaminants	Measured concentration [$\mu\text{mol/mol} \equiv \text{ppm}$]	ISO 14687 / EN 17124 thresholds [$\mu\text{mol/mol}$]
Water (H ₂ O)	19.23 ± 4.24	5
Methane (CH ₄)	Below LOD	100

Total hydrocarbons (except CH ₄)	0.34 ± 0.07	2
Oxygen (O ₂)	2.86 ± 0.54	5
Helium (He)	-	300
Nitrogen (N ₂)	761.68 ± 22.72	300
Argon (Ar)	-	300
Carbon dioxide (CO ₂)	2.90 ± 0.09	2
Carbon monoxide (CO)	1.62 ± 0.11	0.2
Total sulfur with	0.002	0.004
Carbon disulfide (CS ₂)	0.001 (± 0.02 ppb)	
Hydrogen sulfide (H ₂ S)	0.001 (± 0.02 ppb)	
Methanethiol (CH ₃ SH)	Below LOD	
Sulfur dioxide (SO ₂)	Below LOD	
Formaldehyde (HCHO)	Below LOD	0.2
Formic acid (HCOOH)	0.01 ± 0.001	0.2
Ammonia (NH ₃)	Below LOD	0.1
Total halogenated	HCl: below LOD	0.05

The accuracies shown Table 2 result from the measurement accuracy of the mass spectrometer of ± 2 % and the calculated standard deviation from 3 measured values. Total hydrocarbons was calculated on the basis of ethane, ethylene, acetylene, propylene, butane, pentane, benzene, toluene and xylene and given with an accuracy of 20 % for the reasons highlighted in section 2.2. The same applies to the concentration of water due to the pre-calibration. Argon and helium were not considered for the measurement. Below LOD indicates that the measured value is below the limit of detection (Table 1) and therefore does not contribute to the assessment of the degree of contamination.

The contaminants water (H₂O), nitrogen (N₂), carbon dioxide (CO₂) and carbon monoxide (CO) are to be identified from Table 2 as (potentially) critical since they exceed the thresholds from ISO 14687 and EN 17124. Consequently, the value for CO is considered to be particularly critical but is explicitly sensitive to errors due to the reasons mentioned in section 3.2.2. A further assessment of the criticality of the value is only reasonable after further optimizations of the mass spectrometer and was not feasible in this work. According to EN 17124, the overly high measured values of N₂ and CO₂ in the potential fuel cell vehicle cause first of all a dilution of the hydrogen. This will result in lower cell voltages and thus lower power efficiencies, higher H₂ consumption and decreasing efficiency. In addition, fan control may be disrupted due to anodic accumulation of nitrogen and in the fuel cell may be undersupplied areas with

hydrogen. Thus, in addition to power losses, technical components can also be damaged. Furthermore, a high N_2 concentration combined with a high CO concentration is particularly noteworthy, since N_2 blocks the desorption of CO at the anodic catalyst layer. The water-gas shift reaction can also form CO from CO_2 and further intensify the mentioned effect.

For H_2O , the criticality for the fuel cell is much lower. Here, transport mechanisms can be affected by high concentrations in combination with ionic impurities, resulting in overvoltages, power losses, and consequently in system failure. However, high water concentrations are less critical for the fuel cell stack, but much more critical for the HRS and the vehicle's tank components due to a possible formation of ice and corrosion. For high water contents, a safety risk can arise in particular if the check valves of the FCEV freeze due to low temperatures below the freezing point and consequently no longer have proper functionality.

Overall, the authors consider the measured purity of this sample to be critical in terms of compliance with the standards, but still within the tolerable range for the vehicle's fuel cell. Much more relevant are the measured concentrations of N_2 and especially CO. If the measured value for CO would be correct to this extent, this would be a clear sign that no vehicle should be refueled at this HRS. There would be an obvious risk of irreversible deactivation of the fuel cell's catalyst in the vehicle. However, due to the aforementioned limitations concerning the interference from N_2 and CO based on the measurement principle, further optimizations must be carried out on the mass spectrometer, both, software and possibly hardware. For the high N_2 concentration, the measured value must be verified with further samplings at the same HRS. The contamination potentially results from maintenance work on the HRS. Usually, N_2 is used for inerting and purging. Residues from these procedures may be responsible for the high concentrations. Another reason is based on compression at the HRS. The piston compressors used are commonly operated with a gas buffer of N_2 , on the one hand, to protect against contamination containing mineral oil, and on the other hand to protect against possible explosion hazards. Possible leaks cause the N_2 to spill into the compressed hydrogen. Contamination introduced by sampling or analysis due to leakages in hoses, couplings and the tank itself can be excluded since otherwise O_2 would have been detected in an air-like ratio to N_2 . Assuming that approx. 78.08 % N_2 and 20.95 % O_2 are contained in the air, a measured concentration of N_2 of 761.68 ppm should have resulted in the equivalent detection of approx. 204.37 ppm O_2 . Due to the actually determined concentration of 2.86 ppm O_2 , a leakage can be ruled out. Furthermore, a carry-over contamination with N_2 can be excluded, since the

tank was purged 2 times with H₂ 5.0 due to maintenance work prior to sampling, in addition to the purging process demonstrated in this study.

3.3 Identified Next Steps for Hydrogen Sampling and Analysis

The experiments carried out in this study clearly highlight that, apart from the methodology of sampling and subsequent analysis of the purity of hydrogen in the laboratory, some elementary tools for hydrogen-based mobility and economy need to be established. For the sampling container, the sampling methodology, the following transport and the final analysis, round-robin tests have to be performed to check reproducibility and validation. It must be verified to what extent the type of mobile tank, the preparation for sampling (evacuating, purging, ...) and the sampling itself influence the final measurement of the concentrations of the contaminants. First comparative indications of sampling procedures and pre/post preparation are provided by Arrhenius et al. in a review paper on this [48]. The large number of sampling options presented there emphasizes that these must be investigated within a round-robin test about comparability. The methods for analyzing hydrogen also differ substantially, as it is partly written in the international standards. Therefore, it must be possible to guarantee comparability here as well. In addition to the accreditations of the analyzing institutes, a national and international round-robin test is a method to be considered. As a consequence of performing these round robin tests, the measuring instrument and associated laboratory should be validated according to ISO 21087 [32] in order to conform at best to standards. This validation proves that the basic suitability exists to detect all contaminations according to ISO 14687 [12] and EN 17124 [14] with corresponding reliability and comparability with other laboratories investigating the same or different samples.

Following this, it will be necessary to investigate the influence of the mobile tank (or sampling containers in general) on the composition of hydrogen in future tests. In this study, a tank was chosen which is almost identical to that of a fuel cell vehicle. While this is representative of the contamination that eventually reaches and affects the fuel cell in the vehicle, it does not preclude the possibility that the polyethylene liner may still cause a change in composition. In the course of this, the carry-over of contaminants between different samples of various HRS is to be mentioned. Following ASTM D7606-17 [28], the 1 kg used here for purging is sufficient, but this may vary due to different pressure levels applied during sampling and the type of tank.

Other challenges during the analysis of hydrogen relate to the test gases. As shown in Table 1, gases such as formaldehyde and formic acid have limited or no availability in a hydrogen matrix due to their instabilities. This

represents new obstacles to calibration, which must be overcome by appropriate gas flow rates and correction. Correspondingly, the shelf life of certain components is also a hindrance. For example, a concentration of H₂S in hydrogen that showed a concentration of 30 % too low, compared to the analysis certificate, was detected after the test gas cylinder had been stored for just over a year. The concentration of water can also only be represented with a high degree of uncertainty since no test gases for water can be obtained from the gas suppliers. In addition, no individual test gases for all hydrocarbons were included in these tests, since otherwise too many test gases would be necessary due to the diversity and the insufficient specification in the ISO and EN standards.

Finally, an important possibility to be established for checking the methodology of sampling and analysis in the laboratory is the online analysis on-site at the HRS. Employing specifically used analysis devices and/or sensors, the compliance of the hydrogen quality with the ISO/EN standards can be verified, at least in extracts [49]. In this way, it can also be stated directly whether the refueling of a random fuel cell vehicle can be carried out or whether it should not be carried out due to the present impurities.

4 Conclusion

The development of a methodology for the contamination-free sampling of hydrogen with reliable reproducibility is the first essential part of the analysis of hydrogen. In this study, a mobile tank was used for the simplest and most representative sampling of hydrogen, which is in the same form integrated into series production vehicles with fuel cells and may be refueled and transported according to the valid safety regulations even without the presence of a fuel cell vehicle. For this aspect, some safety precautions have been worked out which are not only important for the safe operation of the mobile tank, but the analytical results that can be obtained with it are also influenced by the consistency of the sampling. In this study, a methodology was developed with which it is possible to generate representative and valid measured concentrations of contaminants for HRS in the laboratory. Essentially, this involves purging the mobile tank with 1 kg of H₂ before the actual sample can be collected. This largely guarantees that any contamination previously present in the tank is removed or properly diluted. Since no open end is possible in a carbon fiber tank with an internal liner made of plastic (polyethylene), the procedure described in this paper is a suitable way of using tanks largely similar to those in fuel cell vehicles as sampling containers.

The second important step after sampling is the analysis of hydrogen. For the future and first analysis of hydrogen, a suitable mass spectrometer based on ion molecule reaction mass spectrometry was and will be used. With the help of

this technique, particularly low detection limits of all components mentioned in the internationally valid regulations ISO 14687 [12] and EN 17124 [14] (quality of hydrogen for mobile fuel cells supplied to HRS) are possible, since the method of ionization produces as few fragments of the components as possible. Thus, a uniquely reliable analysis and determination of the concentrations of the contaminants that are particularly harmful to the mobile fuel cell are demonstrated. In this study, a calibration of the mass spectrometer specially prepared for the analysis of hydrogen according to the standards with the composition of test gases was presented and applied based on an example. They form a basis for future measurement tasks with similar components and/or demands on accuracy, reliability and complexity with only one instrument.

With the mobile tank and according to this developed methodology regarding the analysis of hydrogen, an HRS in the Netherlands was probed and the hydrogen was analyzed. The hydrogen at the HRS was largely produced via on-site electrolysis, so a high purity with low contaminants in the form of water, nitrogen and oxygen was expected. The analysis showed that the contaminants water (19.23 ± 4.24 ppm; threshold 5 ppm), nitrogen (761.68 ± 22.72 ppm; threshold 300 ppm), carbon dioxide (2.90 ± 0.09 ppm; threshold 2 ppm) and carbon monoxide (1.62 ± 0.11 ppm; threshold 0.2 ppm) could be identified as critical, as they exceed the limits of ISO 14687 and EN 17124. The hydrogen at this HRS should not have been dispensed according to this present analysis. The further analysis of the measured values provided the insight that the determination of carbon monoxide is not as trivial as anticipated. A high sensitivity of the carbon monoxide signal for nitrogen was detected even though fragmentation could not actually be observed. Here, for future experiments, the resolution of the instrument needs to be further optimized and hardware adaptations are even feasible to a limited extent. For example, to install an additional integrated electron impact mass spectrometer (EI-MS) to completely ionize the nitrogen due to higher possible ionization energies. Thus, an exact concentration of nitrogen can be determined and the cross-sensitivity with carbon monoxide can be calculated. Although this does not solve the problem, it allows the resolution of the instrument to be precisely adjusted. The upgrade with EI-MS, however, additionally allows the exact determination of the concentrations of argon and helium. Continuing, the round robin tests to be performed will investigate the comparability with other laboratories and assist in the validation of the measurement instrumentation with IMR-MS and EI-MS according to valid standards.

In summary, this study demonstrated that a self-developed mobile type IV tank can be used to perform representative sampling of hydrogen at up to 700 bar for hydrogen purity analysis without the need for a simultaneously refueling FCEV, and that based on an exemplary sampling of an HRS high-precision analysis with IMR-MS of contaminants

in unknown hydrogen samples can be applied according to valid international standards. Particular focus was devoted to the strategy of contamination-free sampling, developed procedures for purging the mobile tank, and calibration of the used mass spectrometer. Future experiments will focus on upgrading the laboratory infrastructure, performing round robin tests, validating the measurement instruments, further evaluating the sampling of hydrogen using the mobile tank and the related advancement of the sampling strategy including purging processes with a specific emphasis on water.

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