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Characterization of HCl Primary Reference Gas Standards for Emission Monitoring

Iris de Krom [1*], *Sophie* Schout[1], *Luuk* Meijer[1], *Evtim* Efremov[1], *Stefan* Persijn[1], *Gerard* Nieuwenkamp[1] and *Adriaan* van der Veen[1]

[1] Van Swinden Laboratorium B.V. (VSL), Thijsseweg 11, 2629 JA Delft, Netherlands

Abstract. Hydrogen chloride (HCl) is a key acidic pollutant emitted by waste-to-energy plants, as well as in industrial processes such as cement manufacturing and fossil fuel combustion. Due to its harmful impact on human health and the environment, strict emission limits are enforced under regulations like the European Industrial Emissions Directive (2010/75/EU), revised in 2024, which require regular monitoring of HCl. In Europe, HCl emissions are typically monitored using wet-chemical methods in accordance with EN 1911. These methods exhibit high uncertainty at concentrations below 10 mg m^{-3}, the EU's daily average emission limit, prompting the exploration of more accurate alternatives. Optical gas analysers, already approved by the U.S. Environmental Protection Agency, offer a promising alternative with lower measurement uncertainty. These instruments require calibration with reference gas standards of established metrological traceability. To meet this requirement, VSL employed an optical gas analyser to investigate key factors influencing the development of primary reference materials (PRMs) with HCl. The study focused on stability, adsorption behaviour, and pressure dependence of HCl PRMs. As a result, VSL successfully produced PRMs for HCl in high-pressure cylinders, achieving amount fractions as low as 5 µmol mol^{-1} in nitrogen (approximately 10 mg m^{-3}) with an expanded relative uncertainty of 3% (k = 2). These PRMs are essential for ensuring accurate and reliable calibration of optical gas analysers used in emission monitoring applications.

1 Introduction

Hydrogen chloride (HCl) is a significant contributor to acid pollution, originating from waste-to-energy facilities and industrial activities such as cement production and fossil fuel combustion. Its detrimental impact on human health and ecosystems has led to strict regulatory controls, notably under the European Industrial Emissions Directive (2010/75/EU), which was revised in 2024 to reinforce emission limits and monitoring requirements [1]. Compliance with these regulations typically relies on wet-chemical measurement techniques, as prescribed by EN 1911 [2]. These methods exhibit considerable uncertainty at low concentrations however, particularly near the daily average limit of 10 mg m^{-3}, creating challenges for accurate monitoring.

To address these limitations, optical gas analysers have emerged as a promising alternative, offering improved precision and already gaining approval from the U.S. Environmental Protection Agency. Nevertheless, their effective deployment depends on calibration using reference gas standards with robust metrological traceability. Developing such standards for HCl presents unique challenges due to its reactive nature and adsorption behaviour, especially at low amount fraction levels [3-5]. To evaluate and benchmark the competence for HCl gas standards and analysis the first key comparison (CCQM-K175) was executed between 2020 and 2024 [6]. For the CCQM-K175, travelling gas standards with approximately 30 µmol mol^{-1} HCl in nitrogen were used. During the key comparison, VSL utilised HCl primary gas standards with mole fractions from 100 µmol mol^{-1} to 5 µmol mol^{-1} for the calibration of their analyser [6]. Building on the successful results obtained in the CCQM-K175 key comparison, VSL has undertaken further investigation into the properties of our HCl gas standards. This study focussed on the critical factors influencing the preparation of primary reference materials (PRMs) for HCl, including stability assessment, cylinder wall adsorption, and pressure dependence of the amount fraction HCl. The results obtained in the CCQM-K175 and this study demonstrate the successful production of PRMs in high-pressure cylinders at amount fractions as low as 5 µmol mol^{-1} in nitrogen [6]. These advancements provide a solid foundation for reliable calibration of optical gas analysers, supporting accurate emission monitoring and regulatory compliance.

2 Methods and materials

2.1 Materials for preparing HCl PRMs

HCl gas is highly corrosive and toxic, making the accurate and safe preparation of HCl gas mixtures critically important. To ensure accurate and safe preparation, a dedicated gas filling station was used to prepare static gas mixtures in high-pressure cylinders starting from pure HCl gas. The facility, custom-built in collaboration with Nippon Gases Belgium N.V. and HTR Rotterdam B.V. (Figure 1), was commissioned in 2024. This facility not only ensures a safer working environment but also enables the production of highly accurate static gas mixtures in accordance with ISO 6142-1, with a preparation expanded uncertainty of just

* Corresponding author: idekrom@vsl.nl

0.08% (k = 2) [7]. The gas filling station is specifically designed to sample acid-forming gases, such as HCl, from a gas cylinder. It reduces the cylinder pressure to an outlet pressure with an needle valve. The design allows purging to be carried out with an inert gas (e.g., nitrogen), so it can be used with reactive, toxic and corrosive gases and gas mixtures of middle to high amount fractions. Purging with an inert gas, before initial start-up or while the cylinders are being changed, flushes all the atmospheric air from the system to ensure safe utilization of the process gas. The gas filling station is primarily constructed of electropolished stainless steel.

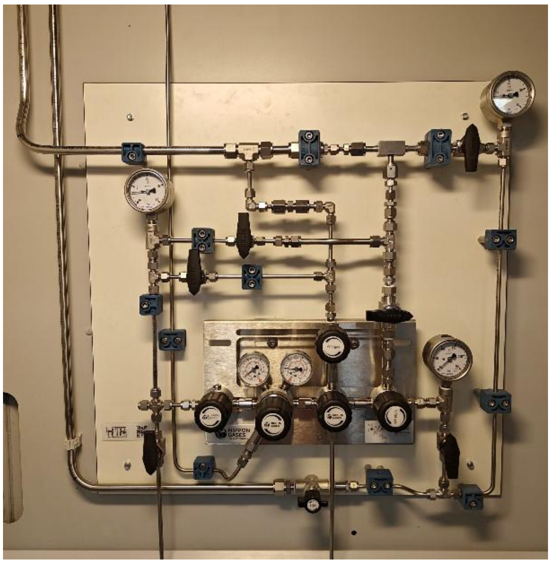

Fig. 1. Dedicated HCl gas filling station.

For mixtures with HCl amount fractions greater than or equal to 1000 µmol mol^{-1} 10 L stainless steel high-pressure cylinders from Nippon Gases (BE) are used. Amount fractions below 1000 µmol mol^{-1} HCl are prepared in 10 L aluminium high-pressure cylinders from Luxfer (UK) with a special HCl passivation from Air Liquide (FR).

Pure HCl gas (quality 5.0, >99.999%) was purchased from Nippon Gases (BE). The purity table provided by the supplier was adopted (Table 1). The pure nitrogen (grade 6.0, >99.9999%, BIP+, Air Products) used for the dilutions was checked for impurities in accordance with ISO 19229 [8, 9].

Table 1. Purity table HCl.

Component	Amount fraction (µmol mol^{-1})	Uncertainty (µmol mol^{-1})
Methane	0.50	0.29
Carbon monoxide	0.50	0.29
Carbon dioxide	1.0	0.6
Water	0.50	0.29
Nitrogen	1.5	0.9
Oxygen	0.50	0.29
Hydrogen chloride	999995.5	1.2

2.2 Gravimetric preparation of HCl PRMs

Two series of HCl PRMs were prepared, using the new gas filling station, starting from pure HCl by dilution with nitrogen (Figure 2). The preparation process complies with ISO 6142-1, which specifies the gravimetric method for producing calibration gas mixtures with high accuracy and traceability [7, 10].

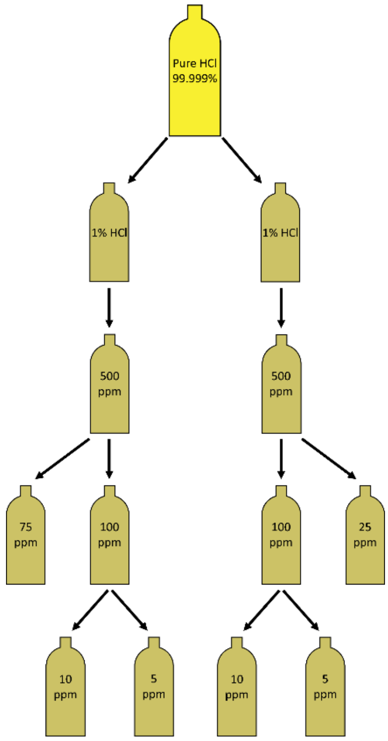

Fig. 2. Series of HCl PRMs prepared.

2.3 Analyser for HCl gas mixtures

For the analysis of the HCl PRMs, a spectrometer based on optical feedback cavity enhanced absorption spectroscopy (OF-CEAS) from AP2E (FR) was used. The cylinders were equipped with a Silconert coated stainless steel pressure regulator and the regulator was flushed prior to use. The measurements are conducted manually by connecting the PRMs to the analyser using short pieces of PFA tubing. A flow of 1000 ml min^{-1}, controlled by a Silconert coated Bronkhorst (NL) thermal mass flow controller, is led to the analyser.

The analyser can be used in the range from 1 µmol mol^{-1} up to 350 µmol mol^{-1}, with a detection limit of 0.6 µmol mol^{-1} and an expanded measurement uncertainty of 1.6% (k = 2), relative. Under dry conditions, the response time of the analyser is between 15 minutes and 60 minutes. The analyser is calibrated with at least 3 primary gas standards for the verification of new PRMs. As a calibration function, a straight-line model was used, established according to ISO 6143 [11].

2.4 Stability study

An important property of reference materials is the stability period, reflected as an expiration date on the certificate [12]. In the case of the static PRMs, this is the period during which the composition of the gas mixture in a cylinder is stable within the range of the measurement uncertainty. A stability study on 10 µmol mol^{-1} and 1 µmol mol^{-1} HCl PRMs was performed with 2 different cylinder passivation treatments. One general passivation and one special HCl passivation (Figure 3). To two of the 1 µmol mol^{-1} PRMs, 2 µmol mol^{-1} of water was added.

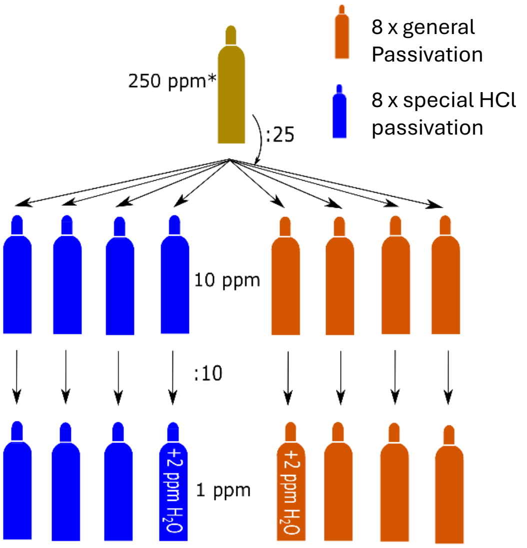

Fig. 3. HCl PRMs prepared for the stability study with two different cylinder passivation treatments.

The 10 µmol mol^{-1} PRMs were analysed five times over a period of more than 500 days, the 1 µmol mol^{-1} PRMs were analysed three times over a period of almost 400 days. Before each analysis the analyser was calibrated with primary gas standards.

2.5 Adsorption behaviour

HCl is very reactive and adsorbs easily on surfaces including the cylinder wall, reducers and tubing. Adsorption can lead to losses during and after preparation. To determine whether this loss is significant the decanting method is typically used [13, 14]. For this test, two 10 µmol mol^{-1} PRMs were used. Approximately half of the gas was decanted into an empty cylinder followed by cross-comparison.

2.6 Pressure dependence

Finally, the influence of pressure on the composition of HCl PRMs was determined. It is important that the amount fraction HCl remains within the coverage interval stated on the certificate when the pressure in the cylinder decreases due to use of the PRM. HCl strongly adsorbs onto the internal surface of the cylinder. As the mixture is consumed, the pressure in the cylinder reduces and the amount faction of the HCl can increase substantially [4].

To determine this, a 10 µmol mol^{-1} PRM was analysed starting at a pressure of 7 MPa in the cylinder. At 3 moments in time the measurement was stopped to determine the pressure in the cylinder. After 2 days of analysis, the cylinder was empty.

3 Results and discussion

3.1 Development HCl PRMs

After preparation of the two sets of HCl PRMs, the composition of the gas standards was verified. Verification took place against existing primary gas standards that were also employed for the CCQM-K175 measurements [7]. The new series of PRMs showed good agreement with each other and were aligned with the primary gas standards used for the CCQM-K175 within the expanded uncertainty of 3% (k = 2) used for CCQM-K175 (Figure 4 and Figure 5).

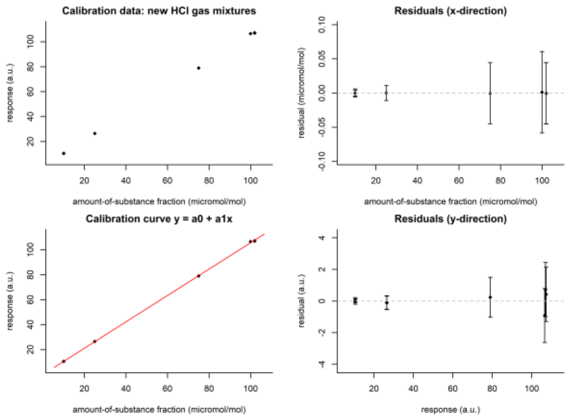

Fig. 4. Linear regression function and residuals for the new HCl PRMs.

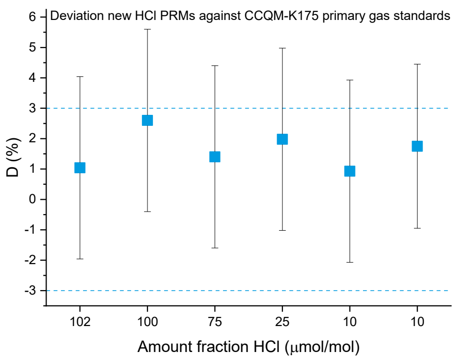

Fig. 5. Deviation of the new HCl PRMs compared to the calibration curve with the CCQM-K175 primary gas standards.

For a satisfactory fit of the data, it is required that the absolute values of the normalized residuals do not exceed 2. The normalized residual is the residual divided by the standard uncertainty [11]. All absolute values of the normalized residuals for new HCl PRMs were smaller than 2. The relative deviations of the new HCl PRMs compared to the calibration curve with the CCQM-K175 primary gas standards are within ± 3.0%.

3.2 Stability study

For the stability study 4 × 4 HCl PRMs were prepared. In Figure 6 the results of the stability study at 10 µmol mol^{-1} HCl are shown and in Figure 7 of the 1 µmol mol^{-1} HCl PRMs.

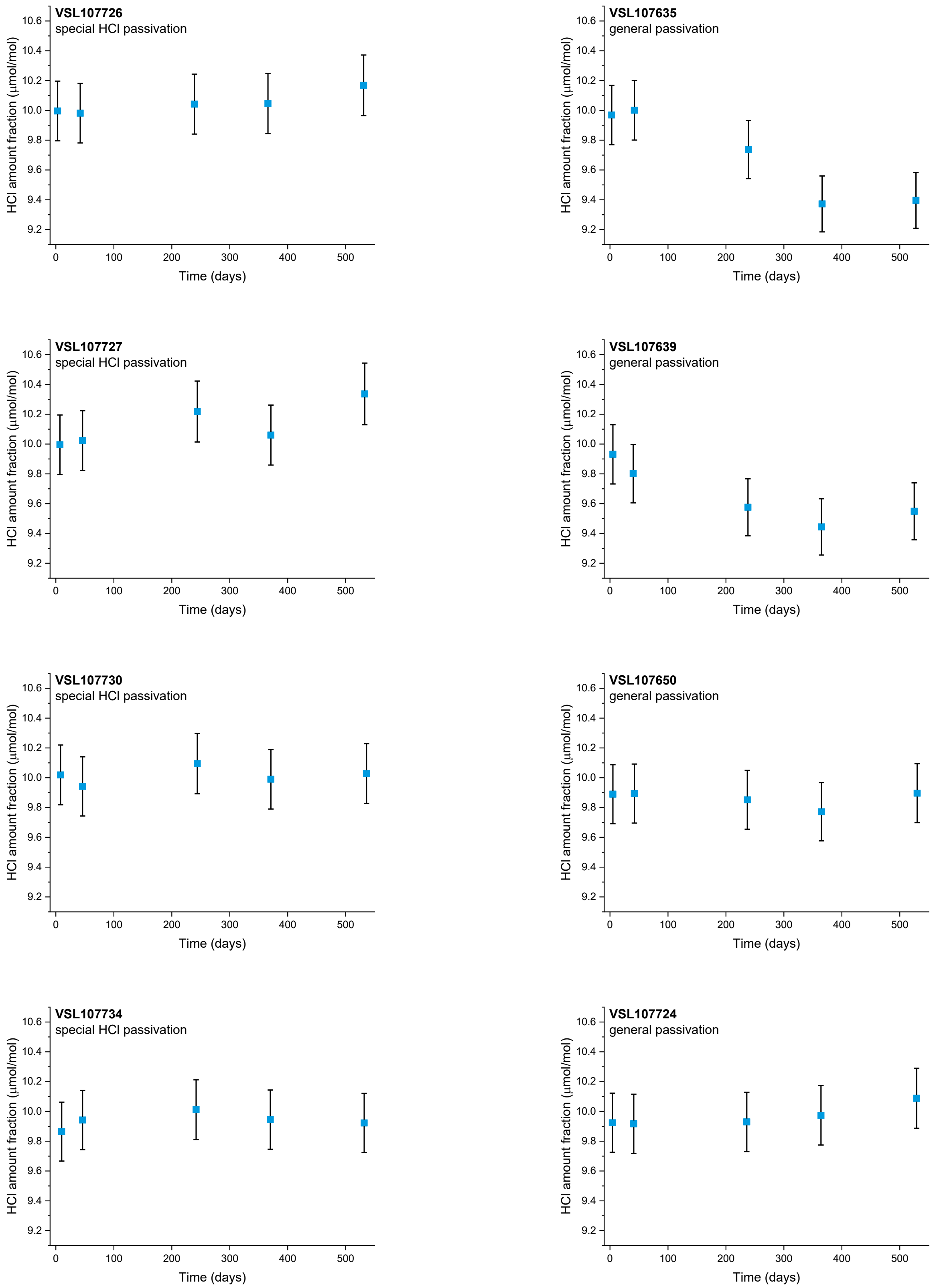

Fig. 6. Results stability study of 10 µmol mol^{-1} HCl. Fraction plotted against the time, uncertainty bars indicating 2.0% stability.

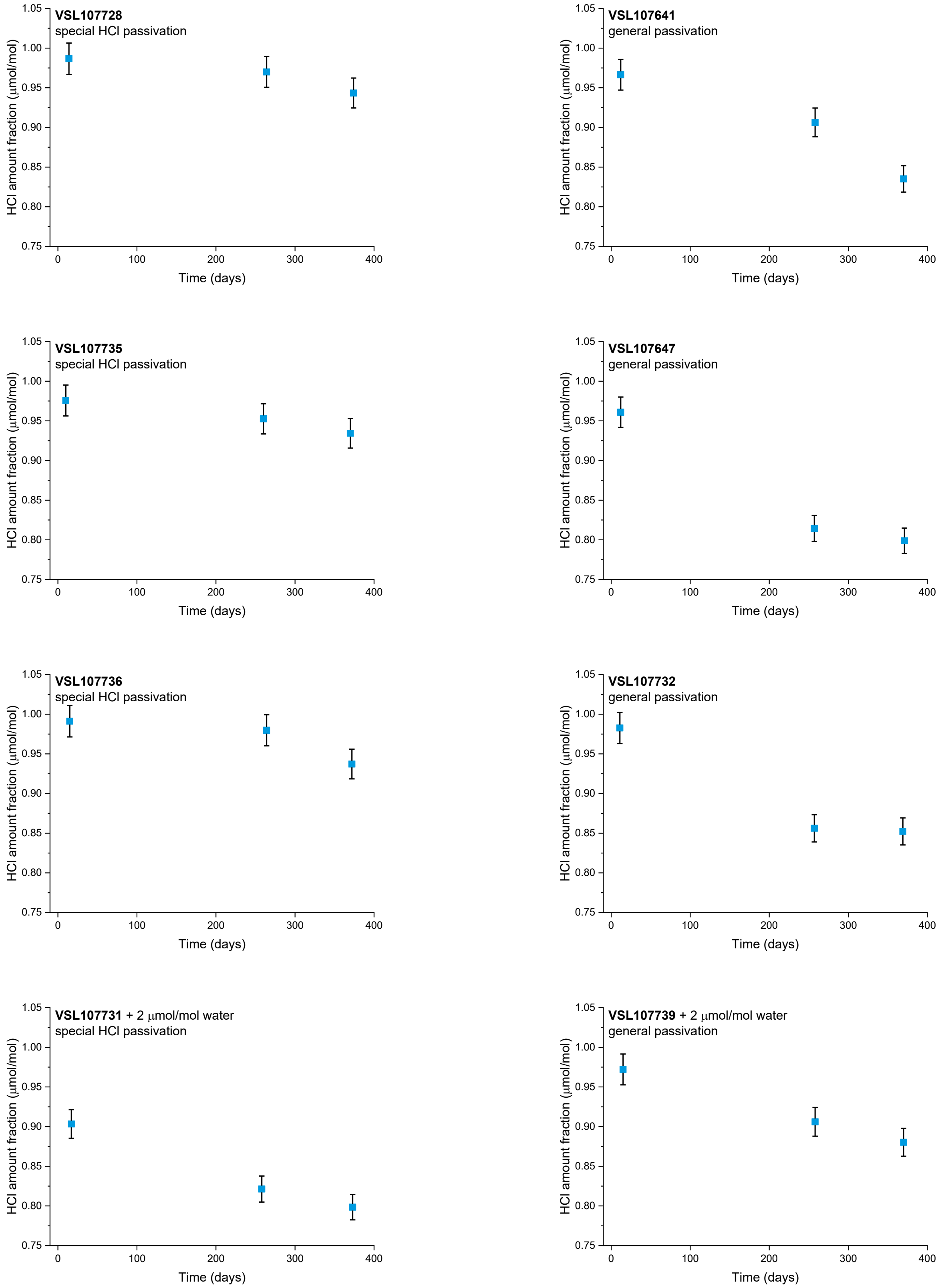

Fig. 7. Results stability study of 1 µmol mol^{-1} HCl. Fraction plotted against the time, uncertainty bars indicating 2.0% stability.

The results show excellent stability over a period of 500 days for the 10 µmol mol^{-1} PRMs in cylinders with a special HCl passivation. Based on the stability data for these mixtures, a 1-year stability within ± 2.0% was determined using regression to assess the data for meaningful instability and a random effects model to evaluate the uncertainty [12]. The calculations were performed in R software.

Two of the 10 µmol mol^{-1} PRMs in cylinders with a general passivation were found to be unstable (VSL107635 and VSL107639).
The 1 µmol mol^{-1} PRMs in cylinders with a special HCl passivation are stable for 200 days. Addition of water (VSL107731) leads to higher losses of HCl and instability of the mixture. The PRMs prepared in cylinders with a general passivation are not stable and addition of water (VSL107739) does not have an influence on the stability, this could indicate that these cylinders already contain water before filling, leading to instability.

3.3 Adsorption behaviour

Two 10 µmol mol^{-1} mixtures were prepared (VSL121486 and VSL207730) approximately half of both gas mixtures was decanted into empty cylinders (VSL121490 and VSL122544). All four mixtures were analysed three times (Figure 8).

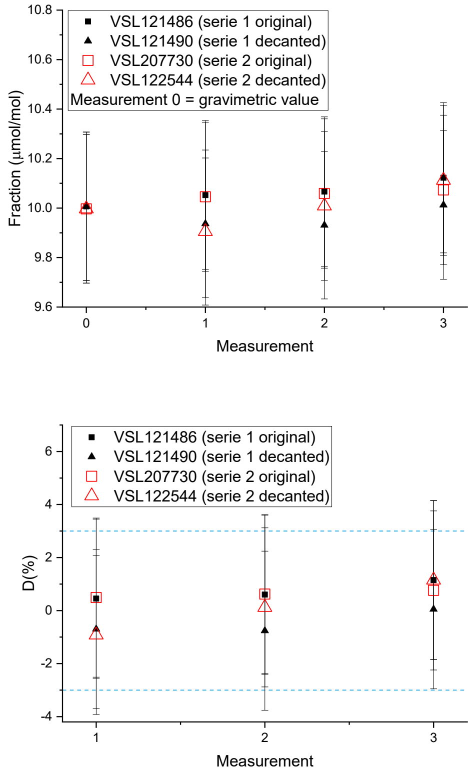

Fig. 8. Top – Fraction of the 10 µmol mol^{-1} mixtures compared to a calibration curve with HCl PRMs. Bottom – Relative deviation of the 10 µmol mol^{-1} mixtures compared to the calibration curve.

The decanted mixtures (VSL121490 and VSL122544) have a lower HCl fraction and more negative deviation compared to the original mixtures, except during measurement 3 where the fraction of VSL122544 is slightly higher compared to the original mixture (VSL207730). The maximum deviation is -1.36% (VSL121490) and -1.41% (VSL122544). This deviation falls well within the 3.0% uncertainty, therefore the loss is insignificant.

3.4 Pressure dependence

VSL307728 was analysed to determine the pressure dependence of the amount fraction HCl when emptying the gas cylinder (Figure 9).

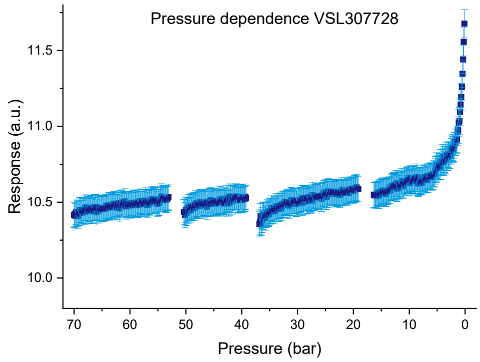

Fig. 9. Pressure dependence of the amount fraction HCl of a 10 µmol mol^{-1} gas standard. Gaps indicate pressure measurement. The dark points indicate the measurement values, the light colour indicates the expanded uncertainty of 3%.

In the beginning, and after pressure measurements, the analyser signal had to stabilize. After stabilisation the signal is stable until a pressure of 0.5 MPa is reached. Based on the results the gas mixtures cannot be used below a pressure of 0.5 MPa. This is below the default limit of 1 MPa for all PRMs and certified reference materials of VSL. The increase in fraction below 0.5 MPa is up to 10%. This effect can be attributed to the strong interaction of HCl with the cylinder surface compared to other gases [4].

3.5 HCl PRM uncertainty

For CCQM-K175 a relative expanded uncertainty of 3% (k = 2) was calculated. Based on the results obtained in this study the uncertainty budget for the HCl PRMs was determined with sources from gravimetry, measurement uncertainty, stability and adsorption (Table 2).

Table 2. Uncertainty budget HCl PRMs

	U_{rel} (%)
Gravimetric uncertainty	0.08
Measurement uncertainty	1.6
Stability	2.0
Adsorption	1.4
HCl PRM	**3**

The relative expanded uncertainty for the HCl PRMs down to 5 µmol mol^{-1} is 3% (k = 2).

4 Conclusion

PRMs for HCl in high-pressure cylinders were successfully developed and characterised. Stability, adsorption and pressure dependence studies confirm the robustness of these mixtures, supporting the claimed expanded uncertainty of 3%. This work is underpinned by the excellent comparison with the primary gas standards used for the CCQM-K175, allowing the continuation of the metrological traceability chain. These PRMs are critical for the traceable calibration of optical gas analysers in emission monitoring, ensuring accurate, reliable, and comparable measurements across laboratories and industries.

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ORCID iDs

Iris de Krom https://orcid.org/0000-0001-5895-5959
Luuk Meijer https://orcid.org/0009-0001-5783-3375
Stefan Persijn https://orcid.org/0000-0002-4356-4266
Adriaan van der Veen https://orcid.org/0000-0002-9648-5123

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