EURAMET TC Project
Final Report

Project Title

Comparison of 100 µmol/mol HCl in N2

Coordinator, Institute, Country

Olav Werhahn

EURAMET Registration No.

1498

Subject Field

Metrology in Chemistry

KCDB Identifier

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Date

2021-12-22

EURAMET 1498 Final Report – Hydrogen Chloride in Nitrogen

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Field
Amount of substance

Subject
Comparison of standards and capabilities for the quantification of 100 µmol/mol HCl in N_2. This comparison prepares participants for participation in the upcoming CCQM-K175[†] (investigating the level of comparability of laboratories' hydrogen chloride in nitrogen gas analytical capabilities at a level of 30 µmol/mol) on the CCQM level.

Content

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† KCDB, https://www.bipm.org/kcdb/comparison?id=1783

1. Introduction

This pilot study was aiming at preparing participants to participate in the key comparison CCQM-K175 to be conducted under the CCQM. Furthermore, it is investigating the level of comparability of laboratories' hydrogen chloride in nitrogen gas analytical capabilities at a level of 100 µmol/mol. Certified reference gas mixtures (100 µmol/mol HCl in N_2) were provided by the Korea Research Institute of Standards and Science (KRISS) and the Physikalisch-Technische Bundesanstalt (PTB). The KRISS and the PTB mixtures were analyzed for the HCl amount fraction by PTB and KRISS, respectively. For the analysis, PTB employed a self-developed laser-spectroscopy based HCl **O**ptical **G**as **S**tandard (OGS)[‡] and KRISS used a non-dispersive infrared (NDIR) spectroscopy analyzer (Model 15i, Thermo Scientific). The comparison is considered similar to a *track C* challenge in the CCQM nomenclature.

The main goals of the study were

1. to investigate the level of comparability of the participating laboratories to analyze the HCl amount fraction in N2 at a HCl level of 100 µmol/mol, including value assignment and gas standard preparation, and

2. to prepare the participating HCl analyzers for the participation in CCQM-K175.

2. Design and organization of the project and comparison

For the comparison, KRISS gravimetrically prepared HCl in N_2 gas mixture, while PTB purchased and subsequently certified a commercial gas mixtures. Both mixtures were analyzed/verified and shipped from the starting participant to the second participant for analysis. The HCl amount fraction assignment was performed using the respective lab-specific analytical techniques. In a second loop, both participants then shipped the cylinders back to the other participant for a post analysis of the mixture.

The mixtures were prepared at KRISS and purchased by PTB in 2020. The KRISS mixture was verified (pre-shipment) and then shipped to PTB. PTB value-assigned the KRISS mixture and certified (pre-shipment) the PTB mixture in May 2020. After shipment of both mixtures to KRISS in 6/2020, the PTB mixture has been value-assigned by KRISS in December 2020 and the KRISS mixture was verified again by KRISS (post-shipment) at the same time. In February 2021 the PTB cylinder was received back at PTB and was certified again by PTB (post-shipment) in March 2021.

[‡] Qu, Z., Nwaboh, J., Werhahn, O. et al. Towards a dTDLAS-Based Spectrometer for Absolute HCl Measurements in Combustion Flue Gases and a Better Evaluation of Thermal Boundary Layer Effects. Flow Turbulence Combust 106, 533–546 (2021). https://doi.org/10.1007/s10494-020-00216-z

2.1 Participants

Table 1 lists the participants for the HCl study in this comparison.

Table 1: List of participants

Acronym	**Country**	**Institute**
PTB	DE	Physikalisch-Technische Bundesanstalt, Germany
KRISS	KR	Korea Research Institute of Standards and Science, Korea

2.2 Measurement protocol

The measurement protocol was previously agreed by the two participants. Each laboratory was requested to perform at least 3 measurements for each mixture. The replicates were to be carried out under reproducibility conditions. The protocol informed the participants about the nominal concentration value. The laboratories were also requested to submit an uncertainty budget summarizing their uncertainty assessment.

2.3 Measurement methods

The analytical measurement methods used by the participants are described in annex A of this report. PTB applied a dTDLAS-based HCl-OGS instrument, operated according to the TILSAM[§] approach, as absolute measuring instrument. The underlying model equation is based on the Beer-Lambert-law and an amount fraction is directly computed from the spectroscopic measurements involving traceable influence quantities. KRISS employed an NDIR instrument (Model 15i, Thermo Scientific), calibrated for the HCl analysis by KRISS's in-house HCl primary gas standards.

2.4 Values to compare

To compare the results, values (CRVs[**]) for the mixtures from PTB and KRISS were assigned by PTB and KRISS, respectively. The CRV value of the PTB mixture was determined via dTDLAS-based HCl-value assignments of a commercial HCl mixture by means of PTB's HCl-OGS and the CRV of the KRISS mixture was determined by KRISS's gravimetric preparation procedure including verification procedures.

[§] TILSAM: Traceable Infrared Laser-Spectrometric Amount fraction Measurement, https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

[**] CRV: comparison reference value – for the specific mixture

2.5 Level of comparability

This comparison report contains the evaluated level of comparability (D) for each participant's mixture. Since there were two mixtures, one from PTB and the other from KRISS, the D values were calculated as follows

- for the KRISS mixture

$$D_{\mathrm{PTB}} = x_{\mathrm{PTB}} - x_{\text{CRV-KRISS}}$$

and

- for the PTB mixture

$$D_{\mathrm{KRISS}} = x_{\mathrm{KRISS}} - x_{\text{CRV-PTB}}$$

The associated expanded uncertainties $U(D_i)$ were computed from

$$U(D_i) = 2 \times \sqrt{u^2(x_i) + u^2\left(x_{\text{CRV-}j}\right)}$$

where $u(x_i)$ and $u(x_{\mathrm{CRV},\,j})$ are the combined uncertainties of the result of lab i and that of the CRV value provided by lab j, respectively (i and j being PTB or KRISS, respectively). The coverage factor of 2 is introduced to report an expanded uncertainty U at a 95 % level.

3. Results

The results of the comparison are summarized in Table 2 where the HCl amount fraction results of the participants given. For the uncertainties of the levels of comparability (D_i), a normal distribution has been assumed, and a coverage factor $k = 2$ has been applied**.**

Table 2: Results of EURAMET 1498. The units of all quantities in the table are µmol/mol.

Cylinder	pre-ship	U	post-ship	U	x_{CRV}	$U(x_{\mathrm{CRV}})$	x_{KRISS}	$U(x_{\mathrm{KRISS}})$	D_{KRISS}	$U(D_{\mathrm{KRISS}})$
PTB (64575)	101.19	2.3	98.1	3.4	99.65	2.10	99.7	0.61	0.1	2.2
Cylinder	pre-ship	U	post-ship	U	x_{CRV}	$U(x_{\mathrm{CRV}})$	x_{PTB}	$U(x_{\mathrm{PTB}})$	D_{PTB}	$U(D_{\mathrm{PTB}})$
KRISS (D866176)	100.0	0.71	99.6	0.61	99.8	0.5	100.1	2.6	0.3	2.6

Estimated uncertainties $U(x_{\mathrm{CRV}})$ in Table 2 do not contain contributions (repeated measurements on the same mixture) from correlations that would reduce $U(x_{\mathrm{CRV}})$. Instead $U(x_{\mathrm{CRV}})$ was computed (conservatively) as two independent measurements.

Figure 1 (plotted using the results in Table 2) depicts the plot of the HCl amount fraction results of the participating laboratories for the KRISS mixture in cylinder D866176. The average of the two KRISS results measured with a 10 months separation (pre-shipment and post-shipment: see details on the KRISS results in the appendix; measurements at KRISS before cylinder was shipped to PTB, and after the cylinder was received back from PTB) is the CRV for this mixture (cylinder D866176). The uncertainties in Fig. 1 are given as 95% confidence intervals (k = 2).

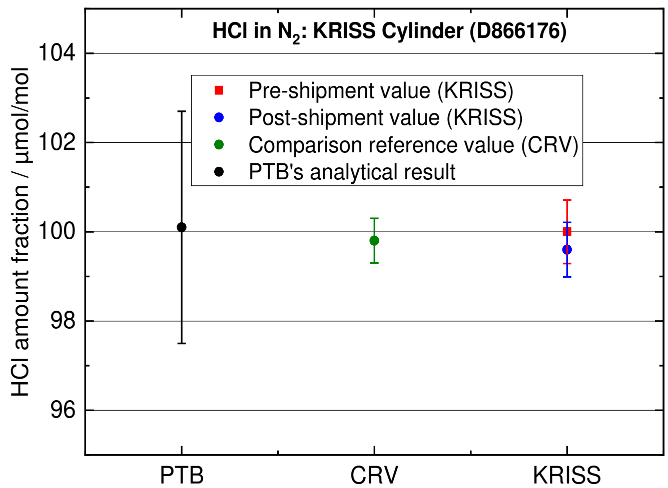

Figure 1: HCl amount fraction results for the KRISS mixture.

Figure 2 (plotted using the results in Table 2) shows the HCl amount fraction results of the participating laboratories for the PTB mixture (cylinder 64575). The average of the two PTB results measured with a 7 months separation (pre-shipment and post-shipment: see details on the KRISS results in the appendix: measurements at PTB before cylinder was shipped to KRISS, and after the cylinder was received back from KRISS) is the CRV for this mixture (cylinder 64575). The uncertainties in Fig. 2 are given as 95% confidence intervals (k = 2).

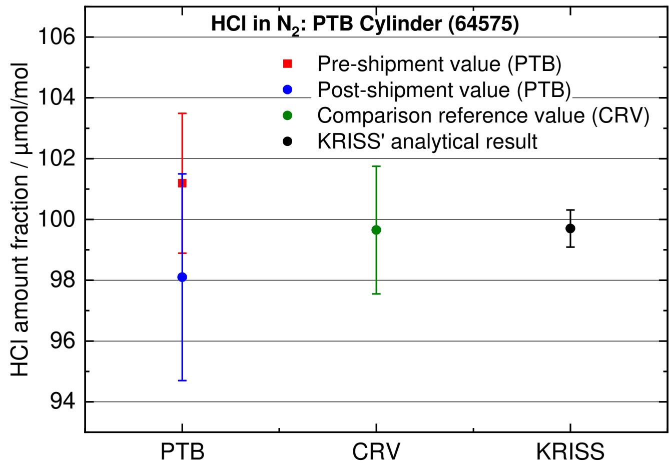

Figure 2: HCl amount fraction results for the PTB mixture.

Figure 3 (plotted using the results in Table 2) depicts the level of comparability (D_i) and the relative level of comparability of the participating laboratories. The uncertainties in Fig. 3 are given as 95% confidence intervals (k = 2).

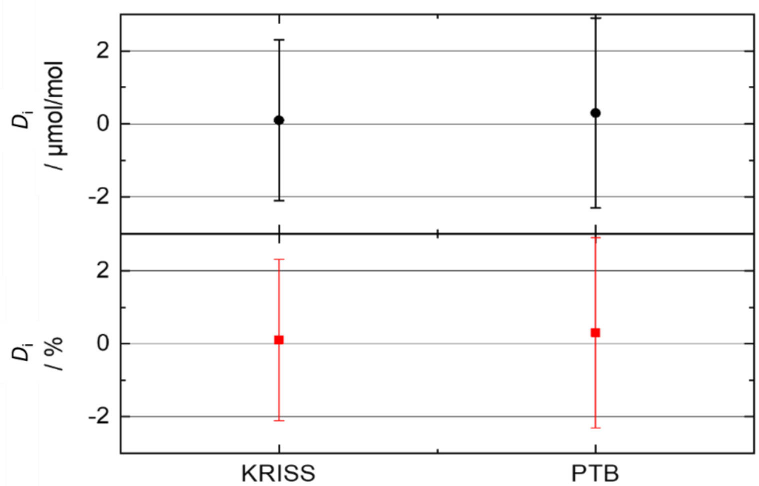

Figure 3: Level of comparability (D_i) of the participating laboratories.

4. Discussion and conclusions

The results of the two participants are in agreement with the respective CRV of the corresponding mixture. The relative level of comparability of the results is 0.3 % and below.

The two main objectives of this study (cf. p. 2) were to

- investigate the level of comparability of laboratories' hydrogen chloride in nitrogen gas analytical capabilities at a level of 100 µmol/mol, including value assignments and gas standard preparations, and
- to prepare PTB's HCl-OGS for the participation in the CCQM-K175.

The former objective has been achieved on the given comparability level of 0.3 %. Nevertheless, in combination with the latter objective, it could be noted here, that PTB has submitted its result and the CRV of the KRISS cylinder with a comparably large uncertainty figure. The major contributor for the uncertainty of the PTB result is resulting from the HCl line strength *S* entering the model equation.[††] Consequently, this PTB-uncertainty then also dominates the uncertainty of both *D* values. The objective of this study has definitely been accomplished by the fact, that PTB's result agrees well with the CRV of the KRISS mixture. However, beyond that, one might argue that PTB may have to check whether there's an overestimation in their uncertainty assessment. In any case, whether with given or improved uncertainty, PTB has achieved the objected preparation for its participation in CCQM-K175 by the present study. References [1-7] are given below on the idea of an OGS as employed by PTB in this study.

Furthermore, it could be noted here that, the HCl amount fraction in the PTB cylinder was observed to drift over time (the last measurements done about 10 months after the gas mixture was initially value-assigned), indicating potential issues with the cylinder treatment of the commercial supplier. Figure 4 displays the time axis of the two cylinders.

Here, one should remember that PTB had purchased cylinder plus gas mixture from Linde PLC. On the contrary, no drift (last measurements done about 10 months after the gas mixture was prepared) was observed for the KRISS mixture, indicating a higher stability of the HCl in N_2 gas mixtures prepared by KRISS in their cylinder.

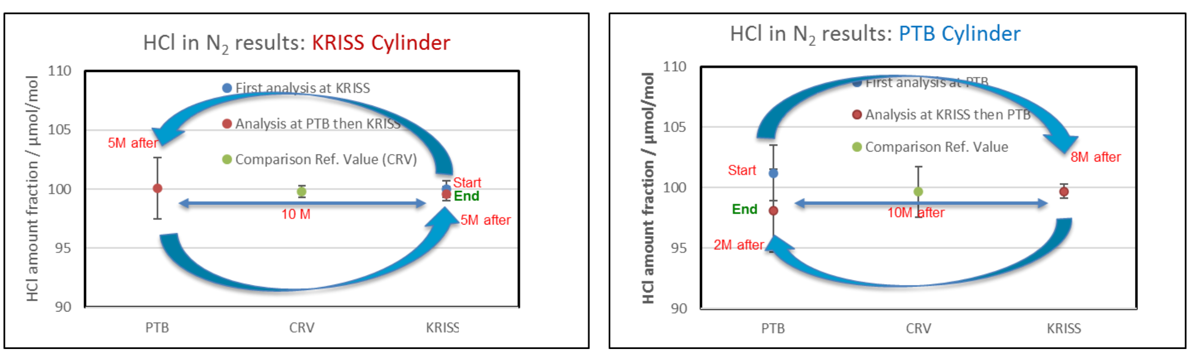

Figure 4: Temporal evolution of the HCl gas inside the cylinders prepared by KRISS and PTB.

[††] The molecular line data was taken from: G. Li et al., JQSRT 121 (2013) 78-90.

The latter conclusion will give rise to even some more confidence in KRISS' capabilities to prepare stable HCl in nitrogen gas standards in cylinders and therefore supports KRISS' expertise in piloting the CCQM-K175. So, the EURAMET 1498 by this, provides some further confidence in the preparations of the upcoming KC.

Generally, the excellent agreement of the results in this study shows the good analytical capabilities of PTB and KRISS. The good performance of the HCl-OGS paves the way to apply the OGS instrument in the CCQM - K175.

Finally, and to give some outlook for further use of the results, this study has proven the participants' capabilities at a 100 µmol/mol HCl level. Based on the technical knowledge of the techniques employed by KRISS and PTB, both labs concluded that this study would provide evidence that the same level of comparability would be achievable throughout the range of 50 to 200 µmol/mol of HCl in nitrogen.

This statement shall bring some similar information as the typical 'How-Far-The-Light-Shine' statement (HFTLS) known from CCQM-GAWG comparisons.

References

[1] O. Werhahn, J.C. Petersen (eds.), 2010, "*TILSAM* technical protocol V1_2010-09-29", Available from:
http://www.euramet.org/fileadmin/docs/projects/934_METCHEM_Interim_Report.pdf

[2] Qu, Z.; Nwaboh, J. A.; Werhahn, O.; Ebert, V. Towards a dTDLAS-Based Spectrometer for Absolute HCl Measurements in Combustion Flue Gases and a Better Evaluation of Thermal Boundary Layer Effects. Flow Turbul. Combust., 2021, 106, 533–546, doi: 10.1007/s10494-020-00216-z.

[4] Nwaboh, J. A.; Qu, Z.; Werhahn, O.; Ebert, V. Interband cascade laser-based optical transfer standard for atmospheric carbon monoxide measurements. Appl. Opt., 2017, 56, nE84–E93, doi: 10.1364/AO.56.000E84.

[5] Buchholz, B.; Böse, N.; Ebert, V. Absolute validation of a diode laser hygrometer via intercomparison with the German national primary water vapor standard. Appl. Phys. B, 2014, 116, 883–899, doi: 10.1007/s00340-014-5775-4.

[6] Pogany, A.; Wagner, S.; Werhahn, O.; Ebert, V. Development and Metrological Characterization of a Tunable Diode Laser Absorption Spectroscopy (TDLAS) Spectrometer for Simultaneous Absolute Measurement of Carbon Dioxide and Water Vapor. Appl. spectrosc., 2015, 69, 257-268.

[7] Nwaboh,J.A.; Qu, Z.;Werhahn,O.; Ebert,V. Towards an Optical Gas Standard for traceable Calibration-Free and Direct NO2 Concentration Measurements. Appl.Sci. 2021,11,5361. https://doi.org/10.3390/app11125361

Appendix (detailed report on participants' results)

Filed by KRISS: Report Form EURAMET 1498, 100 µmol/mol HCl in N_2

General information

Institute	KRISS
Address	267 Gajeong-Ro, Yuseong-Gu, Daejeon 34113, Rep. of Korea
Contact person	Sang Hyub OH
Telephone	82 10 9690 2501
Email	shoh@kriss.re.kr
Comparison results submitted to (institute)	PTB
Comparison results submitted at (date)	2020-01-15

Information on the cylinder

Cylinder number:	64575	D866176
Pressure in cylinder before shipment:	-	-
Cylinder received at:	11-18-2020	11-18-2020
Pressure in cylinder before analysis:	11 MPa	4 MPa
With analysis completed:	8 MPa	<1 MPa
Issues on the cylinder to mention:	_ _ _ _ _	

Description of the procedure used during the analysis

E.g., analyzer, instrumental parameters, analysis procedure, etc.

The experimental conditions are as follows, and it was repeated 4 times in one measurement (Figure 1). Instrument drift was corrected from baseline changes before and after measurement.

Table 1 summarizes detailed information of the cylinders used in this experiments and Figure 2 shows the results of the internal consistency of the cylinders manufactured by KRISS.

Analyzer : HCl Analyzer(Model 15*i*, Thermo Scientific, NDIR type)
Sampling : Multiposition Valve with single regulator
Sample flow rate : 1,000 mL/min with MFC

Injection time : sample 20 min, Nitrogen 10 min
Date collection interval : 5 s
Data acquisition : Last 4 min of 20 min
(The last 3 out of 4 consecutively analyzed was used)

Analysis sequence : 1-2-3-4-5-1-2-3-4-5-1-2-3-4-5-1-2-3-4-5

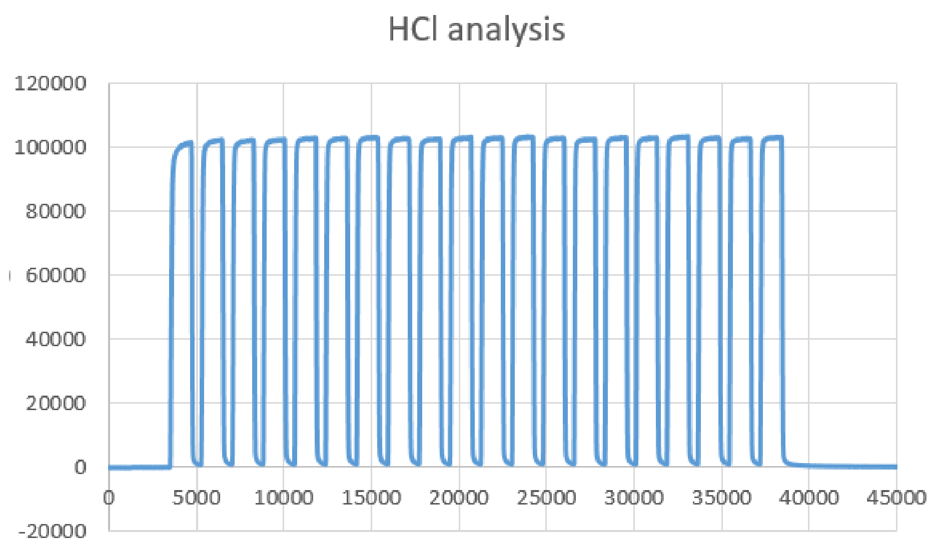

Figure 1. Example of HCl analysis results using NDIR

Table 1: Detailed information of the cylinders used in this experiments

Sampling No.	Cylinder No	Amount-of-substance fraction / µmol/mol	Date of manufacture	Remarks
1	D919873	100.09	2021. 1. 12	Internal use
2	D919880	100.00	2021. 1. 12	Internal use
3	64575	101	2020. 4. 08	PTB cylinder
4	D866176	99.96	2020. 2. 18	KC sample
5	D799711	100.03	2020. 2. 18	Reference
-	D799704	100.01	2020. 2. 18	Internal use

Results

Before shipping to the PTB

Table 3: Results on cylinder number D866175 (expanded uncertainties for coverage factor: k = 2)

#	Amount-of-substance fraction, x_{HCl} / µmol/mol	Expanded uncertainty, $U(x_{HCl})$ / µmol/mol	Relative expanded uncertainty, $U_{rel}(x_{HCl})$ / %
1	99.9	1.0	1.0

2	100.0	1.0	1.0
3			
4			
5			
[redacted]			
[redacted]	100.0	0.71	0.71

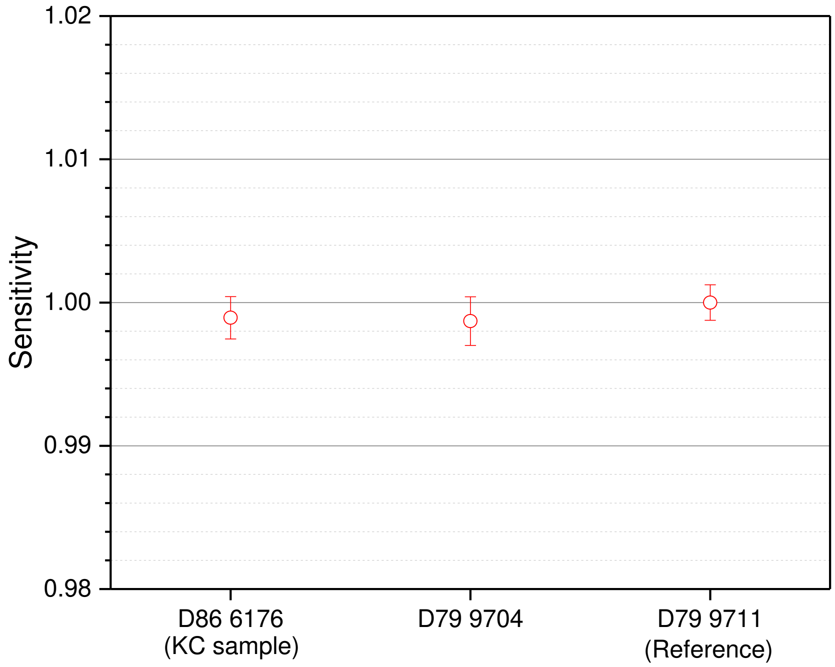

Figure 2. Results from consistency tests of HCl primary standard gas mixtures

Post PTB measurement

Table 3: Single measurement results on cylinder number 64575

Date (dd/mm/yy)	Amount-of-substance fraction, x_{HCl} / µmol/mol	Relative standard deviation on replicas / %	Total-# replicates
12/06/2020	99.3	0.17	3
12/09/2020	99.8	0.15	3
12/14/2020	100.1	0.15	3

Table 4: Results on cylinder number 64575 (expanded uncertainties for coverage factor: k = 2)

#	Amount-of-substance fraction, x_{HCl} / µmol/mol	Expanded uncertainty, $U(x_{HCl})$ / µmol/mol	Relative expanded uncertainty, $U_{rel}(x_{HCl})$ / %
1	99.3	1.1	1.1
2	99.8	1.0	1.0
3	100.1	1.0	1.0
4			
5			
[redacted]			
[redacted]	99.7	0.61	0.61

Table 5: Single measurement results on cylinder number D866176

Date (dd/mm/yy)	Amount-of-substance fraction, x_{HCl} / µmol/mol	Relative standard deviation on replicas / %	Total-# replicates
12/06/2020	99.8	0.23	3
12/09/2020	99.6	0.15	3
12/14/2020	99.5	0.16	3

Table 6: Results on cylinder number D866176 (expanded uncertainties for coverage factor: k = 2)

#	Amount-of-substance fraction, x_{HCl} / µmol/mol	Expanded uncertainty, $U(x_{HCl})$ / µmol/mol	Relative expanded uncertainty, $U_{rel}(x_{HCl})$ / %
1	99.8	1.1	1.1
2	99.6	1.0	1.0
3	99.5	1.0	1.0
4			
5			
[redacted]			
[redacted]	99.6	0.61	0.61

Uncertainty assessment

The contributions of standard uncertainty of CRMs were from preparation of gravimetric method and verification method.

$$u(x_{HCl}) = \sqrt{u_{grav}^2 + u_{ver}^2}$$

Here, x_{HCl} represents the mol fraction of HCl in the cylinder, u is the relative standard uncertainty, u_{grav} and u_{ver} represent uncertainty of gravimetric preparation method and from verification method, respectively.

Table 7: Uncertainty budge of HCl PRMs (Primary reference materials)

Component	Relative standard uncertainty / %		Expanded uncertainty / %	Coverage factor
	Gravimetry	Verification		
HCl	0.10	0.50	0.51	2

Table 8: Purity table of HCl

Component	Amount fraction / µmol/mol	Expanded Uncertainty / µmol/mol (k = 2)	Distribution
H_2	61.6	3.1	normal
O_2	0.14	0.007	normal
N_2	8.99	4.50	normal
CH_4	0.05	0.03	rectangular
CO_2	1.64	0.08	normal
H_2O	5.00	0.25	normal
HCl	999 922.6	5.5	-

Table 9: Purity table of nitrogen

Component	Amount fraction / µmol/mol	Expanded Uncertainty / µmol/mol (k = 2)	Distribution
H_2	0.05	0.03	rectangular
O_2	0.18	0.009	normal
CH_4	0.05	0.03	rectangular
CO	0.10	0.005	normal
CO_2	0.05	0.03	rectangular
H_2O	1.20	0.06	normal
N_2	999 998.4	0.08	

Model equation:

The basic model equation is as follows.
GUM workbench program was used for the uncertainty budget calculation. The formula was too complex to calculate at once, so each step was calculated with Excel and checked, and then calculated step by step using GUM.

$$C_{sample} = \frac{R_{sample}}{R_{std}} \times C_{std}$$

Table 4: Uncertainty budget / or, e.g., copy from GUM workbench file if appropriate.

#	Source of uncertainty	Estimate	Distribution	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution (µmol/mol)	Index
1							
2							
3							
4							
5							
Combined standard uncertainty (µmol/mol)							

Filed by PTB: Report Form EURAMET 1498, 100 µmol/mol HCl in N_2

General information

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Telephone	+495315923420
Email	Olav.werhahn@ptb.de
Comparison results submitted to (institute)	
Comparison results submitted at (date)	

Information on the cylinder

Cylinder number:	64575	D866176
Pressure in cylinder before shipment:	119 bar	--
Cylinder received at:	04.02.2021	24.03.2020
Pressure in cylinder before analysis:	87 bar	88 bar
With analysis completed:	10 bar	52 bar
Issues on the cylinder to mention:	_ _ _ _ _	

Table 1: Detailed information of the cylinders used in these experiments

Sampling No.	Cylinder No	Concentration (µmol/mol)	Date of manufacture	Remarks
3	64575	101.0	2020.04.08	PTB cylinder
4	D866176	99.96	2020.02.18	KC sample

Description of the procedure used during the analysis

E.g., analyzer, instrumental parameters, analysis procedure, etc.

A dTDLAS instrument was used to perform the HCl concentration measurements at PTB. The system consists of a continuous wave interband cascade laser (ICL, Nanoplus) emitting at about 3.6 µm, a single pass gas cell (0.82 m) and a mid-infrared detector (Vigo, model PVI-4TE). For

HCl dTDLAS measurements, a gas sample containing HCl in N_2 continuously flows (volume flow rates: between 0.1- 5 L/min) through the gas cell, controlled by a mass flow controller (MFC), a needle valve and a membrane pump connected to the outlet of the gas cell.

For the gas mixtures containing about 100 µmol/mol HCl in N_2, the dTDLAS HCl amount of substance fraction results (dTDLAS-x_{HCl}) are derived (employing the TILSAM method) by applying a generalized linear regression (using Equation 1, derived from the Beer Lambert law) to the data of the line area plotted as a function of Γ as shown in Fig. 1 (data for cylinder 64575: PTB cylinder).

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

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 line area, $\mathbf{S}_T$ is the HCl line strength at T, L is the optical pathlength in the cell, x_{HCl} is HCl amount of substance fraction.

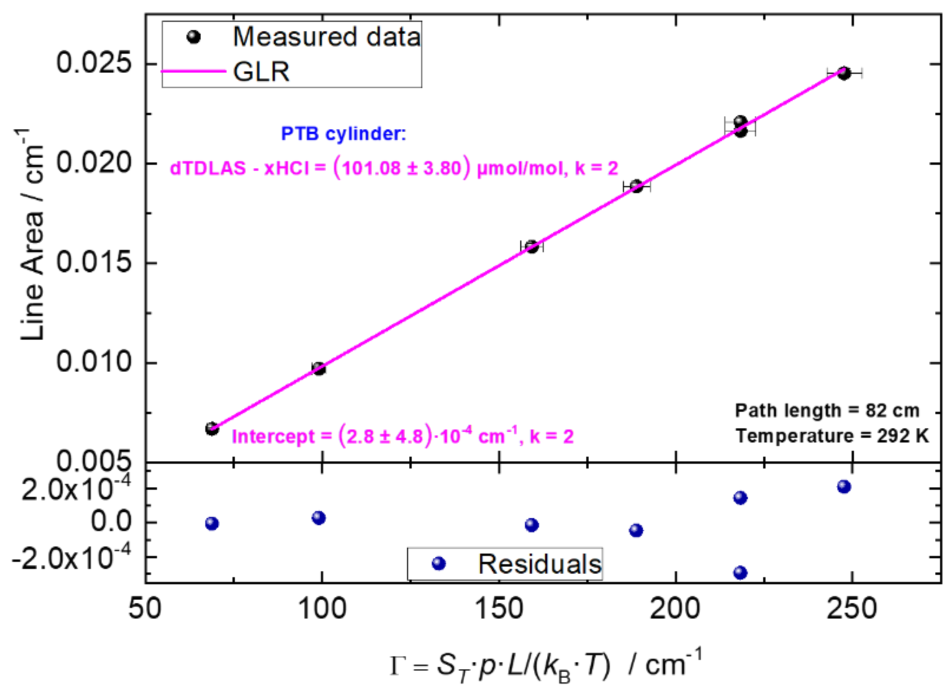


Figure 1: Plot of the line area as a function of Γ. A GLR (uncertainties in both axes are considered) is applied to the data to derive the dTDLAS HCl amount of substance fraction (the slope value according to equation 1).

From the GLR in Fig.1, a slope value (dTDLAS-xHCl) of (101.08 ± 3.80) is derived. It could be noted here that, the change in the quantity Γ is mostly related to the variation in the total gas pressure ($\mathbf{p}_{\text{total}}$). The intercept parameter of $(2.8 \pm 4.8) \cdot 10^{-4}$ cm^{-1} is insignificant (the uncertainty is larger than the value), indicating the experimental conditions were appropriately described (see equation 1).

Results

Table 5: Results on cylinder number _64575 PTB cylinder _ (expanded uncertainties for coverage factor: k = 2) before shipment to KRISS.

Date	x_{HCl} / µmol/mol	$U(x_{HCl})$ / µmol/mol)	$U_{rel}(x_{HCl})$ / %
2020-07-17	101.01	4.00	3.96
2020-07-20	101.08	3.80	3.76
2020-07-21	101.50	4.00	3.94
[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	101.19	2.30	2.27

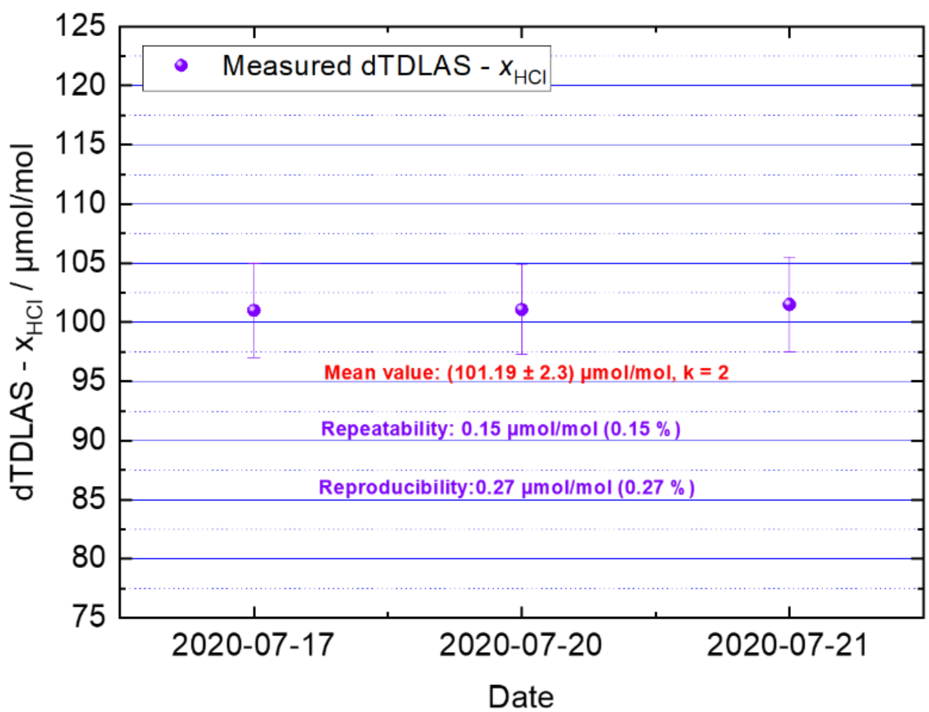


Table 6: Results on cylinder number _ 64575 PTB cylinder_ (expanded uncertainties for coverage factor: k = 2) after cylinder is returned to PTB from KRISS.

Date	x_{HCl} / µmol/mol	$U(x_{HCl})$ / µmol/mol)	$U_{rel}(x_{HCl})$ / %
2021-02-22	97.8	6.2	6.34
2021-02-25	98.0	6.4	6.53
2021-03-02	98.5	5.2	5.28
[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	98.10	3.4	3.47

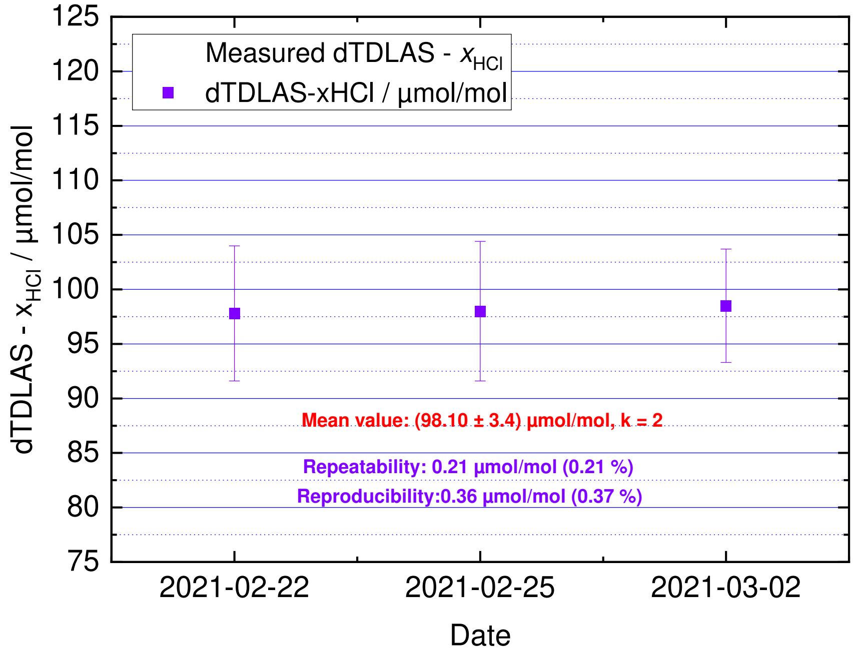
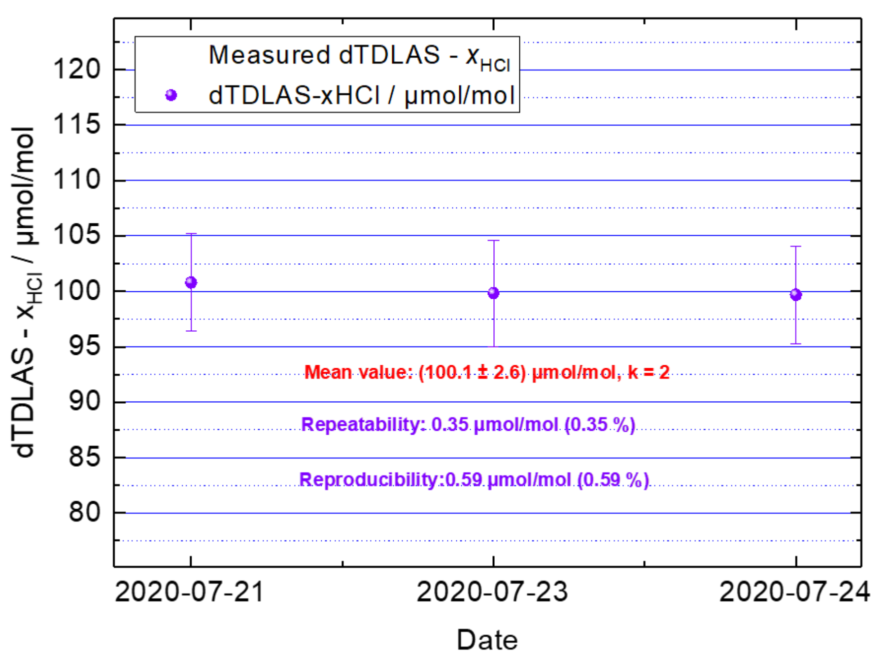


Table 7: Results on cylinder number _ D866176 KRISS cylinder _ (expanded uncertainties for coverage factor: k = 2) after analysis at KRISS and cylinder sent to PTB.

Date	x_{HCl} / µmol/mol	$U(x_{HCl})$ / µmol/mol)	$U_{rel}(x_{HCl})$ / %
2020-07-21	100.80	4.4	4.43
2020-07-23	99.84	4.8	4.81
2020.07-24	99.70	4.4	4.41
[redacted]			
[redacted]	100.1	2.6	2.6



Uncertainty assessment

Model equation: $x_{\mathrm{HCl}} = \frac{A_{\mathrm{line}} \cdot k_B \cdot T}{S_T \cdot L \cdot p_{\mathrm{total}}}$

Example uncertainty budget for the PTB cylinder:

	TILSAM budget x_{HCl}	

Uncertainty Budgets:

x_{HCl}: HCl amount of substance fraction

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L	0.82000 m	0.24 % (rel)	normal	$-120 \cdot 10^{-6}$	$-240 \cdot 10^{-9}$ mol/mol	1.1 %
k_B	$13.8065050 \cdot 10^{-24}$ J/K/molecule	$170 \cdot 10^{-6}$ % (rel)	normal	$7.3 \cdot 10^{18}$	$180 \cdot 10^{-12}$ mol/mol	0.0 %
r_{iso}	1.0	0.0 % (rel)				
xHCl	0.7576					
xHClHITRAN	0.7576					
A_{line}	0.022076 cm^{-1}	1.0 % (rel)	normal	$4.6 \cdot 10^{-3}$	$1.0 \cdot 10^{-6}$ mol/mol	19.6 %
T	291.750 K	0.10 % (rel)	normal	$350 \cdot 10^{-9}$	$100 \cdot 10^{-9}$ mol/mol	0.2 %
p	567.943 hPa	0.15 % (rel)	normal	$-180 \cdot 10^{-9}$	$-150 \cdot 10^{-9}$ mol/mol	0.4 %
S_T	$188.81 \cdot 10^{-21}$ cm/molecule	2.0 % (rel)	normal	$-540 \cdot 10^{12}$	$-2.0 \cdot 10^{-6}$ mol/mol	78.6 %
γ_{HCl}	218.30 cm-1	2.0 % (rel)				
x_{HCl}	$101.13 \cdot 10^{-6}$ mol/mol	$2.28 \cdot 10^{-6}$ mol/mol				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
x_{HCl}	$101.1 \cdot 10^{-6}$ mol/mol	$4.6 \cdot 10^{-6}$ mol/mol	2.00	95% (normal)

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Example uncertainty budget for the KRISS cylinder:

Uncertainty Budgets:

x_{HCl}: **HCl amount of substance fraction**

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
L	0.82000 m	0.24 % (rel)	normal	$-120\cdot10^{-6}$	$-240\cdot10^{-9}$ mol/mol	1.1 %
k_B	$13.8065050\cdot10^{-24}$ J/K/molecule	$170\cdot10^{-6}$ % (rel)	normal	$7.3\cdot10^{18}$	$170\cdot10^{-12}$ mol/mol	0.0 %
r_{iso}	1.0	0.0 % (rel)				
xHCl	0.7576					
xHClHITRAN	0.7576					
A_{line}	0.012922 cm^{-1}	1.0 % (rel)	normal	$7.8\cdot10^{-3}$	$1.0\cdot10^{-6}$ mol/mol	19.6 %
T	292.933 K	0.10 % (rel)	normal	$340\cdot10^{-9}$	$100\cdot10^{-9}$ mol/mol	0.2 %
p	334.802 hPa	0.15 % (rel)	normal	$-300\cdot10^{-9}$	$-150\cdot10^{-9}$ mol/mol	0.5 %
S_T	$189.71\cdot10^{-21}$ cm/molecule	2.0 % (rel)	normal	$-530\cdot10^{12}$	$-2.0\cdot10^{-6}$ mol/mol	78.6 %
γ_{HCl}	128.78 cm-1	2.0 % (rel)				
x_{HCl}	$100.35\cdot10^{-6}$ mol/mol	$2.26\cdot10^{-6}$ mol/mol				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
x_{HCl}	$100.3\cdot10^{-6}$ mol/mol	$4.5\cdot10^{-6}$ mol/mol	2.00	95% (normal)