International Comparison CCQM-K175 – Hydrogen chloride in nitrogen

Jinsang Jung[1], Sanghyub Oh[1], ByungMoon Kim[1], Christina Cecelski[2], Cassie Goodman[2], Jennifer Carney[2], David R. Worton[3], Yoana Hristova[3], Michael Ward[3], Ruth Hill-Pearce[3], Paul Brewer[3], Javis Nwaboh[4], Volker Ebert[4], L.A. Konopelko[5], Y.A. Kustikov[5], A.V. Kolobova[5], I.K. Chubchenko[5], Iris de Krom[6], Evtim Efremov[6], Adriaan van der Veen[6]

[1]Korea Research Institute of Standards and Science (KRISS), Gas Metrology Group, 267 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea
[2]National Institute of Standards and Technology (NIST), Gas Metrology Group, 100 Bureau Drive Building 301, Gaithersburg, MD 20899-3574, United States of America
[3]National Physical Laboratory (NPL), Teddington, Middlesex, TW11 0LW, United Kingdom
[4]Physikalisch-Technische Bundesanstalt (PTB), Spektrometrische Gasanalytik, AG 3.42, Bundesallee 100, 38116 Braunschweig, Germany
[5]D.I. Mendeleyev Institute for Metrology (VNIIM), Department of State Standards in the field of Physical Chemical Measurements, 19, Moskovsky Prospekt, 198005 St-Petersburg, Russia
[6]Van Swinden Laboratorium (VSL), Chemistry Group, Thijsseweg 11, 2629 JA Delft, the Netherlands

Field

Amount of substance

Project reference

CCQM-K175

Subject

Comparison of hydrogen chloride (HCl) in nitrogen (track C)

Organizing body

CCQM-GAWG

Coordinator

KRISS
Jinsang Jung
267 Gajeong-ro, Yuseong-gu
Daejeon 34113
Republic of Korea
Phone +82 42 858 5934
E-mail jsjung@kriss.re.kr

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1 Introduction

Hydrogen chloride (HCl) is a colourless, toxic, and highly corrosive gas that poses risks to both human health and the environment. It is emitted from various sources, including fossil fuel combustion and municipal waste incineration. Consequently, most governments have established stack emission limits for HCl and monitor the emission levels accordingly. To ensure reliable measurement data from chimneys, periodic calibration of HCl monitors is essential using standard gas mixtures. However, due to its highly corrosive nature and strong tendency to adsorb onto the inner surface of cylinders and gas tubes, developing HCl standard gas mixtures in high-pressure cylinders remains a challenge.

This comparison aims to evaluate calibration and measurement capabilities to ensure international equivalence for HCl in nitrogen at an amount fraction of 30 μmol mol^{-1}.

2 Design and organization of the key comparison

2.1 Participants

Table 1 presents the participants in this key comparison. A total of six National Metrology Institutes (NMIs) participated, with KRISS as the coordinating laboratory.

Table 1. List of participants.

Acronym	**Country**	**Institute**
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NIST	US	National Institute of Standards and Technology, Gaithersburg, MD, United States of America
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
PTB	DE	Physikalisch-Technische Bundesanstalt Braunschweig, Germany
VNIIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands

2.2 Measurement standards

KRISS prepared travelling standards in aluminium cylinders gravimetrically according to ISO 6142-1 standard [1]. The pressure in the cylinders was approximately 10 MPa. The nominal amount fraction of HCl in nitrogen was 30 μmol mol^{-1}.

The specification of aluminium cylinders is as follows:

- Manufacturer: Luxfer in UK
- Internal volume: 10 dm^3
- Valve type: G-12, HAMAI industries in Japan, 22 mm diameter Whitworth screw thread

The purity of pure HCl (Tsurumi Soda, Japan) and nitrogen balance gas (Deokyang, Rep. of Korea), expressed as amount fractions, was equal to 99.9923 % and 99.9998 %, respectively. Tables 2 and 3 present the purity tables for pure HCl and N_2, respectively.

Table 2. Purity table for pure HCl.

Component	Amount fraction (μmol mol^{-1})	Standard uncertainty (μmol mol^{-1})
H_2	61.59	15.40
O_2+Ar	0.14	0.04
N_2	8.99	2.25
CH_4	0.06	0.04
CO_2	1.64	0.95
H_2O	5.00	1.25
HCl	999922.58	15.64

Table 3: Purity table for pure N_2.

Component	Amount fraction (μmol mol^{-1})	Standard uncertainty (μmol mol^{-1})
H_2	0.05	0.0289
O_2+Ar	0.35	0.0875
CH_4	0.0005	0.0003
CO	0.0005	0.0003
CO_2	0.0005	0.0003
HCl	0.001	0.0006
H_2O	1.2	0.1200
N_2	999998.40	0.15

The final gas mixtures, with a nominal amount fraction of 30 μmol mol^{-1}, were prepared using a three-step static dilution process (1 cmol mol^{-1} → 500 μmol mol^{-1} → 30 μmol mol^{-1}). The gravimetric amount fractions, $x_{i,\mathrm{grav}}$, of component i were determined based on gravimetry and purity analysis, and their uncertainties, $u(x_{i,\mathrm{grav}})$, were propagated according to the Guide to the expression of Uncertainty in Measurement (GUM) [2] using GUM Workbench (Metrodata GmbH, Germany). Table 4 shows gravimetric amount fractions and standard uncertainties of the CCQM-K175 travelling standards.

Table 4. Summary of the gravimetric amount fractions and standard uncertainties of the CCQM-K175 travelling standards.

Cylinder No	Prepared date (yyyy.mm.dd)	Amount fraction, x_{grav} (μmol mol^{-1})	Standard uncertainty, $u(x_{\mathrm{grav}})$ (μmol mol^{-1})
D63 4067	2021.11.15	29.997	0.011
D63 4090	2021.11.15	30.057	0.011
D64 1531	2021.11.15	29.996	0.011
D64 1550	2021.11.15	30.074	0.012
D98 3267	2021.11.16	30.061	0.011
D98 3274	2021.11.16	30.056	0.011
D98 3403	2021.11.16	30.013	0.011

2.3 Measurement protocol

KRISS is responsible for dispatching the travelling standards to participating laboratories while participants are responsible for returning them to KRISS. The pressure of the returned travelling standards must be at least 5 MPa.

KRISS drafts the report for the CCQM-K175 key comparison. Participants are required to report their measurement data (at least three independent results for statistical analysis) to KRISS in the specified reporting format. Additionally, participants must submit detail information regarding their calibration standards, analytical methods, and uncertainty evaluation.

2.4 Schedule

Table 5. shows the schedule of the CCQM-K175 key comparison.

Table 5. The schedule of the CCQM-K175 key comparison.

Date	Stage
September 2020	Proposal of draft protocol
May 2021	Agreement of draft protocol
June 2021	Registration of participants
September 2021	Preparation of travelling standards
October-November 2021	Analysis of travelling standards by KRISS
December 2021	Shipment of travelling standards to NMIs
January-March 2022	Measurement by NMIs
January 2023	Return of travelling standards to KRISS
December 2022	Measurement report due
January 2023	Re-analysis of travelling standards by KRISS for stability
August 2023	Report individual results to participants
September 2023	Received confirmation from all participants about their reported results
January 2024	Draft A available

2.5 Determination of gravimetric amount fractions and associated expanded uncertainties

The prepared amount fraction of component *i* in a gas mixture, $x_{i,\mathrm{prep}}$, is calculated using Equation (1) by incorporating the stability of component *i* according to the ISO 6142-1 standard [1].

$$x_{i,\mathrm{prep}} = x_{i,\mathrm{grav}} + \Delta x_{i,\mathrm{stab}} \quad (1)$$

Its uncertainty, $u(x_{i,\mathrm{grav}})$, is calculated using Equation (2).

$$u(x_{i,\mathrm{grav}}) = \sqrt{\sum_{j=1}^{q}\left(\frac{\partial x_i}{\partial M_j}\right)^2 \times u^2(M_j) + \sum_{k=1}^{r}\left(\frac{\partial x_i}{\partial m_k}\right)^2 \times u^2(m_k) + \sum_{k=1}^{r}\sum_{j=1}^{q}\left(\frac{\partial x_i}{\partial y_{j,k}}\right)^2 \times u^2(y_{j,k})} \quad (2)$$

where $u(x_{\mathrm{i,grav}})$ is obtained by combining the uncertainties from molar mass of component *j* (M_j), weighing of mass added of the parent gas *k* (m_k), and amount fraction of component *j* in the parent gas *k* ($y_{j,k}$) using the GUM Workbench (Metrodata GmbH, Germany).

The stability of component *i* in a gas mixture consists of:

- Short-term stability ($\Delta x_{i,\mathrm{stab\_S}}$): Due to initial adsorption of component *i* onto the inner surface of the gas cylinder.
- Long-term stability ($\Delta x_{i,\mathrm{stab\_L}}$): Arising from interactions with impurities in the parent gases, reactions with the cylinder's inner surface, further adsorption, or desorption of previously adsorbed component i.

Short-term stability is assessed using the cylinder-to-cylinder division method [3], while long-term stability is evaluated by re-verifying the travelling standards upon their return to the coordinating laboratory, using newly prepared reference gas mixtures.

$$\Delta x_{i,\mathrm{stab}} = \Delta x_{i,\mathrm{stab\_S}} + \Delta x_{i,\mathrm{stab\_L}} \tag{3}$$

The uncertainty of $x_{i,prep}$ is calculated using Eq. (4).

$$u(x_{i,\mathrm{prep}}) = \sqrt{u^2(x_{i,\mathrm{grav}}) + u^2(x_{i,\mathrm{stab\_S}}) + u^2(x_{i,\mathrm{stab\_L}})} \tag{4}$$

If travelling standards are stable, $\Delta x_{i,\mathrm{stab}}$ becomes zero.

$$x_{i,\mathrm{prep}} = x_{i,\mathrm{grav}} \tag{5}$$

$$u(x_{i,\mathrm{prep}}) = \sqrt{u^2(x_{i,\mathrm{grav}})} \tag{6}$$

ISO 6143 standard [4] describes the general procedure for the verification of the preparation of a gravimetric gas mixture. The validity of the gravimetric gas mixtures is demonstrated by verifying the composition as calculated from the preparation data with that obtained from analytical measurement. The verification criterion is shown in Equation (7).

$$\left|x_{i,\mathrm{prep}} - x_{i,\mathrm{ver}}\right| \leq 2\sqrt{u^2(x_{i,\mathrm{prep}}) + u^2(x_{i,\mathrm{ver}})} \tag{7}$$

Where the verification uncertainty $u(x_{i,ver})$ consists of analytical repeatability and reproducibility.

$$u(x_{i,\mathrm{ver}}) = \sqrt{u^2(x_{i,\mathrm{repeat}}) + u^2(x_{i,\mathrm{reprod}})} \tag{8}$$

When the verification criterion shown in Equation (7) is not satisfied with the best analytical techniques, gas mixtures should be prepared again. If the verification criterion shown in Equation (7) is still not satisfied, the standard uncertainty caused by inhomogeneity between gas mixtures, $u(x_{i,\mathrm{homo}})$ can be added to $u(x_{i,\mathrm{ver}})$ as following Equation (9).

$$u(x_{i,\mathrm{ver}}) = \sqrt{u^2(x_{i,\mathrm{repeat}}) + u^2(x_{i,\mathrm{reprod}}) + u^2(x_{i,\mathrm{homo}})} \tag{9}$$

Where $u(x_{i,\mathrm{homo}})$ can be calculated from standard deviation of sensitivity ratios of the travelling standards during verification measurements. The sensitivity ratio is calculated as following Equation (10).

$$\text{Sensitivity ratio} = {}^{(S/x)_{sample}}\Big/_{(S/x)_{reference}} \tag{10}$$

Where *S* represents NDIR HCl response.

Finally, the reference value of a component *i* in gas mixture, $x_{i,\mathrm{ref}}$, is expressed as Equation (11):

$$x_{i,\mathrm{ref}} = x_{i,\mathrm{prep}} \tag{11}$$

The standard uncertainty of $x_{i,\mathrm{ref}}$ is calculated using Equation (12).

$$u(x_{i,\mathrm{ref}}) = \sqrt{u^2(x_{i,\mathrm{prep}}) + u^2(x_{i,\mathrm{ver}})} \tag{12}$$

2.6 Measurement methods

The coordinating laboratory (KRISS) analyzed the HCl amount fractions in the travelling standards using an NDIR HCl analyzer (Thermo scientific, model 15i). The gas flow rate was controlled by a mass flow controller (MFC) (Brooks, 5850), which was calibrated against a displacement flow meter (MesaLabs, 530+ H). A SilcoNert-coated gas regulator and an MFC were used to control the gas sample flow rate, which was maintained at 1.0 L min^{-1} for the NDIR HCl analyzer. SilcoNert-coated stainless-steel lines were employed to minimize HCl adsorption losses during gas sample transport from the cylinder to the analyzer.

A-B-A sequence was used for sample analysis as follows:

Pure N_2 – KRISS HCl standard – pure N_2 - KC cylinder – pure N_2 – KRISS HCl standard

Pure N_2 was analyzed for 10 minutes, while the travelling standards were analyzed for 20 minutes. This cycle was repeated three times per day over three independent days. The raw response signal from the NDIR HCl analyzer was averaged using data from the last 4 minutes of each measurement period.

The measurement methods, measurement dates, and traceability information provided by the participating laboratories are summarized in Table 6.

Table 6. Summary of calibration methods and metrological traceability of participants.

Laboratory	Measurement date	Calibration	Traceability	Balance gas	Measurement technique
KRISS	12-14 April 2022	Single point	Own standards (ISO 6142-1)	Nitrogen	NDIR (Thermo, 15i)
NIST	21-25 April 2022	Multipoint	Standards generated by permeation (ISO 6145-10) [5]	Nitrogen	CRDS (Tiger Optics, Halo)
NPL	6-29 June 2022	Single point	Own standards (ISO 6142-1) diluted dynamically using sonic nozzles (ISO 6145-6) [6]	Nitrogen	CRDS (Picarro, G2108)
PTB	7 April-9 June 2022	HCl absorption line	PTB HCl Optical Gas Standard [7]	Nitrogen	PTB TDLAS
VNIIM	22 April-20 June 2022	Single point	Own standards (ISO 6142-1)	Nitrogen	Electrochemical sensor (Polytron, 700 or Satellite XT)
VSL	10 March-26 April 2022	Multipoint	Own standards (ISO 6142-1)	Nitrogen	OF-CEAS (AP2E, ProCeas HCl)

2.7 Degrees of equivalence

The degree of equivalence of the participant is defined as:

$$D_i = x_{i,\mathrm{Lab}} - x_{\mathrm{i,KCRV}} \tag{13}$$

where D_i is the degree of equivalence between laboratory result and the key comparison reference value (KCRV) while $x_{i,Lab}$ and $x_{\mathrm{i,KCRV}}$ are the values reported by each participant and the key comparison reference value, respectively.

The standard uncertainty of D_i ($u(D_i)$) is calculated as follows.

$$u(D_i) = \sqrt{u^2(x_{i,\mathrm{Lab}}) + u^2(x_{i,\mathrm{KCRV}})} \tag{14}$$

where $u(x_{i,Lab})$ and $u(x_{i,KCRV})$ are the standard uncertainties of $x_{i,\mathrm{Lab}}$ and $x_{i,\mathrm{KCRV}}$, respectively.

3 Results

3.1 Stability and verification of the travelling standards

The short-term stability of HCl in the travelling standards was evaluated using the cylinder-to-cylinder division method [3]. For this assessment, two sets of 30 μmol·mol^{-1} HCl in nitrogen gas mixtures were prepared and sequentially divided twice into similar type of cylinders. The mother cylinder was prepared 24 days after the preparation of the grandmother (G.M.) cylinder, and the daughter cylinder was prepared 3 days after the preparation of the mother cylinder. Figure 1 compares the sensitivity ratios of HCl in the grandmother (original), mother (1st division), and daughter (2nd division) cylinders. A decreasing trend in sensitivity ratios was clearly observed in both cases.

The adjusted amount fractions in the original gas cylinders were calculated using the sensitivity ratios from Figure 1 and Equation (10) in the reference [3]. The calculated values are presented in Table 7. The average decreases in HCl amount fractions during the 1st and 2nd experiments were 0.79% and 0.69 %, respectively. Despite using the same type of gas cylinders in both experiments, the relative decreases were not consistent. Consequently, the changes in amount fraction of the travelling standards were not corrected but were instead incorporated into the uncertainty term.

The relative standard uncertainty due to short-term stability, $u_{\mathrm{rel}}(x_{i,\mathrm{stab\_S}})$ was equal to 0.39 %, calculated as half of the average decreases of amount fractions from Table 7.

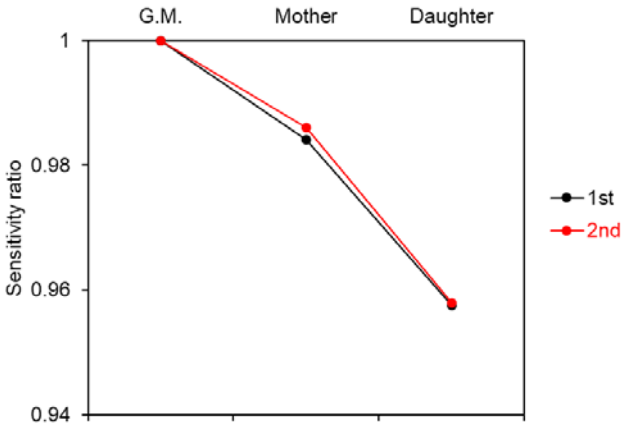

Figure 1. Comparison of sensitivity ratios of HCl in grandmother (G.M.), mother, and daughter cylinders during the cylinder-to-cylinder division experiment to evaluate the short-term stability of HCl in cylinders.

Table 7. Gravimetric and analytical amount fractions of 30 μmol mol^{-1} HCl in N_2 gas mixtures determined from the cylinder-to-cylinder division.

	Gravimetric amount fraction (μmol mol^{-1})	Analytical amount fraction (μmol·mol^{-1})	Relative decrease (%)
1st experiment	30.02	29.79	0.79
2nd experiment	29.993	29.78	0.69

After the travelling standards were returned to KRISS, the long-term stability of HCl in the travelling standards was evaluated by comparing them with a newly prepared gas standard. Figure 2 presents a comparison of the sensitivity ratios of the travelling standards and the newly prepared gas standard

(D06 7998). The error bars in Figure 2 represent expanded analytical uncertainties, which include both analytical repeatability and reproducibility.

As shown in Figure 2, the sensitivity ratios of the travelling standards were in good agreement with those of the newly prepared standard, within an expanded analytical uncertainty of 0.36 %. These results indicate that the travelling standards remained stable throughout the key comparison period. Since the analytical uncertainty is included in $u(x_{i,\text{stab\_S}})$, both $\Delta x_{i,\text{stab\_L}}$ and its associated uncertainty, $u(\Delta x_{i,\text{stab\_L}})$ were set to zero.

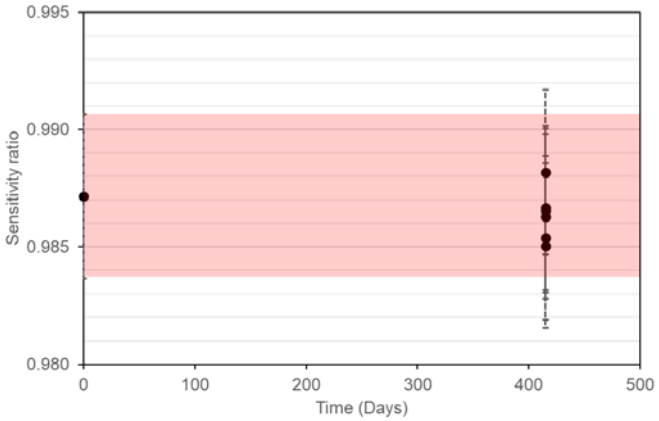

Figure 2. Comparison of sensitivity ratios of HCl in returned travelling standards (prepared on 15 November 2021) and newly prepared standard (prepared on 4 January 2023) to evaluate the long-term stability of HCl inside cylinders.

According to the short-term and long-term stability studies, the gravimetric amount fraction becomes the preparation values (i.e., $x_{i,\text{prep}} = x_{i,\text{grav}}$) and the preparation uncertainty, $u(x_{i,\text{prep}})$, is calculated from gravimetric uncertainty and short-term stability as follows:

$$u(x_{i,prep}) = \sqrt{u^2(x_{i,\text{grav}}) + u^2(x_{i,\text{stab\_S}})} \tag{15}$$

All travelling standards were verified three times over three separate days before being shipped to the participants. Figure 3 presents the verification results of the travelling standards. The verification amount fraction was determined by comparing the response areas of the travelling standards with that of the reference gas mixture (D64 1550).

The prepared amount fractions ($x_{i,\text{prep}}$) showed good agreement with the calculated amount fractions ($x_{i,\text{ver}}$) within an expanded uncertainty of 0.81 %. The expanded uncertainty in Figure 3 was derived from the preparation uncertainty and verification uncertainty, as defined in Equations (7) and (8).

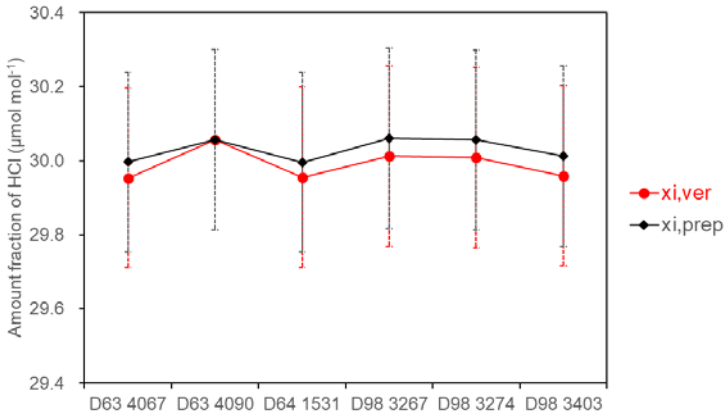

Figure 1. Comparison of prepared ($x_{i,\mathrm{prep}}$) versus analytical amount fractions ($x_{i,\mathrm{ver}}$) of the travelling standards.

Finally, the preparation amount fractions become the reference values ($x_{i,\mathrm{ref}} = x_{i,\mathrm{prep}}$), and the standard uncertainty of the reference value, $u(x_{i,\mathrm{ref}})$, is determined by combining the preparation uncertainty and the verification uncertainty as follows:

$$u(x_{i,ref}) = \sqrt{u^2(x_{i,\mathrm{prep}}) + u^2(x_{i,\mathrm{ver}})} \tag{16}$$

Here, the verification uncertainty used is the one obtained prior to shipping to participants.

3.2 Key comparison reference values (KCRVs) and degrees of equivalence

The reference amount fractions and uncertainty budget of the travelling standards are summarized in Table 8. The relative preparation standard uncertainty was estimated to be 0.40 %, primarily attributed to the short-term stability of HCl in gas cylinders. In contrast, the relative verification standards uncertainty was estimated to be equal to 0.14 %. Finally, the relative expanded uncertainty of the reference values was determined to be equal to 0.84 %.

Table 8. Summary of reference amount fractions and expanded uncertainty of the travelling standards.

Cylinder No	Amount fraction, $x_{i,\mathrm{ref}}$ (µmol mol^{-1})	Preparation uncertainty, $u(x_{i,\mathrm{prep}})$				Verification uncertainty, $u(x_{i,\mathrm{ver}})$				$U_{\mathrm{rel}}(x_{i,\mathrm{ref}})$ (%) (k = 2)	$U(x_{i,\mathrm{ref}})$ (µmol mol^{-1}) (k = 2)
		Gravi-metry	Short-term stability	Long-term stability	$u(x_{i,\mathrm{prep}})$ %	Repeat-ability	Repro-ducibility	Homogenity	$u(x_{i,\mathrm{ver}})$ %		
		$u(x_{i,\mathrm{grav}})$ (%)	$u(x_{i,\mathrm{stab\_S}})$ (%)	$u(x_{i,\mathrm{stab\_L}})$ (%)		$u(x_{i,\mathrm{repeat}})$ (%)	$u(x_{i,\mathrm{reprod}})$ (%)	$u(x_{i,\mathrm{homo}})$ (%)			
D63 4067	29.997	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253
D63 4090	30.057	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253
D64 1531	29.996	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253
D98 3267	30.061	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253
D98 3274	30.056	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253
D98 3403	30.013	0.04	0.39	0.0	0.40	0.13	0.07	0.0	0.14	0.84	0.253

In this comparison, the gravimetric amount fractions ($x_{i,\mathrm{ref}}$) are set to the KCRV ($x_{i,KCRV}$) as expressed in the following.

$$x_{i,KCRV} = x_{i,ref} \tag{17}$$

The KCRV ($x_{i,KCRV}$) and the reported results ($x_{i,\mathrm{Lab}}$) along with their expanded uncertainties are summarized in Table 9. Additionally, the difference (D_i) and their expanded uncertainties, calculated using Equations (12) and (13), are also presented in Table 9 and Figure 4.

Table 9. Key comparison reference values, participants' results, and the degrees of equivalence.

NMI	Cylinder No	$x_{i,\mathrm{KCRV}}$ (µmol mol^{-1})	$U(x_{i,\mathrm{KCRV}})$ (µmol mol^{-1})	$x_{i,\mathrm{Lab}}$ (µmol mol^{-1})	$U(x_{i,\mathrm{Lab}})$ (µmol mol^{-1})	D_i (µmol mol^{-1})	$U(D_i)$ (µmol mol^{-1})
NIST	D63 4067	29.997	0.253	28.27	0.44	-1.73	0.51
NPL	D63 4090	30.057	0.253	31.27	1.28	1.21	1.30
VNIIM	D64 1531	29.996	0.253	31.10	0.40	1.10	0.47
VSL	D98 3267	30.061	0.253	30.10	0.90	0.04	0.93
PTB	D98 3274	30.056	0.253	30.11	0.42	0.05	0.49
KRISS	D98 3403	30.013	0.253	29.98	0.32	-0.03	0.41

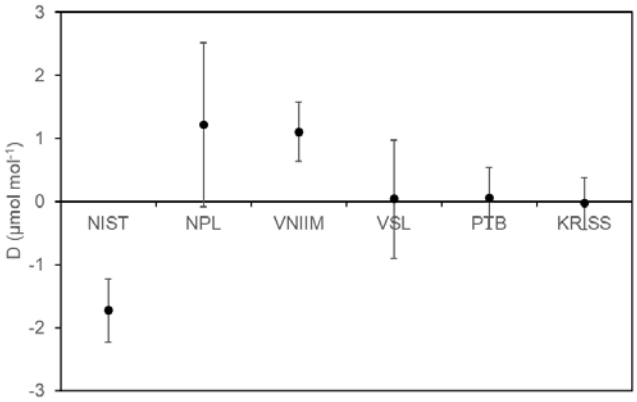

Figure 4. Degrees of equivalence at a nominal value of 30 µmol mol^{-1} for HCl amount fractions. The error bar represents the expanded uncertainty at a 95 % level of confidence.

A consensus value was computed using the hierarchical model from CCQM-K118. This model takes the reported results ($y_{\mathrm{lab},j}, u(y_{\mathrm{lab},j})$) and the results from the homogeneity study ($y_j, u(y_j)$) were treated as fixed constants. The observation equation underlying the Bayesian hierarchical model takes the form [8]

$$y_{\mathrm{lab},j} = \mu + \lambda_j + \beta_j + \epsilon_j \tag{18}$$

where μ denotes the consensus value, λ_j denotes an effect due to laboratory j, β_j an effect due to the batch homogeneity of the travelling standards, and ϵ_j a random effect due to laboratory j. It is assumed that the laboratory and homogeneity effects are mutually independent for each j. The β_j are modelled as fixed effects.

In the model as given, $\epsilon_j \sim \mathcal{N}(0, u_{\mathrm{lab},j}^2)$ where $u_{\mathrm{lab},j} = U_{\mathrm{lab},j}/k_{\mathrm{lab},j}$. The estimation of the λ_j separately from the β_j is possible because the latter effects are estimated from a different data set.

The likelihood of the $y_j'|\theta_j, \sigma_j$ can be described as [9][10]

$$y_j'|\theta_j \sim \mathcal{N}(\theta_j, \sigma_j^2) \tag{19}$$

where θ_j denotes the fitted adjusted laboratory mean and σ_j the standard uncertainty associated with y'_j. This standard deviation is computed from [8]

$$\sigma_j^2 = u^2(y_{\text{lab},i}) + u^2(\beta_j) \quad (20)$$

The θ_j are assumed to be drawn from a normal distribution with mean μ and standard deviation τ, where μ denotes the consensus value and τ the standard deviation of the laboratory effects λ_j. Conditional on these parameters, the θ_j are normally distributed [10]

$$\theta_j|\mu,\tau,\mathbf{y} \sim \mathcal{N}(\hat{\theta}_j, V_j) \text{ [20]}$$

with mean $\hat{\theta}_j$ and variance V_j, where

$$\hat{\theta}_j = \frac{\frac{1}{\sigma_j^2}y'_j + \frac{1}{\tau^2}\mu}{\frac{1}{\sigma_j^2}+\frac{1}{\tau^2}}; V_j = \frac{1}{\frac{1}{\sigma_j^2}+\frac{1}{\tau^2}} \quad (21)$$

The hierarchical model has two parameters, the mean μ and between-laboratory standard deviation τ. The Bayesian model is complete after specifying the prior probability distributions for μ and τ. The priors are specified as follows [8]

$$\mu \sim \mathcal{N}(\mu_0, 0.1\mu_0) \quad (22)$$

and

$$\tau \sim \text{Cauchy}(0, 0.02\tau_0) \quad (23)$$

Both priors are weakly informative about μ and τ, respectively. The model was coded in the Stan language [11] and the data were fitted using R [12]. The warm-up was 200 000 iterations and 2 000 000 samples were generated. Before calculating μ and τ, the data set was thinned by taking every fifth sample to reduce the autocorrelation in the output of the Markov Chain Monte Carlo method [10].

The consensus value, as the mean of the largest consistent subset, is 30.20 µmol mol^{-1} with a standard uncertainty of 0.28 µmol mol^{-1}. The between-laboratory standard deviation is 0.33 µmol mol^{-1}. The consensus value of the complete data set is 30.09 µmol mol^{-1} with a standard uncertainty of 0.47 µmol·mol^{-1}. The consensus value agrees well with the key comparison reference values.

4 Supported CMC claims

The results of this comparison support the Calibration and Measurement Capability (CMC) claims for HCl in nitrogen for standards and calibration over the amount fraction range of 10 µmol mol^{-1} to 100 µmol mol^{-1}. As shown in Annex A, the 10 µmol mol^{-1} HCl in nitrogen remained stable within an expanded analytical uncertainty of 0.39% over a period of 111 days. Since this uncertainty is smaller than the reference value uncertainty of 0.84% for 30 µmol mol^{-1} HCl in nitrogen listed in Table 8, the same relative uncertainty can be applied when extrapolating from 30 µmol mol^{-1} to 10 µmol mol^{-1}.

5 Discussion and conclusions

The CCQM-K175 result showed that four participants (NPL, VSL, PTB, and KRISS) agreed with their KCRV, but two participants (NIST and VNIIM) were discrepant. The consensus value underlined the showed agreement.

References

[1] International Organization for Standardization, “ISO 6142-1 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods”, ISO Geneva, 2015

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Annex A: Long-term stability evaluation of 10 µmol mol^{-1} HCl in nitrogen

The long-term stability of 10 µmol mol^{-1} HCl in nitrogen (D014780) was evaluated by comparing it with newly prepared gas standards (D285202, D298617). As shown in Figure A1, the sensitivities of 10 µmol mol^{-1} HCl in nitrogen was in good agreement with those of the newly prepared standards, within an expanded analytical uncertainty of 0.50 % over a period of 111 days.

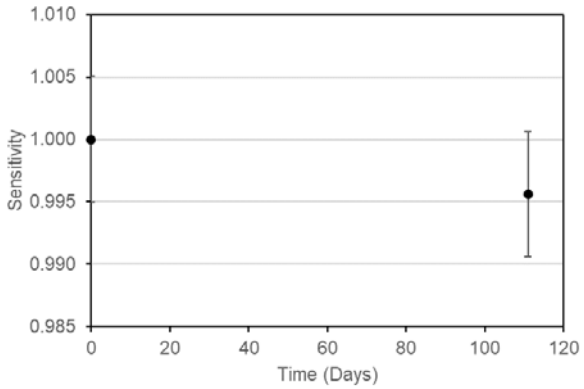

Figure A1. Comparison of sensitivities of 10 µmol mol^{-1} HCl in nitrogen (D014780: prepared on 22 November 2024) and newly prepared standard (D285202, D298617: prepared on 13 March 2025) to evaluate the long-term stability of HCl inside cylinders.

Annex B: Addendum to NIST Report for CCQM-K175 Measurement reports

The measurement results submitted by NIST revealed an underestimation of the amount fraction of HCl assigned to the CCQM-K175 sample (cylinder # D634067). NIST's measurements for this comparison included two sets of equipment: (1) a permeation system to produce on-demand standards for calibration, and (2) a commercial dilution system to dilute the CCQM-K175 sample to within the operating range of the cavity ring-down analyser. After a thorough review of the data, NIST has determined that the discrepant result for this comparison was most likely due to insufficient passivation of the dilution system.

Before the key comparison measurements began, the permeation system was set up with the HCl permeation device, and given several days for the temperature, flows, etc. to stabilize. This stabilization period also enabled passivation of the permeation chamber and associated tubing. The dilution system, on the other hand, which does not require an extended stabilization period, was set up shortly before the comparison measurements began. As a result, it is likely that the dilution system and associated sample lines were not adequately passivated prior to starting the analysis.

In addition to the measurements submitted for this comparison, NIST performed another set of analyses on the CCQM-K175 sample before returning the cylinder to KRISS. By the time these measurements were taken, the dilution system had been running (and therefore passivating) for nearly a week. The data from these additional analyses were not included in the final results submitted by NIST, due a large change in value assignment to the CCQM-K175 sample, and uncertainty surrounding whether these new measurements were sound. Although further reanalysis would have provided more clarity and confidence to these new measurements, this would have put the cylinder below the minimum required return pressure. Therefore, the seemingly discrepant results were excluded, and the cylinder was returned.

Figure B1 shows the instrument response of the diluted CCQM-K175 sample over the course of all measurements performed at NIST. Points numbered 1 through 58 (blue and orange) include the measurements obtained for the key comparison, whereas points 59 through 117 (green and purple) are measurements taken as part of the additional (excluded) analyses. The corresponding amount fraction values assigned to the CCQM-K175 sample are included in Figure B2 and Table B1.

Upon re-review of the measurement results, it is apparent that some of the HCl from the CCQM-K175 sample may have been lost to the interior surfaces of the dilution system and sample tubing, resulting in a lower amount fraction reading from the instrument. Since the permeation system was operated independently of the dilution system, the readings for the on-demand standards were not similarly impacted. Once the dilution system had been sufficiently passivated, the resulting amount fraction of the CCQM-K175 sample appeared to be very close to that of the key comparison reference value.

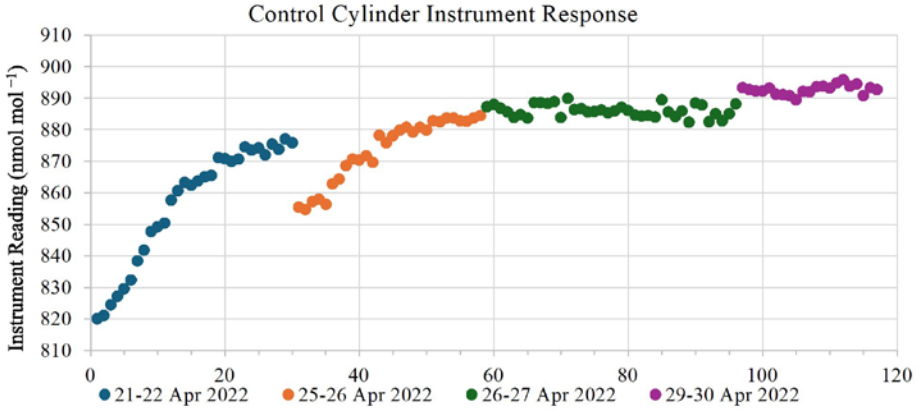

Figure B1: Instrument readings for the diluted CCQM-K175 sample over the duration of measurements performed at NIST.

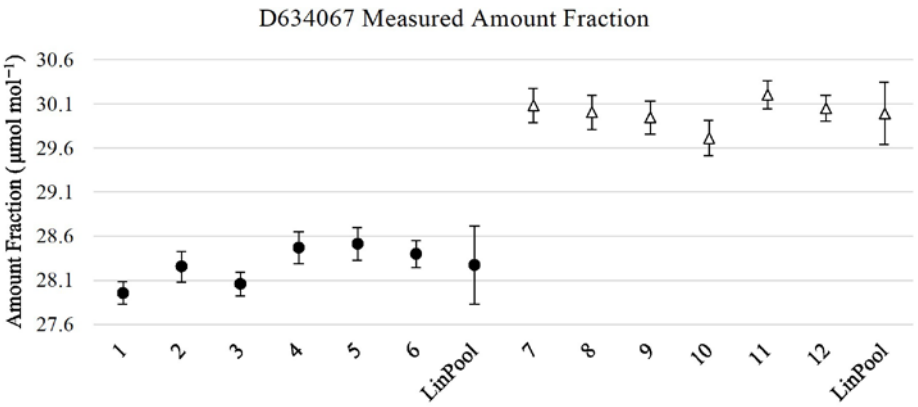

Figure B2: Amount fraction values assigned to the CCQM-K175 sample, as originally submitted for the key comparison (solid circles), and as reanalyzed before returning the cylinder to KRISS (open triangles). The numbered points represent replicated measurements, which were then combined using the NICOB Linear Pool consensus-building procedure (LinPool).

Table B1: Submitted and reanalyzed amount fraction values for the CCQM-K175 sample, as compared to the key comparison reference value (KCRV), with associated uncertainties for 95 % confidence (k = 2).

Measurement Result	Amount Fraction (µmol mol^{-1})	Expanded Uncertainty (µmol mol^{-1})
Submitted	28.27	0.44
Reanalyzed	29.99	0.35
KCRV	30.00	0.25

Annex C: Measurement reports

Acronym	Country	Institute
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NIST	US	National Institute of Standards and Technology, Gaithersburg, MD, United States of America
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
PTB	DE	Physikalisch-Technische Bundesanstalt Braunschweig, Germany
VNIIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands

Report Form CCQM-K175 HCl in nitrogen at 30 µmol mol^{-1}

Laboratory name: Korea Research Institute of Standards and Science (KRISS)
Cylinder number: D98 3403

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	12.04.2022	29.96	0.03	4

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	13.04.2022	29.97	0.15	4

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	15.04.2022	30.00	0.07	4

Final result

Component	Result (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Coverage factor
HCl	29.98	0.32	2

Calibration standards

From pure HCl and N_2, primary reference materials were prepared in accordance with [1]. All the mixtures were prepared in Luxfer cylinders (UK).

The scheme of preparation of calibration mixtures from pure substances is shown on figure 1.

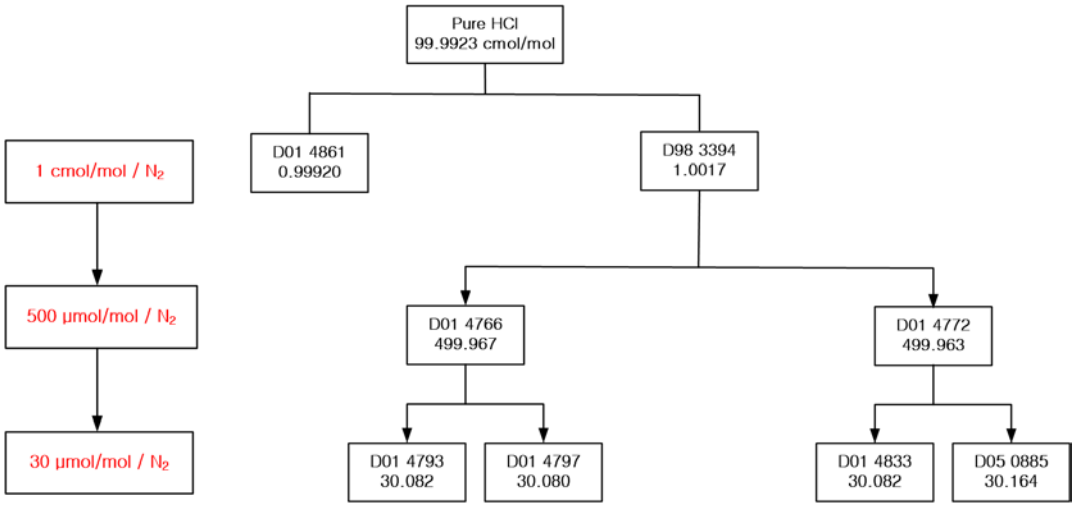

Figure 1. The scheme of preparation of calibration mixtures

The purities of pure HCl (Tsurumi Soda, Japan) and balance gas (Deokyang, Rep. of Korea) were determined by KRISS. The purities of pure HCl and N_2 balance were 99.9923% and 99.9998%, respectively.

Table 1: Purity table for HCl

Component	Amount fraction, µmol mol^{-1}	Standard uncertainty, µmol mol^{-1}
H_2	61.59	15.40
O_2+Ar	0.14	0.04
N_2	8.99	2.25
CH_4	0.06	0.04
CO_2	1.64	0.95
H_2O	5	1.25
HCl	999922.58	15.64

Table 2: Purity table for N_2

Component	Amount fraction, µmol mol^{-1}	Standard uncertainty, µmol mol^{-1}
H_2	0.05	0.0289
O_2+Ar	0.35	0.0875
CH_4	0.0005	0.0003
CO	0.0005	0.0003
CO_2	0.0005	0.0003
HCl	0.001	0.0006
H_2O	1.2	0.1200
N_2	999998.40	0.15

30 μmol/mol level of calibration cylinders were verified using a NDIR analyzer (Thermo, model 15i). Four cylinders were agreed within a relative standard uncertainty of 0.17 %. Amount fraction of HCl and their standard uncertainties in calibration standards are shown in Table 3.

Table 3: The values of HCl amount in the calibration standards

Cylinder ID	Amount fraction ($\mu mol\ mol^{-1}$)	Standard uncertainty ($\mu mol\ mol^{-1}$)
D01 4793	30.082	0.160
D01 4797	30.080	0.160
D01 4833	30.082	0.163
D05 0885	30.164	0.162

Instrumentation

1) HCl concentration measurement
   - HCl concentration was analyzed using a NDIR HCl analyzer (Thermo scientific, model 15i).
   - HCl concentration in a KC sample cylinder was determined by comparing response areas of the KC sample cylinder versus those of the KRISS calibration standard (D01 4793).
2) Flow rate measurement
   - Gas flow rate was controlled by a mass flow controller (MFC) (Brooks, 5850).
   - The MFC was calibrated against a displacement flow meter (MesaLabs, 530+ H).
   - The displacement flow meter was calibrated against the KRISS traceable flow rate standard.
3) Measurement configuration
   - SilcoNet coated gas regulator and MFC were used to control the flow rate of gas sample from the KC sample cylinder. The flow rate of gas sample was maintained at 1.0 L min^{-1}.
   - SilcoNet coated SS lines were used to minimize adsorption loss of HCl.

Calibration method and value assignment

1) Conditioning of a KC sample cylinder
   - KC cylinder was stored more than two days in a temperature-controlled laboratory at 22±1°C before analysis.
2) Analytical procedure
   - A-B-A sequence was used for sample analyses as follows
     Pure N_2 – KRISS HCl standard – pure N_2 - KC cylinder – pure N_2 – KRISS HCl standard
   - Pure N_2 was analyzed for 10 min whereas both the KRISS HCl standard and KC cylinder were analyzed for 20 minutes
   - This cycle was repeated 3 times a day
   - The KC sample cylinder was analyzed three independent days
3) Data processing
   - Raw response signals of the KRISS HCl standard and KC cylinder were averaged using last 4 min data.

Single point calibration method was used to determine HCl amount fraction in the comparison

gas mixture.

Uncertainty budget

Component	Abbreviation	Standard uncertainty (μmol mol^{-1})
*The uncertainty from the KRISS calibration standard (gravimetric preparation, verification)	$u_{\_ref}$	0.16
The uncertainty from repeatability of KC cylinder measurement	$u_{\_repeat}$	0.03
The uncertainty from reproducibility of KC cylinder measurement	$u_{\_reprod}$	0.01
Combined standard uncertainty	$u_{\_merg}$	0.16

*The uncertainty of the KRISS calibration standard was evaluated as described in Section 2.5 of this report.

Expanded uncertainty, U (k = 2) = 0.32 μmol/mol

References

[1] International Organization for Standardization. “ISO 6142-1 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods. ISO Geneva. 2015.

Authorship

Authorship: Jinsang Jung, Sanghyub Oh, ByungMoon Kim

Measurement report NIST

CCQM-K175: HCl in nitrogen at 30 µmol mol^{-1}
Laboratory: National Institute of Standards and Technology
Laboratory code: NIST
Cylinder number: D634067

Measurement 1#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	21/4/22	27.96	0.5 %	6

Measurement 2#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	21/4/22	28.25	0.6 %	6

Measurement 3#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	21/4/22	28.06	0.5 %	6

Measurement 4#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	25/4//22	28.47	0.6 %	6

Measurement 5#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	25/4/22	28.51	0.7 %	6

Measurement 6#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	25/4/22	28.40	0.5 %	6

Results

Component	Result (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Coverage factor
HCl	28.27	0.44	2

Calibration standards

Since NIST does not house primary standard mixtures (PSMs) of hydrogen chloride (HCl) in the amount fraction of 30 µmol mol^{-1}, standards were prepared by the use of a permeation device system (PDS). A permeation wafer device was purchased with a nominal permeation rate of 1900 ng min^{-1} ± 25 % at 30 ºC. The purchased wafer device was stated to be ≥ 99.0 % pure from the manufacturer. Additional impurity analysis was not performed by NIST, due to the inability to make such measurements at the

time of this study. Therefore, the manufacturer's purity specifications were converted into amount fraction as described in ISO 19229 [1].

The permeation wafer device was inserted into the PDS, which was set up in continuous-weighing-mode in compliance with ISO 6145-10 [2] and internal procedures. The mass of the HCl permeation wafer device was measured every 15 min using a Rubotherm magnetic suspension balance. The mass resolution of the balance is 0.001 mg. The total gas flow from the PDS was measured by a DH Instruments (DHI) MolBloc (1E3 Series) flow meter. The MolBoc had been previously calibrated by flowing known volumes of nitrogen across the flow meter following internal procedures. See Figure 1 for the permeation schematic setup.

The gas flow over the permeation wafer device (nitrogen, nominal purity ≥ 99.999 %) was kept constant at 800 mL min^{-1} at 38 °C. By varying the nitrogen dilution gas flow, a suite of HCl standards could be produced on demand. A permeation rate (q_{m}) in µmol min^{-1} was determined for the mean amount fraction to be analyzed using Eq. 1.

$$q_{\mathrm{m}} = \frac{slope \left|\frac{\Delta m}{\Delta t}\right| \cdot 10^{6}}{M} \qquad \text{(Eq. 1)}$$

q_{m}	Permeation rate (µmol min^{-1})
Δm	Change in mass (g)
Δt	Change in time (min)
M	Molar mass of HCl (g mol^{-1})

Instrumentation

The HCl component of the CCQM-K175 sample (cylinder #: D634067) was analyzed by cavity ring-down spectroscopy (CRDS) (Tiger Optics, Model Halo, HCl). Sample delivery pressure was controlled using a high-purity, two-stage stainless steel regulator dedicated to HCl service (DIN 477 No. 6). The regulator was passivated for one hour at a sample gas flow rate of approximately 300 mL min^{-1} prior to any measurements taken.

Due to the limited operating range of the CRDS (0 µmol mol^{-1} to 10 µmol mol^{-1}), the CCQM-K175 sample was diluted prior to analysis using an Environics Series 4040 gas dilution system. The delivery pressure of the sample was set to 0.137 MPa (20 psig). Sample gas flow was set to 30 mL min^{-1}, and the nitrogen dilution gas flow was set to 970 mL min^{-1}, producing a total flow (1000 mL min^{-1}) with a nominal amount fraction of 0.9 µmol mol^{-1}. The analyzer was purged for 5 min before sample data was collected.

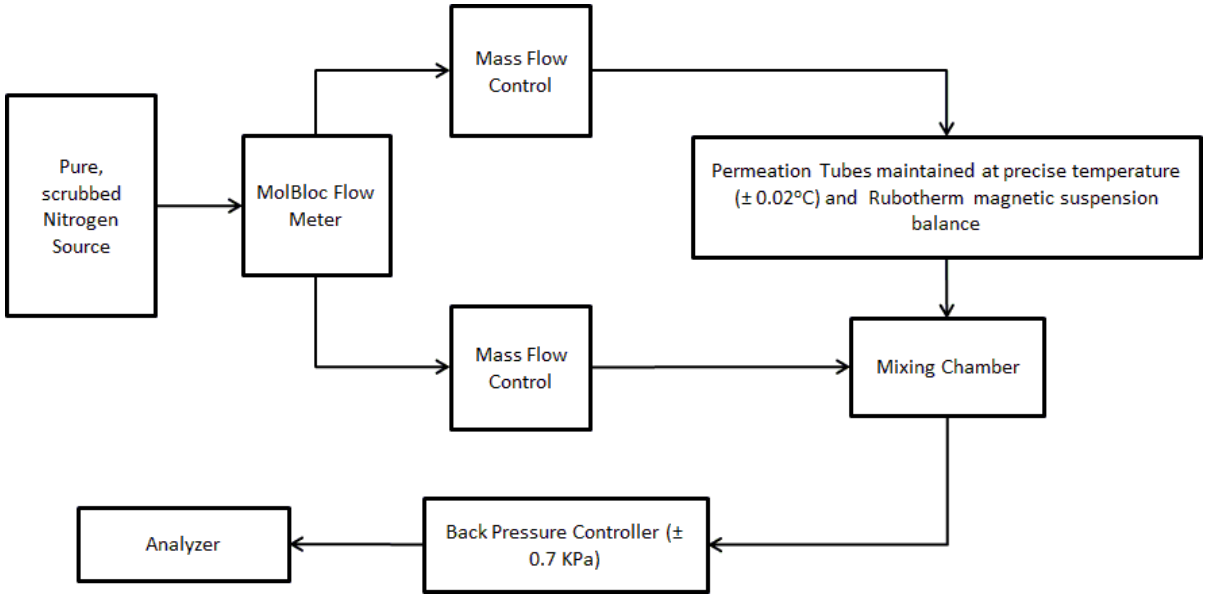

Figure 1: Schematic of the basic elements of the permeation device system.

Calibration method and value assignment

The CCQM-K175 sample was analyzed against a set of on-demand HCl standards (from the PDS) ranging from 0.7 µmol mol^{-1} to 1.0 µmol mol^{-1}. The diluted CCQM-K175 sample (from the gas dilution system) was used as the analytical control throughout the analysis.

Sample selection of the control or the on-demand standard was achieved using a computer operated gas analysis system (COGAS). This COGAS was configured so that the control was always flowing at 1000 mL min^{-1}, either to the analyzer (when the standard from the PDS flowed to vent) or to vent (when the standard from the PDS was flowing to the analyzer).

The analytical sequence was control, standard 1, standard 2, control, standard 3, *et cetera*, until all standards had been bracketed by the control. Each data point was an average of 60 readings taken at 1 s intervals, with six replicated measurements recorded for each sample in the sequence.

The above sequence was repeated a minimum of six times over two days (with the order of the standards being randomized in each set collected), giving six independent analyses from which the amount fraction of the CCQM-K175 sample could be determined.

Each analytical sequence of control, standard, standard, control was corrected for linear instrument drift by using Eq. 2. The corrected instrument response for each control in the sequence was then ratioed to each sample response in the sequence (Eq. 3).

$$R_C = R_{C1} + \frac{(R_{C2} - R_{C1})}{(N-1)} \cdot (n-1) \qquad \text{(Eq. 2)}$$

R_C	Drift-corrected control response (µmol mol^{-1})
R_{C1}	Average of repeat responses, control response 1 (µmol mol^{-1})
R_{C2}	Average of repeat responses, control response 2 (µmol mol^{-1})
N	Number of samples in sequence
n	Sample number in sequence

$$r = \frac{R_{Sn}}{R_C} \quad \text{(Eq. 3)}$$

r	Response ratio
R_{Sn}	Average n^{th} sample response (µmol mol^{-1})
R_C	Drift-corrected control response (µmol mol^{-1})

The average flow was also calculated for each sample response, which was then converted to a molar flow volume using Eq. 4.

$$\dot{n}_n = \frac{Q}{v_{\text{m}}} \quad \text{(Eq. 4)}$$

$\dot{n}_n$	Molar flow for n^{th} sample in sequence (mmol min^{-1})
Q	Average Flow (mL min^{-1})
v_{m}	Molar Volume (L mol^{-1})

The amount fraction for each on-demand standard was then calculated utilizing Eq. 5, also taking into account the manufacturer's reported impurity of the HCl wafer device.

$$x = \left(\frac{q_{\text{m}}}{\dot{n}_n}\right) \cdot 1000 \quad \text{(Eq. 5)}$$

x	Amount fraction (µmol mol^{-1})
q_{m}	Permeation rate (µmol min^{-1})
$\dot{n}$	Molar flow (mmol min^{-1})
n	Sample number in sequence

The data for each of the six analytical sequences were evaluated using a first-order generalized least-squares regression (GenLine) compliant with ISO 6143 [3,4]. The average ratio and uncertainty were plotted on the *x*-axis, and the gravimetric amount fraction and uncertainty were plotted on the *y*-axis for each on-demand standard.

Each of the resulting regression equations was then used to predict the HCl amount fraction of the control from a response ratio $r = 1.0000$ in Eq. 6. The regression parameters and corresponding amount fraction values are included in Table 1.

$$y_C = Ar + B \quad \text{(Eq. 6)}$$

y_C	Predicted amount fraction of control (µmol mol^{-1})
r	Response ratio
A	Slope
B	Intercept

A dilution factor (DF) was calculated for the dilution of the CCQM-K175 sample by dividing the sample flow by the total gas flow.

$$DF = \frac{Q_{\mathrm{K175}}}{Q_{\mathrm{TOT}}} \quad \text{(Eq. 7)}$$

DF	Dilution factor
Q_{K175}	Flow of the CCQM-K175 sample (mL min^{-1})
Q_{TOT}	Total flow (mL min^{-1})

The predicted value of the control from each regression equation was divided by the dilution factor to give the predicted amount fraction value (y) of the CCQM-K175 sample (see Table 1).

$$y = \frac{y_C}{DF} \quad \text{(Eq. 8)}$$

Table 1: HCl regression coefficients and predicted amount fractions for the control (y_C) and for the CCQM-K175 sample (y), with associated standard uncertainties.

Measurement	$y_C = Ar + B$		y_C (µmol mol^{-1})	DF	y (µmol mol^{-1})
	A	B			
1	0.8249 ± 0.0071	0.0145 ± 0.0067	0.8394 ± 0.0017	0.03002 ± 0.00004	27.96 ± 0.07
2	0.8216 ± 0.0089	0.0267 ± 0.0080	0.8483 ± 0.0024	0.03002 ± 0.00004	28.25 ± 0.09
3	0.8330 ± 0.0069	0.0093 ± 0.0067	0.8424 ± 0.0017	0.03002 ± 0.00004	28.06 ± 0.07
4	0.8507 ± 0.0179	0.0039 ± 0.0162	0.8547 ± 0.0025	0.03002 ± 0.00004	28.47 ± 0.09
5	0.8482 ± 0.0196	0.0078 ± 0.0178	0.8560 ± 0.0026	0.03002 ± 0.00004	28.51 ± 0.09
6	0.8338 ± 0.0168	0.0187 ± 0.0157	0.8526 ± 0.0021	0.03002 ± 0.00004	28.40 ± 0.08

The six individual values assigned to the CCQM-K175 sample were combined using the Linear Pool consensus-building procedure, as implemented in the NIST Consensus Builder (NICOB) [5], to produce the final amount fraction value and its associated uncertainty.

The Linear Pool procedure is a mixture model, which aggregates a set of measured values expressed in the form of probability distributions, thereby producing a consensus distribution. The probability distributions assigned to each of the six measurement results were assumed to be Gaussian, with means equal to their measured values, y, and standard deviations equal to the associated standard uncertainties, $u(y)$.

The probability distribution of the consensus value was determined as a mixture of the probability distributions associated with the measurements, with all measurements given equal weights. The sample size drawn from the mixture distribution was $K = 10^6$.

The results of the NICOB Linear Pool are summarized in Figure 2, and the final value assigned to the CCQM-K175 sample is listed in Table 2.

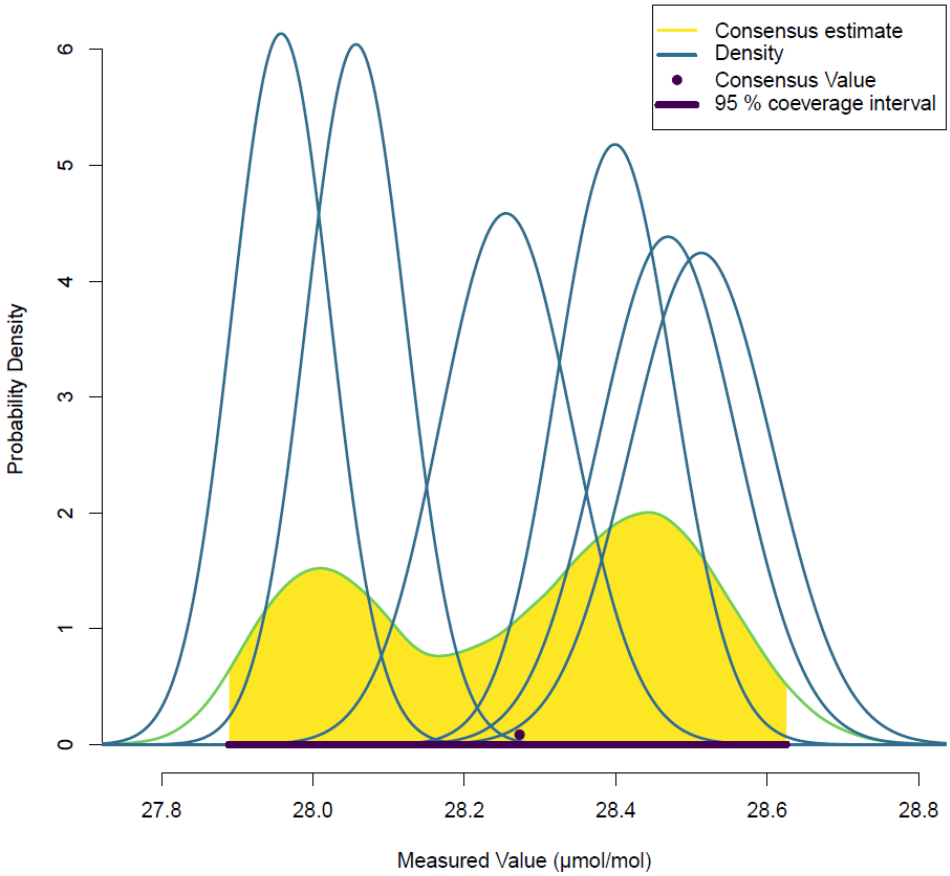

Figure 2: Probability density of the consensus value based on a sample of size $K = 10^6$ drawn from the equally-weighted mixture of Gaussian distributions assigned to the six measurements of the CCQM-K175 sample. The dark purple point marks the estimate of the consensus value, and the yellow shaded region under the curve comprises 95 % of the area under the curve: its projection onto the horizontal axis (dark purple line segment) is a 95 % coverage interval for the true value.

Table 2: Final HCl value assignment for the CCQM-K175 sample and associated uncertainty for 95 % confidence (k = 2).

Sample Number	Amount Fraction (μmol mol^{-1})
D634067	28.27 ± 0.44

Uncertainty evaluation

All measured data and calculations for the final amount fraction of HCl were reviewed for sources of systematic and random error. The following uncertainties were considered contributors to the overall uncertainty of the assigned value of the sample.

The uncertainty of the permeation rate was determined using the LINEST function in Excel (Eq. 9), as the uncertainty of the slope of the line from the calculation of the mass change of the permeation wafer over time.

$$u(q_{\mathrm{m}}) = \text{LINEST slope uncertainty} \quad \text{(Eq. 9)}$$

q_{m}	Permeation rate

The uncertainty of the calculated ratio of the sample to control was determined from the uncertainties of the replicated measurements for the two bracketing controls and the sample for which the ratio was being calculated (Eq. 10).

$$u(r) = r\sqrt{u^2(R_{C1}) + u^2(R_{Sn}) + u^2(R_{C2})} \quad \text{(Eq. 10)}$$

$u(R_{C1})$	Relative uncertainty of repeat responses for control 1
$u(R_{C2})$	Relative uncertainty of repeat responses for control 2
$u(R_{Sn})$	Relative uncertainty of repeat responses for the n^{th} sample
r	Response ratio

The average flow uncertainty was then calculated as a molar flow uncertainty using Eq. 11.

$$u(\dot{n}_n) = \dot{n}_n\sqrt{u^2(Q) + u^2(v_{\mathrm{m}})} \quad \text{(Eq. 11)}$$

$\dot{n}_n$	Molar flow for associated n^{th} sample
$u(Q)$	Relative uncertainty of average flow
$u(v_{\mathrm{m}})$	Relative uncertainty of molar volume

The uncertainty of the calculated amount fraction for each on-demand standard was determined from the uncertainties of the molar flow and the permeation rate (Eq. 12), also taking into account the uncertainty of the HCl purity.

$$u(x) = x\sqrt{u^2(\dot{n}_n) + u^2(q_{\mathrm{m}})} \quad \text{(Eq. 12)}$$

$u(q_{\mathrm{m}})$	Relative uncertainty of permeation rate
$u(\dot{n}_n)$	Relative uncertainty of molar flow for the n^{th} sample
x	Amount fraction from calculated permeation rate

The uncertainty of the dilution factor was determined from the measured uncertainties of the CCQM-K175 sample flow and the total gas flow using Eq. 13.

$$u(DF) = DF\sqrt{u^2(Q_{\mathrm{K175}}) + u^2(Q_{\mathrm{TOT}})} \quad \text{(Eq. 13)}$$

$u(Q_{\mathrm{K175}})$	Relative uncertainty of CCQM-K175 sample flow
$u(Q_{\mathrm{TOT}})$	Relative uncertainty of total flow
DF	Dilution factor

The uncertainty associated with each predicted amount fraction of the control was calculated using GenLine, based upon the uncertainties of the ratios and corresponding amount fractions of the on-demand standards. This uncertainty was then combined with the uncertainty of the dilution factor using Eq 14.

$$u(y) = y\sqrt{u^2(y_C) + u^2(DF)} \quad \text{(Eq. 14)}$$

$u(y_C)$	Relative uncertainty of predicted amount fraction of control (from GenLine)
$u(DF)$	Relative uncertainty of dilution factor
y	Calculated amount fraction of CCQM-K175 sample

The final uncertainty, u, assigned to the CCQM-K175 sample was computed by the NICOB Linear Pool procedure as the standard deviation of the K samples drawn from the consensus distribution, and is depicted in Figure 2. The expanded uncertainty is expressed as:

$$U = ku \quad \text{(Eq. 15)}$$

where the coverage factor k is equal to 2. The true value is therefore asserted to lie in the interval defined by the assigned amount fraction ± U, with a confidence of approximately 95 %. [6].

References

[1] International Organization for Standardization, ISO 19229:2019 Gas analysis – Purity analysis and the treatment of purity data, 2nd edition.

[2] International Organization for Standardization, ISO 6145-10:2002 Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 10: Permeation method.

[3] M.J.T. Milton, P.M. Harris, I.M. Smith, A.S. Brown, and B.A. Goody, Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures, *Metrologia*, 4(4), S291–S298 (2006).

[4] International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition.

[5] A. Koepke, T. Lafarge, A. Possolo, and B. Toman, Consensus building for interlaboratory studies, key comparisons, and meta-analysis, *Metrologia*, 54(3), S34–S62 (2017).

[6] JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (Gum 1995 with minor corrections), Joint Committee for Guides in Metrology, BIPM, Sèvres, France (2008).

Authorship

Cassie A. Goodman, Jennifer Carney

Measurement report NPL

CCQM-K175: HCl in nitrogen at 30 µmol mol^{-1}
Laboratory: National Physical Laboratory
Laboratory code: NPL
Cylinder number: D634090

Measurement 1[#]

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	06/06/2022	31.60	0.43	3

Measurement 2[#]

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	08/06/2022	31.51	0.21	3

Measurement 3[#]

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	09/06/2022	31.65	0.39	3

Measurement 4

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	29/06/2022	30.31	0.17	5

Results

Component	Result (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Coverage factor
HCl	31.27	1.28	2

Calibration standards
Two NPL primary reference materials (NPL PRMs) of nominally 30 µmol mol^{-1} and 5 µmol mol^{-1} hydrogen chloride (HCl) in nitrogen were prepared in accordance with ISO 6142-1 from one source of pure hydrogen chloride (99.9 %, BOC, UK). The NPL PRMs were prepared in 10 litre aluminium cylinders treated with BOC Spectraseal passivation (BOC, UK). The nominally 5 and 30 µmol mol^{-1} hydrogen chloride in nitrogen mixtures were prepared by exchange dilution [Brewer et al., 2019] of a nominally 1 cmol mol^{-1} hydrogen chloride in nitrogen (BIP^{+}, Air Products) parent mixture, which had been prepared by dilution of the pure hydrogen chloride source (shown schematically in figure 1). Both mixtures were used in determining the amount fraction of the comparison mixture. The amount fractions of the two NPL PRMs (3111R1 and HCL012) are 30.18 ± 0.03 and 5.00 ± 0.01, respectively (standard uncertainties from gravimetry only are stated).

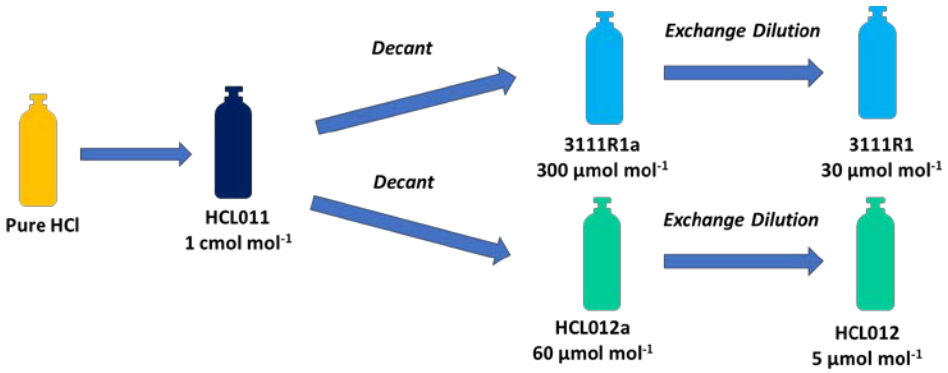

Figure 1. Schematic of the preparation of the NPL mixtures used to assign the travelling standard. Amount fractions given are nominal amounts.

Purity tables for the hydrogen chloride and nitrogen used are provided below. The purity of hydrogen chloride and nitrogen were taken from the manufacturer's certificate of analysis in accordance with ISO 19229:2015.

Table 1. Hydrogen chloride purity table

Component	Amount Fraction (µmol mol^{-1})	Standard Uncertainty (µmol mol^{-1})
HCl	999420	107
H_2O	5.0	2.5
N_2*	82.5	41.25
O_2*	82.5	41.25
CO_2*	82.5	41.25
H_2*	82.5	41.25
CO*	82.5	41.25
CH_4*	82.5	41.25
Cl_2#	10.0	5.0
CH_2Cl_2#	10.0	5.0
HBr	60.0	30.0

*These impurities were group together in the certificate of analysis and given as a total, which was divided equally between all components.
#These impurities were group together in the certificate of analysis and given as a total, which was divided equally between all components.

Table 2 – Nitrogen purity table

Component	Amount Fraction (µmol mol^{-1})	Standard Uncertainty (µmol mol^{-1})
N_2	999999.4846	0.8735
Ar	0.50	0.05
O_2	0.005	0.0025
H_2O	0.0050	0.0020
C_xH_y	0.0050	0.0025
CH_4	0.0004	0.0001

Analytical methods

Instrumentation

The amount fraction of hydrogen chloride was measuring using a Picarro G2108 cavity ring-down spectrometer (CRDS) that has been modified by the manufacturer to include a high concentration range mode (1 - 15 μmol mol^{-1}) which is the chosen mode for the measurements presented here. Due to the limitation of the analyser measurement range, it was necessary to dilute the comparison mixture below the upper limit. Therefore, an existing single stage dilution system was used that produced a nominal value for the comparison mixture of 5 μmol mol^{-1}.

Calibration method and value assignment

Before measuring any gas mixture, the analyser response to the balance gas (nitrogen) was recorded. The analyser response to an NPL in-house calibration standard either 3111R, a nominally 5 μmol mol^{-1} hydrogen chloride in nitrogen mixture, which was sampled directly and compared against the diluted comparison mixture or HCL012 a nominally 30 μmol mol^{-1} hydrogen chloride in nitrogen mixture which was sampled via the same dilution system as the comparison mixture, was recorded for at least forty-five minutes until a stable signal was recorded. The CCQM-K175 mixture (cylinder D634090) was then measured for an equivalent time. This sequence was repeated between two and three times. The last 84 points from each measurement were averaged. Separate measurements of the balance gas showed that the analyser drift was below 0.001 μmol mol^{-1} and therefore negligible over the measurement run.

Dynamic dilution system set-up

A single-stage dynamic dilution device was used to dilute the CCQM K175 mixture and the 30 μmol mol^{-1} inhouse calibration standard (3111R). The dynamic system was based on a critical orifice array [Brewer et al., 2010] comprising two sonic nozzles, which provided a 1:6.24 dilution of the nominally 30 μmol mol^{-1} HCl mixtures. Upstream of the nozzles, sample and diluent gases were supplied by high precision pressure regulators (LNI Swissgas, Switzerland)), critical flows through the sonic nozzles were generated by maintaining, P_{inlet}/P_{outlet} across the nozzles of > 2. Downstream pressure was maintained using a back pressure regulator (Swagelok).

The HCl mixtures were sampled *via* pressure regulators compatible for use with trace HCl. SilcoNert-2000 treated fittings were used for the standard side of the array to minimise HCl loss from adsorption onto the wetted surfaces. The standard and diluent sides were connected using a three-way valve to create a by-pass allowing the system to be continually purged with a constant flow of dry nitrogen (BIP Nitrogen, Air Products) thus, preventing water vapour from being introduced when breaking connections.

Calibration of dynamic dilution device and evaluation of dilution factor

The dilution device was calibrated for flow using molbloc-L Laminar Flow Elements. The calibration was independently validated gravimetrically via the dilution of, and comparison with, NPL PRMs of carbon monoxide in nitrogen. A calibration curve containing four points across the range 0.001-0.3 μmol mol^{-1} was generated from a CO in nitrogen PRM at nominally 10 μmol mol^{-1} using a validated dynamic dilution device in accordance with ISO 6143:2006. A separate carbon monoxide in nitrogen PRM (NPL1135R) was diluted through the dilution system used in the CCQM K175. An amount fraction value was assigned to NPL1135R based on an inverse evaluation using XLGENLINE (in the GDR mode) (Cox et al., 2003) from the calibration curve generated. This value was then compared to the predicted one determined from the flow calibrations.

Agreement between the dilution factor obtained from the flow calibration and the one from the gravimetric calibration method was within 0.3 %. The standard uncertainty of the dilution factor from the gravimetric calibration and the flow calibration combined was estimated and a conservative uncertainty of 1 % (k=1) was assigned. This was done to take into consideration the slight discrepancy between the two calibration techniques and to account for any potential drift downstream of the sonic nozzles.

Uncertainty evaluation

The ratio of the CRDS instrument response from the travelling standard (V_{unk} - V_{zero}) and the NPL PRM (V_{std} – V_{zero}) is calculated by:

$$r = \left(\frac{V_{unk} - V_{zero}}{V_{std} - V_{zero}}\right)$$

And the average ratio ($\bar{r}$) is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Where n is the number of ratios. The amount fraction of the hydrogen chloride in the travelling standard mixture, x_u, is calculated by:

$$x_u = x_s \bar{r} D$$

Where x_s is the amount fraction of hydrogen chloride in the NPL PRM. The standard uncertainty of the measurand, $u(x_u)$, is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{{x_s}^2} + \frac{u(\bar{r})^2}{\bar{r}^2} + \frac{u(D)^2}{D^2}}$$

The table below shows the uncertainty analysis for an example measurement.

Table 3 – Example HCl value assignment uncertainty analysis

	unit	example value	standard unc	Sensitivity coefficient	unc contribution	unc type	Distribution
x_s	µmol mol^{-1}	4.998	0.016	6.323	0.099	A	Normal
$\bar{r}$	-	1.013	0.004	31.189	0.134	A	Normal
D	-	6.24	0.0624	5.065	0.316	A	Normal
$\boldsymbol{x_u}$	µmol mol^{-1}	31.60					
$\mathbf{u}(\boldsymbol{x_u})$	µmol mol^{-1}	0.357					
$\mathbf{U}(\boldsymbol{x_u})$	µmol mol^{-1}	0.714					

To obtain the final result, an average of the four measurement results was determined and the corresponding standard deviation of this average was reported as the expanded uncertainty after multiplication by a coverage factor of 2.

References

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Brewer, P. J., Goody, B. A., Gillam, T., Brown, R. J. C., and Milton, M. J. T.: High-accuracy stable gas flow dilution using an internally calibrated network of critical flow orifices, Measurement Science & Technology, 21, 10.1088/0957-0233/21/11/115902, 2010.

Cox, M. G., Forbes A B, Harris P. M. and Smith I. M. (2003). The classification and solution of regression problems for metrology. Technical Report CMSC 24/03 (Teddington, UK: National Physical Laboratory).

Authorship

Yoana Hristova, Michael Ward, Ruth Hill-Pearce, Paul Brewer, David R. Worton.

Measurement Report PTB

CCQM-K175: HCl in nitrogen at 30 µmol mol^{-1}
Laboratory: PTB, Dep 3.4, WG 3.42
Laboratory code: -
Cylinder number: D983274

Measurement 1#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
HCl	07.04.2022	29.76	0.30

Measurement 2#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
HCl	03.05.2022	29.70	0.30

Measurement 3#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
HCl	06.05.2022	30.39	0.30

Measurement 4#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
HCl	03.06.2022	30.29	0.30

Measurement 5#

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard uncertainty (µmol mol^{-1})
HCl	09.06.2022	30.43	0.30

Final Result

Component	Result (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Coverage factor
HCl	30.11	0.42	2

Note: The final HCl results is calculated as the average of the results measured at the different dates above. The uncertainty of the results is calculated using the individuals' combined uncertainties for the different days and the relative repeatability of the results (0.5 %).

Analytical method

The PTB Optical gas standard (OGS), based on direct tunable diode laser absorption spectroscopy, was used to perform absolute HCl concentration measurements. The laser spectrometer consists of a continuous-wave wavelength-tunable interband cascade diode laser emitting at about 3.6 µm (P6 HCl line in the 1-0 fundamental band), a double pass gas cell (1.64 m) and a mid-infrared detector. The setup used here is - aside of the optical double pass configuration - identical with the EURAMET 1498 Pilot study. Here in K175, we used the double path configuration to achieve a higher signal to noise ratio. The gas sample containing about 30 µmol/mol HCl in N_2 was continuously flown through the gas cell with volume flow rates between 0.1 - 5 L/min, while recording the total gas pressure and gas temperature. The flow is controlled by a mass flow controller (MFC flow range: 5000 sccm), a needle valve and a membrane pump connected to the outlet of the optical gas cell. The sampling lines as well

as the gas cell of the instrument are coated with Dursan™ to minimize surface interaction (adsorption, contamination, and loss of HCl).
To derive the HCl amount fraction of the gas sample, a generalized linear regression (using Equation 1, derived from the Beer-Lambert-law) is applied to the data. Fig. 1 shows the area underneath the HCl absorption line (*"line area"*) plotted as a function of Γ, which is defined in equation 1:

$$A_{\text{line}} = x_{\text{HCl}} \cdot \left(\frac{S_T \cdot L \cdot p_{\text{total}}}{k_B \cdot T}\right) = x_{\text{HCl}} \cdot \Gamma \qquad (1)$$

Here, the quantity k_B is the Boltzmann constant, T is the gas temperature, p_{total} is the total gas pressure, A_{line} is the measured integrated line area (spectral area underneath the targeted absorption line), S_T is the HCl line strength of the P6 HCl line at T, L is the optical pathlength in the cell, and x_{HCl} is the HCl amount of substance fraction. Direct traceability of the dTDLAS HCl amount fraction results is addressed via the traceability of measured input parameters (in equation 1) i.e. the measured gas pressure (p_{total} traceable to the PTB pressure standard), temperature (T traceable to the PTB temperature standard), line area (A_{line} traceable to PTB's wavenumber (1/wavelength) standard) and optical path length (L traceable to the PTB length standard). The constant k_B is taken from the CODATA database (traceability to the CODATA recommended values of the fundamental physical constants, P. J. Mohr et al, Review of Modern Physics, 77, 2005), and S_T from HITRAN (traceable to the HITRAN20 entry for HCl from Li et al. JQSRT 121, 78–90,2013) which has been validated in separate HCl measurements at PTB.

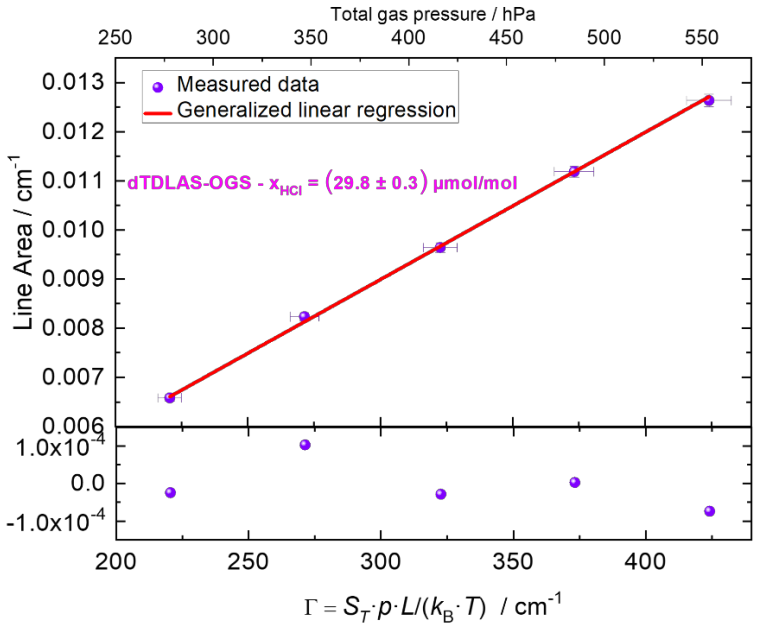


Figure 1: Plot of the measured line area as a function of Γ. A generalized linear regression (GLR) is applied (uncertainties in both axes are considered) to the data to derive the dTDLAS-OGS HCl amount of substance fraction (which is the slope value according to equation 1). The variation in Γ is mostly related to the variation in absorber number density which scales with the total gas pressure (p_{total}).

Uncertainty evaluation

The generalized linear regression (GLR) in Fig. 1 was done using the "B_Least" software (supporting implementation of ISO standard 6143) that is recommended for purposes like this. Applying the GLR to the data in Figure 1 yielded the HCl amount fraction (dTDLAS-OGS x_{HCl}; slope value) and the intercept value with their respective uncertainties. Due to an insignificant intercept, a second GLR was performed to derive the final HCl amount fractions with the intercept forced to zero. The table below

show the uncertainty budget (model equation: $x_{HCl} = A_{line}/ \Gamma$) for a single point in Figure 1, i.e at p_{total} of 352.439 hPa, corresponding to $\Gamma = 271.38$ cm^{-1}.

Uncertainty budget

Authorship

Author: Javis Nwaboh, Volker Ebert

Measurement report VNIIM

CCQM-K175: HCl in nitrogen at 30 µmol mol^{-1}

Laboratory name: D.I.Mendeleyev Institute for Metrology (VNIIM)

Cylinder number: D641531

Measurement 1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	22.04.2022	31.05	0.32	4

Measurement 2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	06.05.2022	31.33	0.52	4

Measurement 3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	12.05.2022	31.20	0.36	4

Measurement 4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	25.05.2022	31.13	0.19	4

Measurement 5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	17.06.2022	30.98	0.12	4

Measurement 6

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
HCl	20.06.2022	31.01	0.15	4

Final result

Component	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
HCl	31.1	0.4	2

Calibration standards

Calibration gas mixtures were prepared in accordance with [1]. Preparation was carried out from pure substances in 2 dilution stages:
1-st stage – 4 mixtures HCl/N_2 –level 0.5 %;
2-nd stage – 5 mixtures HCl/N_2 –level 30 μmol/mol.
All the mixtures were prepared in Luxfer cylinders ($V=5\ dm^3$).

The mixtures at 0.5 % and 30 μmol/mol level have been prepared again in cylinders D804128 and D804145 accordingly to check the sorption and quality of preparation of the inner surface of the cylinders. The successful results of verification of gas mixtures D804745 #1 and D804745 #2, indicated below, confirmed the absence of sorption in the cylinders.

The scheme of preparation of calibration mixtures from pure substances is shown on figure 1.

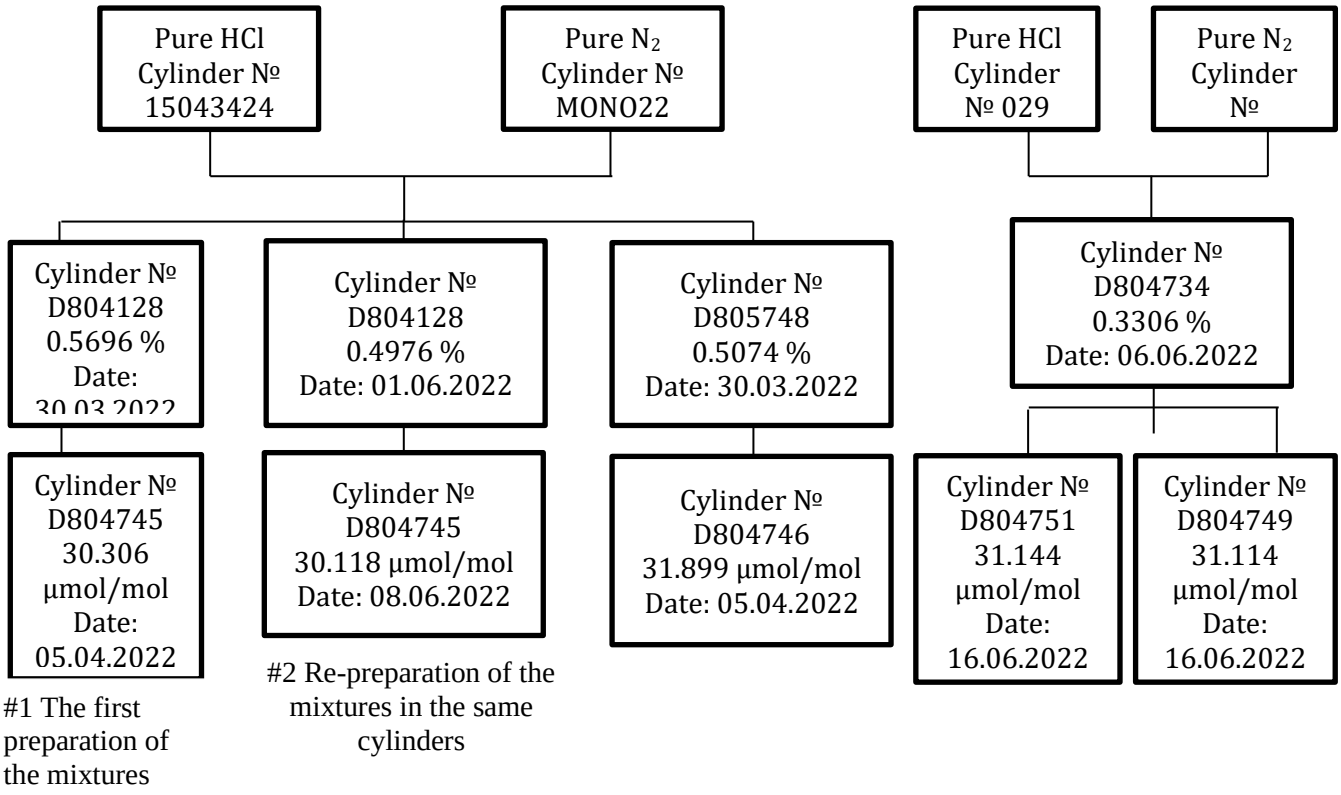


Figure 1. The scheme of preparation of calibration mixtures

The characteristics of the pure substances used for preparation of the calibration standards are shown in the tables 1 and 2.

Table 1: Purity table for HCl

Cylinder №	Component	Amount fraction, μmol/mol	Standard uncertainty, μmol/mol
15043424	HCl	999900	46
	H_2O	25	14
	Other impurities	75	43
029	HCl	999900	46
	H_2O	25	14
	Other impurities	75	43

Table 2: Purity table for N_2

Component	Amount fraction, μmol/mol	Standard uncertainty, μmol/mol
N_2	999999.38	0.05
Ar	0.0802	0.0020
CH_4	0.0025	0.0009
CO	0.0010	0.0004
CO_2	0.0204	0.0006
H_2	0.0025	0.0014
O_2	0.0156	0.0008
H_2O	0.50	0.05

Verification measurements of the premixtures (0.5 %) were carried out by means of FTIR FSM-1201 (Russia), $u_{ver} \approx 0.14$ % rel.
Verification measurements of the final mixtures (30 μmol/mol) were carried out by means of two facilities based on Polytron 7000 (Germany) and Satellite XT (UK) sensors, $u_{ver} \approx 0.5$ % rel.

All verification measurements consisted of checking consistency between the batch of similar prepared mixtures.
The values of HCl amount fraction in the calibration gas mixtures and their standard uncertainties are shown in the table 3.

Table 3: The values of HCl amount in the calibration standards

Cylinder number	Component	Amount fraction (μmol/mol)	Standard uncertainty due to weighing and purity (μmol/mol)
D804745 #1	HCl	30.306	0.023
D804745 #2	HCl	30.118	0.023
D804746	HCl	31.899	0.024
D804751	HCl	31.144	0.023
D804749	HCl	31.114	0.023

The homemade permeation tubes of HCl were used for the validation of the final mixtures. Two permeation tubes with a total permeation rate of 23.07 microgram/min were inserted into generator GGS-K (Russia) at 35.0 °C purged by carrier flow (Pure N_2, Cylinder № MONO22) at 0.5 dm^3/min to generate gas mixture at 30,44 μmol/mol.

To validate the calibration standards the mixtures from cylinder D804745 #1 and permeation tubes were analyzed alternately using facility based on Polytron 7000 (Germany) sensor. The relative difference between cylinder and permeation tubes was less 0.8 % while the uncertainty

of validation was 1.5 %. Thus, the calibration standard was validated with the permeation tubes and measuring facility within its analytical uncertainty.

Instrumentation

The instruments used for the measurements of the HCl content in the comparison mixture (cylinder № D641531) were two facilities based on Polytron 7000 (Germany) and Satellite XT (UK) sensors.

Each facility consists of electrochemical sensor of HCl (Polytron 7000 or Satellite XT), homemade automated system for the supply of gas mixtures to the sensor and homemade software to control the supply of gas mixtures and the processing of the measurement results.

Calibration method and value assignment

Single point calibration method was used to determine HCl amount fraction in the comparison gas mixture.

Measurement sequence was in the order: $standard_i$ - sample - $standard_i$.

Each of the 6 measurement results was received under repeatability conditions with the different calibration standards (table 3). Each of these 6 results is the mean from 4 replicates.

Measurements 1-4 were carried out by means of facility based on Polytron 7000 (Germany) sensor and calibration standards D804745 #1, D804746. Measurements 5-6 were carried out by means of facility based on Satellite XT (UK) sensor and calibration standards D804745 #1, D804746, D804751, D804749.

The amount of substance for each replicate was calculated according to the formula

$$X_x = X_{st} \frac{A_x}{(A'_{st}+A''_{st})/2},$$

where X_x and X_{st} – amount of substance of HCl in the comparison and calibration mixtures;

A_x – analytical signal of HCl in the comparison gas mixture;

A'_{st} and A''_{st} analytical signals of HCl in the calibration standard before and after measurement of the comparison mixture.

Temperature corrections were not applied due to use of above-mentioned measurement sequence.

Uncertainty evaluation
Uncertainty table:

Component	Abbreviation	Standard uncertainty μmol/mol
The uncertainty from gravimetric preparation of calibration standards (weighing + purity)	u_{prep}	0.023
The uncertainty from verification of calibration standards	u_{ver}	0.14
The uncertainty from measurement	u_{meas}	0.14
Combined standard uncertainty	u	0.20
Expanded uncertainty (k = 2)	U	0.4

The uncertainty associated with the stability of calibration gas mixtures is not indicated in the table, as it is included in the uncertainty of verification and measurements. The measurements were carried out in the period from 22.04.2022 to 20.06.2022 and all the measurements were used in calculating the result and the corresponding measurement uncertainty.

References

[1] International Organization for Standardization. “ISO 6142-1 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods. ISO Geneva. 2015.

Authorship

Authorship: L.A. Konopelko, Y.A. Kustikov, A.V. Kolobova, I.K. Chubchenko

Measurement report VSL

CCQM-K175: HCl in nitrogen at 30 µmol mol^{-1}
Laboratory: Van Swinden Laboratorium
Laboratory code: VSL
Cylinder number: D983267

Measurement 1

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	10/03/2022	29.77	0.8	1 (5-minute average)

Measurement 2

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	08/04/2022	30.10	0.8	1 (5-minute average)

Measurement 3

Component	Date (dd/mm/yy)	Result (µmol mol^{-1})	Standard deviation (% relative)	Number of replicates
HCl	26/04/2022	30.46	0.8	1 (5-minute average)

Results

Component	Result (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Coverage factor
HCl	30.1	0.9	2

Calibration standards

Value assignment 1 % HCl in N_2

A gas mixture of 1 % HCl in N_2 has been purchased (Linde Gas, LI5241). The amount fraction HCl in the gas mixture has been measured in a two-step procedure using pure HCl gas and a static 6 % HCl in N_2 gas mixture. For the measurement, dilutions of the gas mixtures are prepared according to ISO 6145-4:2004 [1]. This method allows the preparation of gas mixtures starting from pure HCl gas or HCl gas mixtures at atmospheric conditions. A gas-tight syringe is filled with pure HCl gas or a HCl gas mixture and fitted into a syringe motor. The motor delivers a constant flow rate of gas which is further diluted with a known stream of pure nitrogen controlled by a calibrated Bronkhorst mass flow controller. The obtained gas mixture is led to the analyser using short pieces of FEP tubing.

Pure HCl (grade 5.0 > 99.999 %, Praxair, PA0022) was used to measure the composition of 6 % HCl in N_2 (VSL100161 x_{grav} (6.0442 ± 0.0036) cmol mol^{-1} (k = 2)). The pure HCl was diluted with N_2 to obtain calibration gas mixtures with 5 different amount fractions in the range of 50 µmol mol^{-1} - 120 µmol mol^{-1} HCl in N_2. The 6 % HCl in N_2 gas mixtures was diluted with N_2 to obtain 3 different amount fractions in the same range (x_{dil}). For the data processing a straight line model has been applied to fit the data from the pure HCl gas and calculate the composition of the 6 % HCl in N_2 gas mixture according to ISO 6143:2001 [2] ($x_{\mathrm{dil/ver}}$ and x_{ver}). The average for the amount fraction HCl in the nominally 6 % mixture $x_{\mathrm{VSL100161}}$ is (5.74 ± 0.05) cmol mol^{-1} (k = 2).

Measurement results dilution pure HCl and 6 % HCl in N_2

Mother mixture	Dilution factor	x_{dil} (µmol mol^{-1})	r (a.u.)	$x_{dil/ver}$ (µmol mol^{-1})	$x_{VSL100161}$ (cmol mol^{-1})
Pure HCl	20000	50.0	1283		
Pure HCl	14992	66.7	1704		
Pure HCl	12005	83.3	2112		
Pure HCl	10000	100	2539		
Pure HCl	8547	117	2941		
6 % HCl	910	66.4	1604	62.8	5.71
6 % HCl	733	82.5	1997	78.6	5.76
6 % HCl	601	101.6	2423	95.7	5.75

After determining the composition of the 6 % HCl in N_2 gas mixture (VSL100161) this mixture was used to calibrate the composition of the 1 % HCl in N_2 gas mixture (LI5241). Both gas mixtures were diluted with N_2 to obtain amount fractions in the range of 5 µmol mol^{-1} – 15 µmol mol^{-1} HCl in N_2. For the data processing, a straight line model has been applied to fit the data from the dilutions from the 6 % HCl in N_2 gas mixture and calculate the composition of the 1 % HCl in N_2 gas mixture according to ISO 6143:2001 [2]. The average for x_{LI5241} is (1.011 ± 0.012) cmol mol^{-1} (k = 2).

Measurement results dilution 6 % and 1 % HCl in N_2

Mother mixture	Dilution factor	x_{dil} (µmol mol^{-1})	r (a.u.)	$x_{dil/ver}$ (µmol mol^{-1})	x_{LI5241} (cmol mol^{-1})
6 % HCl	4047	14.2	14.55		
6 % HCl	6198	9.3	9.64		
6 % HCl	12360	4.64	4.80		
6 % HCl	3996	14.4	14.56		
6 % HCl	6122	9.4	9.45		
6 % HCl	12230	4.69	4.81		
6 % HCl	4096	14.0	14.26		
6 % HCl	4083	14.0	14.32		
6 % HCl	6247	9.2	9.55		
6 % HCl	12467	4.60	4.78		
1 % HCl	984	10.2	10.34	10.1	0.99
1 % HCl	660	15.2	15.64	15.3	1.01
1 % HCl	969	10.3	10.53	10.3	1.00
1 % HCl	2001	5.00	5.20	5.03	1.01
1 % HCl	2045	4.89	5.20	5.03	1.03
1 % HCl	999	10.0	10.46	10.2	1.02
1 % HCl	672	14.9	15.52	15.2	1.02

HCl fractions in the mixtures used

Mixture number	x (cmol mol^{-1})	U x (cmol mol^{-1}) (k = 2)
PA0022	99.999	0.001
VSL100161	5.74	0.05
LI5241	1.011	0.012

PSM preparation method

Five PSMs were used as calibration gas standards for this comparison. The PSMs were prepared gravimetrically according to ISO 6142-1:2015 [3]. The mixtures were prepared in three stages, from the 1 % HCl in N_2 mixture (LI5241), via 2 or 3 dilutions into an evacuated cylinder with nitrogen balance gas the end mixtures were obtained in 10 Litre passivated cylinders. The 1 % HCl in N_2 mixture was first diluted to 500 µmol mol^{-1}, this gas mixture was diluted to 100, 60, 30 and 15 µmol mol^{-1} and the 100 µmol mol^{-1} was also diluted to 5 µmol mol^{-1}.

HCl fractions PSMs

Mixture number	$xHCl$ (µmol mol^{-1})	U $xHCl$ (µmol mol^{-1}) (k = 2)
VSL207727	101.0	1.2
VSL207736	60.6	0.7
VSL207728	30.3	0.4
VSL207735	15.16	0.18
VSL207731	5.06	0.06

Purity information

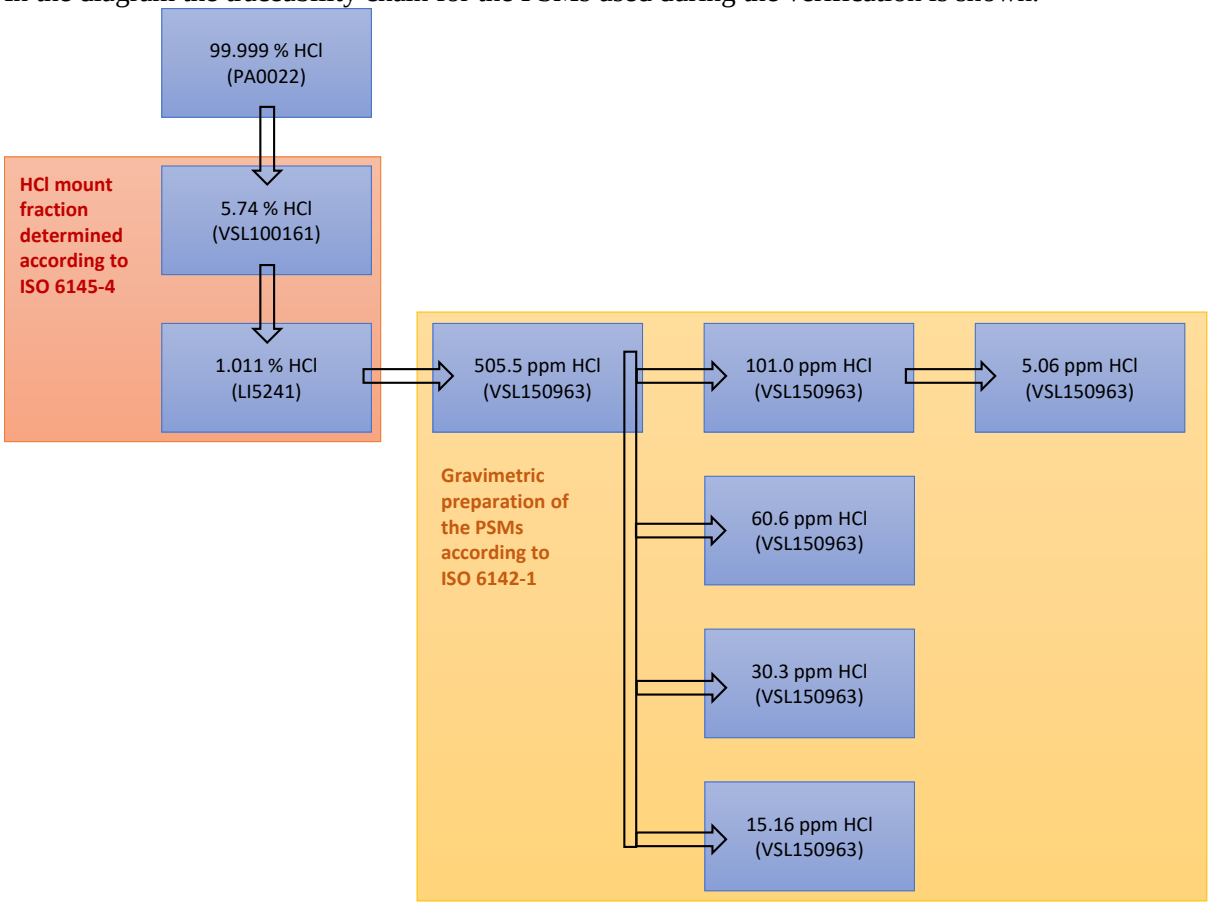
The pure nitrogen (grade 6.0 >99.9999 %, BIP+, Air Products) used has been checked for impurities in accordance with ISO 19229 [4].

Purity table nitrogen (APN26B)

Component	Amount fraction (mol mol^{-1})	Uncertainty (mol mol^{-1})
Argon	0.000035000	0.000005000
Methane	0.000000050	0.000000030
Carbon monoxide	0.000000015	0.000000009
Carbon dioxide	0.000000010	0.000000006
Hydrogen	0.000000500	0.000000300
Water	0.000000010	0.000000006
Nitrogen	0.999964410	0.000010000
Oxygen	0.000000005	0.000000003

PSM Traceability chain

In the diagram the traceability chain for the PSMs used during the verification is shown.



Analytical method

For the HCl analysis the ProCeas HCl Trace Analyser from AP2E was used based on Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS). During one measurement at least 5 static Primary Standard Materials (PSM), prepared according to ISO 6142-1:2015 [3], have been analysed to calibrate the analyser in the range of 100 – 5 µmol mol^{-1} HCl in N_2. The cylinders have been equipped with a Silconert coated stainless steel pressure regulator and the regulator is flushed prior to use. The measurements are conducted manually by connecting the gas mixtures to the analyser using short pieces of FEP tubing. A flow of 1000 ml min^{-1}, controlled by a Silconert coated Bronkhorst mass flow controller, is led to the analyser. On the same day as the PSMs the gas mixture for the K175 has been analysed. The response of the analyser is stabilised for 30 – 60 minutes after which the average response over the next 5 minutes is recorded. For the data processing a straight line model has been applied according to ISO 6143:2001 [2].

In the table below the measurement data from the first measurement on 10-03-2022 is given.

Mixture number	x **(µmol mol^{-1})**	r **(a.u.)**	**U** r **(a.u.)** (k **= 2)**	x_{meas} **(µmol mol^{-1})**
VSL207727	101.0	103.3	0.8	
VSL207736	60.6	62.4	0.5	
VSL207728	30.32	31.09	0.25	
VSL207735	15.16	15.54	0.12	
VSL207731	5.061	5.01	0.04	
CCQM mixture		30.50	0.25	29.77

Uncertainty evaluation

The uncertainty of the pure HCl gas is based on information from the supplier. The uncertainty of the 6 % HCl and 1 % HCl gas mixtures is the standard deviation of the verification measurements.

The uncertainty budget for the CCQM mixture contains uncertainty sources from the verification according to ISO 6143:2001 [2].

The mean and the standard deviation of the 3 verification measurements has been calculated using a Bayesian hierarchical model as implemented in the NIST Consensus Builder. The dark uncertainty, expressed as standard uncertainty is 0.22 µmol mol^{-1}. The dark uncertainty includes drift, measurement bias and stability.

Uncertainty source	**Distribution**	**Expanded uncertainty (µmol mol^{-1})**
Gravimetric uncertainty PSMs	k = 2	0.36
Standard deviation measurements	k = 2	0.72
Dark uncertainty	k = 2	0.44
x	**k = 2**	**0.9**

Reference

1. ISO 6145-4:2004, *Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – part 4: Continuous syringe injection method*
2. ISO 6143:2001, *Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures*
3. ISO 6142-1:2015, *Gas analysis – Preparation of calibration gas mixtures – part 1: Gravimetric method for Class I mixtures*
4. ISO 19229:2019: *Gas analysis – Purity analysis and the treatment of purity data*

Authors: Iris de Krom, Evtim Efremov, Adriaan van der Veen