Low-concentration HCl gas mixtures in H_2: preparation and analysis

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Abstract. Measuring hydrogen chloride (HCl) impurities in hydrogen (H_2) produced by alkaline electrolysers is crucial in current "green" hydrogen systems. It aims to develop new gas standards and analytical methods, integrating both online and onsite monitoring and calibration at alkaline electrolyser facilities. These efforts are fundamental for setting industry-standard metrological practices that ensure reliable and consistent monitoring of hydrogen quality. Following strict standards such as ISO 14687:2019, which sets the quality requirements for hydrogen fuel and defines permissible contaminant levels like hydrogen chloride (HCl), highlights the importance of these initiatives. This study at Spanish Metrology Institute (CEM) aims to establish advanced capabilities for preparing and detecting hydrogen chloride (HCl) in hydrogen matrix mixtures at µmol/mol levels and below, as part of projects EPM 21GRD05 Met4H2 and the national Hydrogen Project-PRTR. To validate the in-house method, static gravimetric mixtures of HCl in hydrogen were prepared and analysed over a concentration range from 5 µmol/mol to 1 000 µmol/mol, revealing that while both gravimetric and analytical values align quite well at high concentrations, analytical measurements at lower levels report reduced HCl values-likely due to losses during successive dilutions.

1 Introduction

The transition to green hydrogen as a key energy source is growing rapidly, driven by its potential to decarbonize various sectors, including energy, transportation, and industry [1]. The EMP 21GRD05 Met4H2 project [2] addresses a critical need in the emerging hydrogen economy through one of the work packages, aims to address the challenges associated with hydrogen gas quality by developing methodologies and metrological frameworks that can be implemented at every stage of the hydrogen supply chain. The outcomes of this work will not only support the transition towards green hydrogen but will also facilitate the creation of a reliable infrastructure for hydrogen-based energy systems, strengthening trust in its role as a clean energy solution for the future.

As electrolysis becomes a key method for generating green hydrogen [3], the presence of impurities such as hydrogen chloride (HCl) in the produced hydrogen presents significant challenges [4]. Even trace amounts of HCl can negatively impact the purity and performance of hydrogen, potentially damaging infrastructure and limiting its use in sensitive applications. Therefore, ensuring the quality of hydrogen produced by electrolysis is essential, not only for optimizing process efficiency but also for ensuring the safety and reliability of hydrogen systems. In this aspect, ISO 14687:2019 [5] and UNE-EN 17124:2022 [6] provide essential guidelines for hydrogen fuel quality specifications and assurance.

As part of its involvement in the 21GRD05 Met4H2 project [2], the Reference Gas Laboratory of the National Metrology Institute of Spain (CEM) has carried out the preparation of primary reference gas mixtures (PRGM) of hydrogen chloride in hydrogen (HCl/H_2). These mixtures are prepared using the static gravimetric method, in accordance with ISO 6142:2015 [7], by carefully weighing the calculated mass of each component before introducing it into a gas cylinder. The PRGM will support the development and validation of a new analytical technique and provide traceable reference values for hydrogen quality testing laboratories.

2 Experimental

2.1 Preparation of standard gas mixtures

In the first place, as a preliminary step to preparation, an exhaustive study of cylinder passivation techniques was conducted, leading to the selection of ACULIFE® IV from Air Liquide wall treatment cylinders for the process (internal work carried out in CEM Reference Gas Laboratory within 21GRD05 Met4H2 EMP project) [2].

CEM has prior experience in preparing this type of mixture and has already set up an outdoor gas shed for

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storing the pure gases, including H_2, N_2 and HCl. There, the pure HCl gas is connected to a control panel, where 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. Additionally, modifications were made to the gas shed system to enable purging with dry nitrogen after replacing an empty HCl cylinder, ensuring precise and contamination-free gas preparation [8].

Standard gas mixtures are gravimetrically prepared at high pressure in 5 L aluminium alloy cylinders with appropriate passivation (ACULIFE® IV). To obtain low-concentration mixtures (µmol/mol), a multi-step dilution process is carried out, starting with pure hydrogen chloride (3.0 quality, Linde) and pure hydrogen (5.5 quality Praxair, 6.0 quality Linde). A detailed description of the filling process can be found in reference [8].

Before use, the cylinders were 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.

2.2 Analysis of standard gas mixtures

The analytical measurements were performed with a ProCeas® analyser from AP2E/DURAG. It is an infrared spectrometer, based on optical feedback cavity enhanced absorption spectroscopy (OFCEAS) [9]. This custom-built instrument allows low level HCl and water (H_2O) analysis in various matrices (hydrogen, nitrogen, dry air and helium). It is equipped with two lasers: laser 1 for HCl concentrations below 10 µmol/mol and H_2O between 0 µmol/mol and 50 µmol/mol and laser 2 for HCl concentrations above 10 µmol/mol (up to 1 000 µmol/mol).

The measurement process begins by passing dry nitrogen through the OFCEAS analyser system for a minimum of 24 hours to reduce humidity as much as possible. Before starting the analysis, if the matrix of the mixture is another gas (H_2 in most cases), this gas is injected until the measurement stabilises. Furthermore, the pressure regulator is purged with the sample of interest (pressurising the dead volume and then depressurising it multiple times). After completing these steps, the cylinder is connected to the analyser system, and the gas sample is introduced with an outlet pressure of 1 bar with excess gas flow coming out of the vent (this is controlled with a rotameter).

3 Results and discussion

Previously, CEM gas laboratory was unable to analyse low-concentration mixtures, as the detection limit of the gas chromatography method used was approximately 900 µmol/mol [8]. This limitation has been overcome through the acquisition of the OFCEAS analyser mentioned above [10, 11].

For the purpose of testing the device three initial families of HCl/N_2 mixtures were prepared and analysed. Within the collaborative work of the project, one of the mixtures of 10 µmol/mol (HCl/N_2) was sent to the National Metrology Institute of the Netherlands (VSL). The measured HCl concentration reported by VSL was coherent with the analytical result obtained by CEM. Therefore, these mixtures served as a reference for assessing the system's response under controlled conditions.

Lately, several mixtures of HCl/H_2 were prepared and analysed over a wide concentration range as illustrated in Fig. 1.

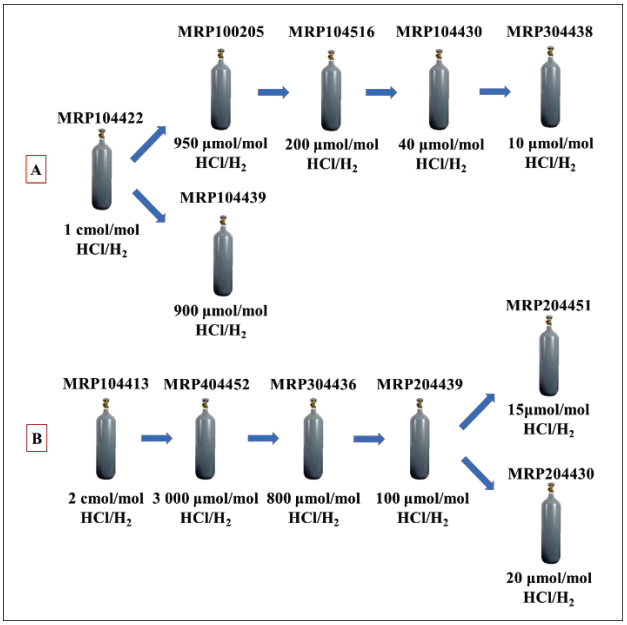

Fig. 1. Schematic representation of two sets of mixtures prepared through dilution steps, with the target HCl concentration indicated.

After preparation and analysis, the gravimetric and analytical values of HCl concentration in the mixtures were compared against each other. Although both values are similar for higher concentrations (e.g., around 900 µmol/mol), discrepancies were observed at lower levels (table 1). This is particularly notable in the low µmol/mol range, where the analytical results are below those expected according to gravimetry. There are several factors that could explain this discrepancy, most notably the loss of HCl during the successive dilutions required to prepare the low-concentration mixtures.

Table 1. Summary of the analysed samples.

Cylinder code	[HCl] (gravimetry) (µmol/mol)	[HCl] (OFCEAS) (µmol/mol)
MRP104439	920.91	919.78
MRP100205	919.11	919.56
MRP204430	20.17	13.90
MRP204451	16.08	9.23
MRP304438	9.71	4.03

Achieving a stable concentration value is a critical requirement for all these measurements. Due to the highly reactive nature of HCl, it was essential to use a short pipeline, and thoroughly purge the entire system, including the pressure regulators, prior to conducting measurements [12, 13].

A key challenge in OFCEAS analysis is the high gas consumption during measurement. The cylinders

employed at CEM have a volume of 5 L, and despite preparing the standard gas mixtures at the maximum achievable pressure (close to 200 bar), this still constitutes a limiting factor. Fig. 2 and Fig. 3 present representative results of HCl determination carried out using the OFCEAS analyser.

Moreover, under these conditions, 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, as initially planned.

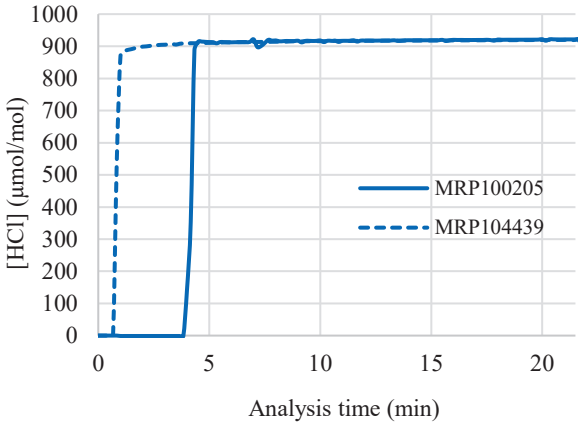

Fig. 2. OFCEAS measurement of two high-concentration mixtures.

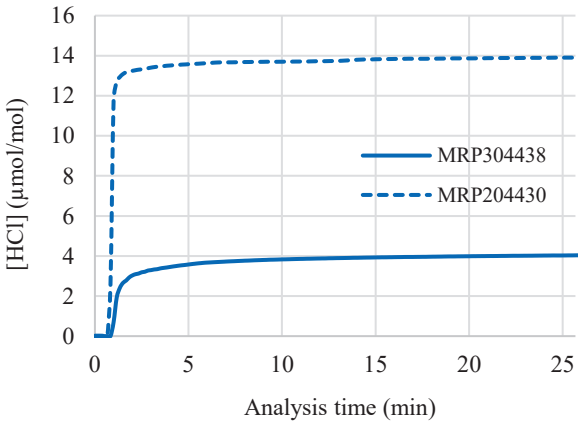

Fig. 3. OFCEAS analysis of two low-concentration mixtures.

4 Conclusion and further work

The CEM Reference Gas Laboratory has made significant progress in analytical techniques through the successful preparation and measurement of HCl/H_2 mixtures at the µmol/mol level. This achievement is especially significant as it represents an improvement over the previous analytical limit of 900 µmol/mol for HCl concentrations [8]. This current study builds upon that work, establishing a basis for the further development of the laboratory's hydrogen analysis methods, with a specific focus on detecting trace-level impurities such as HCl and H_2O in hydrogen. These impurities are critically important, as even small amounts can significantly affect the performance and quality of hydrogen, especially in applications such as fuel cell technology, hydrogen storage, and industrial processes.

A primary objective of this study is to address and optimize the preparation and analysis of low-concentration HCl mixtures (µmol/mol). We observed a discrepancy between the gravimetric values and analytical measurements, particularly at lower concentrations. This has been reported in previous works [13]. This discrepancy highlight the need for improvements in the preparation technique, especially during the final dilution steps, to ensure that the analytical results more accurately represent the true concentration of HCl in hydrogen mixtures. By optimizing the final dilution steps, we aim to reduce losses due to adsorption, enhance the reproducibility of results, and ensure that the analytical methods produce values more closely aligned with gravimetric concentrations. This refinement will not only improve the precision of HCl measurements but also strengthen the laboratory's capacity to detect trace-level impurities in hydrogen with greater accuracy and consistency.

Moreover, the improvement of the analysis process is crucial too. The use of treated sampling lines and pressure regulators with an appropriate coating such as SilcoNert® 2000 has demonstrated a reduction in HCl losses due to adsorption [12, 13]. It is also important to maintain minimal humidity both in the measurement system and in the mixtures [12, 13]. For the measurement system, this is already achieved by passing a continuous flow of dry nitrogen or hydrogen, as appropriate, before the analyses. For the mixtures, this could be improved by introducing a vacuum pump in the HCl filling station.

Moving forward, several key areas of focus will guide the next phase of this study. First, we will undertake a comprehensive validation of the existing analytical method to ensure its accuracy and precision across a broad spectrum of HCl concentrations. This validation process will involve refining the methodology to address potential limitations, particularly at trace concentrations.

Additionally, an ongoing stability study will be conducted to assess the long-term behavior and stability of HCl in H_2 mixtures at varying concentrations. This will ensure that prepared mixtures remain consistent over time, providing reliable analytical results.

We will also focus on improving the methodology for uncertainty evaluation. This will involve developing more robust procedures for quantifying uncertainties at different stages of the analytical process, thus improving the overall reliability and reproducibility of the results. Lastly, efforts will be made to expand the laboratory's capabilities to prepare and analyse HCl mixtures at the nanomol concentration level, enabling even greater sensitivity and precision in the detection of HCl impurities in hydrogen.

Through these efforts, this study aims to contribute significantly to advancing the laboratory's hydrogen analysis capabilities, ensuring more accurate and consistent impurity detection in hydrogen used for fuel and industrial applications.

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