


 Cite this: *Analyst*, 2021, **146**, 1402

## Accurate analysis of HCl in biomethane using laser absorption spectroscopy and ion-exchange chromatography

 Javis A. Nwaboh,<sup>a</sup> Heleen Meuzelaar,<sup>b</sup> Jiawen Liu,<sup>b</sup> Stefan Persijn,<sup>b</sup> Jianrong Li,<sup>b</sup> Adriaan M. H. van der Veen,<sup>b</sup> Nicolas Chatellier,<sup>c</sup> Arnaud Papin,<sup>c</sup> Zhechao Qu,<sup>a</sup> Olav Werhahn<sup>a</sup> and Volker Ebert<sup>a</sup>

Biomethane is a renewable energy gas with great potential to contribute to the diversification and greening of the natural gas supply. Ideally, biomethane can directly be injected into the natural gas grid system. For grid injection, specifications such as those in EN 16723-1 shall be met. One of the impurities to be monitored is hydrogen chloride (HCl). To assess conformity with the specification for HCl, accurate and reliable test methods are required. Here, we report the development of three novel test methods, based on a variety of laser absorption spectroscopy techniques (Direct absorption spectroscopy-DAS and wavelength modulation spectroscopy-WMS) and ion-exchange chromatography, for the measurement of HCl in biomethane. Gas mixtures of HCl in biomethane were used to demonstrate the performance of the spectroscopic systems in the nmol mol<sup>-1</sup> to low μmol mol<sup>-1</sup> ranges, achieving uncertainties in the 4% range,  $k = 2$ . For ion-exchange chromatography analysis, HCl was first collected on an alkali-impregnated quartz fiber filter. The analysis was performed according to ISO 21438-2 and validated using synthetic biomethane spiked with HCl. The relative expanded uncertainties for the ion exchange chromatography HCl measurements are in the 10–37% range,  $k = 2$ . The results presented for the 3 test methods demonstrate that the respective methods can be used for HCl conformity assessment in biomethane.

 Received 1st October 2020,  
 Accepted 10th December 2020  
 DOI: 10.1039/d0an01955k

[rsc.li/analyst](http://rsc.li/analyst)

### 1. Introduction

There is an increased need from the European Union (EU) to diversify its energy supply, thereby targeting renewable sources such as biomethane.<sup>1,2</sup> Biomethane (composed mostly of methane, nitrogen and carbon dioxide produced by upgrading biogas, *i.e.* removing molecules such as carbon dioxide, hydrogen sulfide and water from biogas) is a renewable energy gas that can be used for equipment and applications designed for natural gas, and can be injected into the natural gas network if certain specifications are met. To preserve the integrity of the natural gas grid infrastructure, the specification (EN 16723-1<sup>3</sup>) for biomethane injection provides threshold values for the contents of impurities such as siloxanes, hydrogen chloride (HCl), hydrogen fluoride (HF), and halogenated volatile organic compounds in biomethane. As an example, high concentrations of halogenated compounds are generally found in

biogas from industrial landfills and sewage treatment which need to be removed.

In this work, we describe dedicated methods for the analysis of HCl in biomethane and biogas, aiming to achieve analytical performance characteristics better than those provided by the methods specified in EN16723-1. The method cited in the specification is developed for measurements in air, thus not specifically developed and validated for measurements in biomethane. In fact, a recent study indicates the potential inadequacy of current standard methods for chlorine sampling in particular in biogas but also in biomethane.<sup>4</sup>

With the growing number of biomethane plants in Europe,<sup>5</sup> there is a need to develop a metrological infrastructure for traceable biomethane conformity assessment<sup>2</sup> thereby supporting policy makers to make decisions on the supply and use of biomethane. Within the EMPIR project “*Metrology for Biomethane*”,<sup>1</sup> test methods are being developed for accurate and reliable measurements of the impurities. Accurate measurements of the concentration of HCl in biomethane (threshold for chlorinated compounds in EN 16723-1: 1 mg m<sup>-3</sup>; 1 μmol mol<sup>-1</sup> HCl corresponds to approximately 1.5 mg m<sup>-3</sup> at reference conditions 25 °C and 101.325 kPa) for quality control are of particular importance as HCl leads to

<sup>a</sup>Physikalisch-Technische Bundesanstalt (PTB), 38116 Braunschweig, Germany.

E-mail: javis.nwaboh@ptb.de

<sup>b</sup>VSL, Thijssseweg 11, 2629 JA Delft, The Netherlands

<sup>c</sup>INERIS: Parc Technologique Alata BP 2, Verneuil en Halatte, 60550, France


corrosion in gas transport pipelines and appliances. Across Europe threshold values vary for chlorinated compounds in biomethane.<sup>3,6</sup> As indicated, to support conformity assessment of biomethane, there is currently no dedicated method for HCl in biomethane. Laser absorption spectroscopy and ion-exchange chromatography are techniques that enable the developing of selective, accurate and reliable tests methods for this purpose.

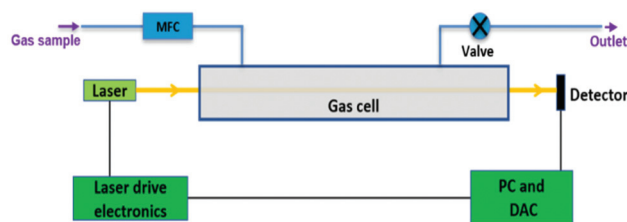
Laser absorption spectroscopy has been demonstrated for accurate HCl and other gas species amount fraction measurements in a variety of applications.<sup>7–14</sup> So far, reports on laser spectroscopic measurements of HCl in biomethane, addressing traceability of the results to the international system of units (SI), are lacking. Direct tunable diode laser absorption spectroscopy (dTDLAS) and wavelength modulation spectroscopy (WMS) with comparably higher sensitivity<sup>2,9</sup> specifically as demonstrated in other applications<sup>2,8,9,11</sup> are good candidates for the development of test methods for HCl concentration measurements in biomethane. dTDLAS is a variant of TDLAS that combines this spectroscopic technique with a special, first principles data evaluation approach to directly extract absolute species amount fraction (concentration) without calibration of the sensor with a calibration gas mixture, under the provision that a metrologically traceable line strength parameter is available.<sup>7,11,15</sup> Ion exchange chromatography on the other hand is an analytical technique that is widely used to measure the concentration of gases with very low limits of quantification,<sup>16,17</sup> and therefore also a good candidate to develop a test method for HCl concentration measurements in biomethane. Due to the biomethane matrix, a dedicated sampling approach and data analysis procedure is required.

In the following subsections, two laser spectroscopy methods (based on dTDLAS and WMS) and an ion exchange chromatographic method have been described for accurate and reliable measurements of the amount fraction of HCl (nmol mol<sup>-1</sup> to μmol mol<sup>-1</sup>) in biomethane. The performance characteristics (*e.g.*, repeatability and reproducibility) of the methods were determined to demonstrate their applicability for HCl impurity measurements at these low levels in biomethane. The measurement methods are validated by comparing the measurement results with values assigned to the amount fraction of HCl in calibration gas mixtures. These gas mixtures have been prepared using static or dynamic gravimetric gas mixture preparation methods. An in-depth description of one of the dynamic-gravimetric gas mixture preparation method, developed for this purpose is based on the permeation method as described in ISO 6145-10,<sup>18</sup> is presented. Uncertainty evaluations are presented for the analytical values reported for all measurements.

## 2. Experimental results

### 2.1. The dTDLAS measurements

In dTDLAS, the relation between the incident radiation and the transmitted radiation across an absorbing medium (*e.g.*,



**Fig. 1** Schematic of the ICL-dTDLAS instrumentation for HCl concentration measurements in CH<sub>4</sub> and biomethane (DAC: data acquisition card).

gas molecules in a gas cell, see Fig. 1) can be expressed by the extended Beer–Lambert law,<sup>11</sup>

$$\Phi(\tilde{\nu}, L) = Tr(t) \times \Phi_0(\tilde{\nu}) \times \exp\{-S_T \times g(\tilde{\nu} - \tilde{\nu}_0) \times L \times n\} + E(t) \quad (1)$$

where the quantity  $\Phi_0$  is the incident radiation,  $\Phi$  the transmitted radiation,  $Tr(t)$  and  $E(t)$  describe the effect of variation of the cell broadband transmission and an additive detector signal (*e.g.*, caused by background radiation) with time  $t$ ,  $S_T$  is the line strength of the probed molecular transition at gas temperature  $T$ ,  $L$  is the optical path length of the light beam transmitted through the absorbing medium,  $g$  is a normalized absorption line profile centred at  $\nu_0$ , and  $n$  is the absorber number density,<sup>11,14,19</sup> As already described elsewhere,<sup>11,14,19</sup> making use of the area-normalization of  $g$  and employing the ideal gas law (assuming ideal gas behaviour), eqn (1) can be written in integral form:<sup>11</sup>

$$\begin{aligned} x_{\text{species}} &= \frac{k_B \times T}{S_T \times L \times r_{\text{iso}} \times p_{\text{total}}} \int_{-\infty}^{\infty} A(\tilde{\nu}) d\tilde{\nu} \\ &= \frac{k_B \times T}{S_T \times L \times r_{\text{iso}} \times p_{\text{total}}} \times A_{\text{line}} \end{aligned} \quad (2)$$

where the quantity  $A(\tilde{\nu}) = -\ln(\Phi(\tilde{\nu})/\Phi_0(\tilde{\nu}))$  is the spectral absorbance,  $k_B$  the Boltzmann constant,  $p_{\text{total}}$  the total gas pressure and  $A_{\text{line}}$  the line area.<sup>11</sup> The quantity  $r_{\text{iso}}$  is an isotopic correction factor, given *e.g.* as  $r_{\text{iso}} = x_{\text{H-35Cl}}/x_{\text{H-35Cl-HIT}}$ , for a probed H<sup>35</sup>Cl line, where  $x_{\text{H-35Cl}}$  and  $x_{\text{H-35Cl-HIT}}$  are the abundances of H<sup>35</sup>Cl in the sample and the conventional abundance value used by HITRAN,<sup>20</sup> respectively. The amount fraction of a gas species  $x_{\text{species}}$  (*e.g.*,  $x_{\text{HCl}}$ , for HCl) can be made metrologically traceable to the international system of units (SI), if all input quantities, *e.g.*,  $S_T$ ,  $L$ ,  $p_{\text{partial}}$  and  $T$ , are determined with metrological traceability as well, the measurement uncertainty is duly propagated, and the impact of all assumptions underlying the measurement model have been taken into account in the evaluation of the measurement uncertainty.

**2.1.1. The dTDLAS instrument.** Fig. 1 shows a schematic of the dTDLAS instrument used to perform the HCl concentration measurements at PTB. The system in Fig. 1 consists of a continuous wave interband cascade laser (ICL, Nanoplus) emitting at about 3.6 μm (2752.04 cm<sup>-1</sup>), 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 CH<sub>4</sub>/biomethane flows (volume flow rates: between 0.1–2 L min<sup>-1</sup>, controlled by the mass flow controller (MFC), a needle valve and a membrane pump connected to the outlet in Fig. 1) through the gas cell. The laser wavelength was swept at 140 Hz across the probed HCl absorption line (1-0, P6-line centred at 2752.04 cm<sup>-1</sup>). The sampling line and the gas cell are all coated with Dursan™ to reduce surface interaction (adsorption, contamination and loss of HCl) as the gas flows and to minimize the response time of the instrument.

**2.1.2. Measurements of HCl amount fractions.** Fig. 2a depicts typical recorded signal of HCl in CH<sub>4</sub> measured using the setup in Fig. 1. The measurement was performed using a gas mixture with a nominal amount fraction of 110 μmol mol<sup>-1</sup> HCl in CH<sub>4</sub>. Fig. 2b shows absorbance data derived from the signal in Fig. 2a. A Voigt profile is fitted to the data in Fig. 2b in order to derive the line area ( $A_{\text{line}} = 0.00829 \text{ cm}^{-1}$ , area underneath the absorption line). The fitting was performed with the Lorentzian and Gaussian line widths fixed by means of a CH<sub>4</sub>-HCl broadening coefficient (measured in a separate experiment) and the measured gas temperature, respectively. The fit software used is capable of accounting for interferences due to absorption by other gas molecules, e.g. methane, in the gas mixture. Using the line area, and by means of eqn (2) an amount fraction of (112.0 ± 2.6) μmol mol<sup>-1</sup> is evaluated for the data in Fig. 2b, where the uncertainty is stated as standard uncertainty. The measured HCl amount fraction of (112.0 ± 5.2) μmol mol<sup>-1</sup> (coverage factor

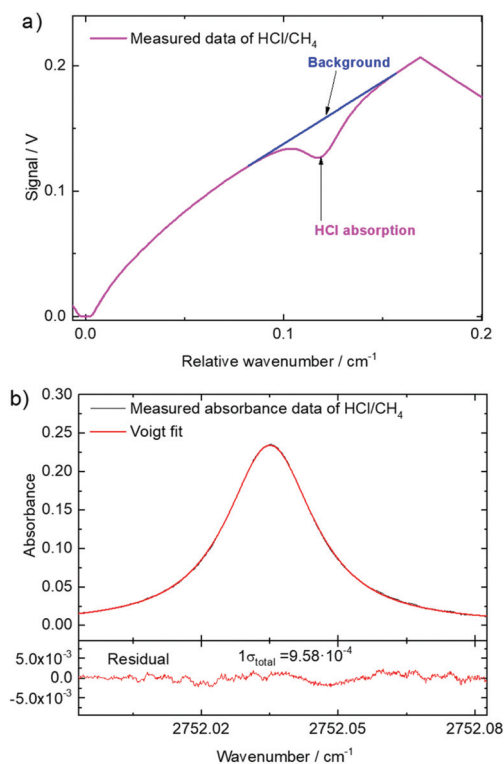
$k = 2^{21}$ ) is in good agreement with the value of (110 ± 5.5) μmol mol<sup>-1</sup>,  $k = 2$ , reported for the gas mixture by the manufacturer (information on the metrological traceability not reported). By means of the peak absorbance (0.2342) and the total residual ( $\sigma_{\text{total}} = 9.58 \times 10^{-4}$ ) in Fig. 2b, a signal to noise ratio (S/N) of 245 is calculated. Using the measured HCl amount fraction of 112 μmol mol<sup>-1</sup> and the S/N of 245, a snapshot precision of 0.46 μmol mol<sup>-1</sup> ( $\Delta t = 2 \text{ s}$ ) is evaluated for the data in Fig. 2b.

Table 1 holds the uncertainty budget of the dTDLAS 112 μmol mol<sup>-1</sup> HCl amount fraction results evaluated from the data in Fig. 2b. As shown in Table 1 (with eqn (2) as model function), the relative standard uncertainty of the result of 2.3% ( $k = 1$ ) is dominated by the uncertainty of the line strength values (traceable to ref. 22 and validated at the PTB) of 2.0%,<sup>7,20,22–24</sup> followed by the relative standard deviation of the line area ( $A_{\text{line}}$ ) of 1%, and the rest of the other quantities (including the uncertainty associated with the assumption of an ideal gas for eqn (1)) with sub-percent uncertainties.

To determine the repeatability and the detection limit of the dTDLAS spectrometer, Fig. 3a and b depict results of repeated dTDLAS measurements and dTDLAS- $x_{\text{HCl}}$  Allan deviation plot, respectively. The repeatability (calculated as the standard deviation of the mean) of the HCl amount fraction results is 0.065 μmol mol<sup>-1</sup> (0.058% relative). The detection limit of the instrument is 25 nmol mol<sup>-1</sup> at a time resolution ( $\Delta t$ ) of 24 s. Here, time resolution means the averaging time.

Regarding the reproducibility of the dTDLAS results, HCl amount measurements were carried out at three consecutive months. Fig. 4a depicts dTDLAS measurements performed at months 1, 2 and 3. The mean value of the dTDLAS results is 112.6 μmol mol<sup>-1</sup>. The reproducibility (standard deviation) of the results is 0.31 μmol mol<sup>-1</sup> (0.28% relative). As shown in Fig. 4a, all dTDLAS results are in good agreement with the value assigned to the commercial gas mixture (110 ± 5.5) μmol mol<sup>-1</sup> ( $k = 2$ ).

Similar dTDLAS measurements of HCl amount fractions were performed in the amount fraction range of 10–500 μmol mol<sup>-1</sup> achieving good agreements (see Fig. 4b, linearity in the range (10–500 μmol mol<sup>-1</sup>: slope: 1.038 ± 0.071, intercept: (-2.41 ± 5.57) μmol mol<sup>-1</sup>) with the values reported for the gas mixtures used, further demonstrating the capability of the dTDLAS test method for HCl concentration measurements in biomethane. The intercept is insignificant (*i.e.*, its uncertainty

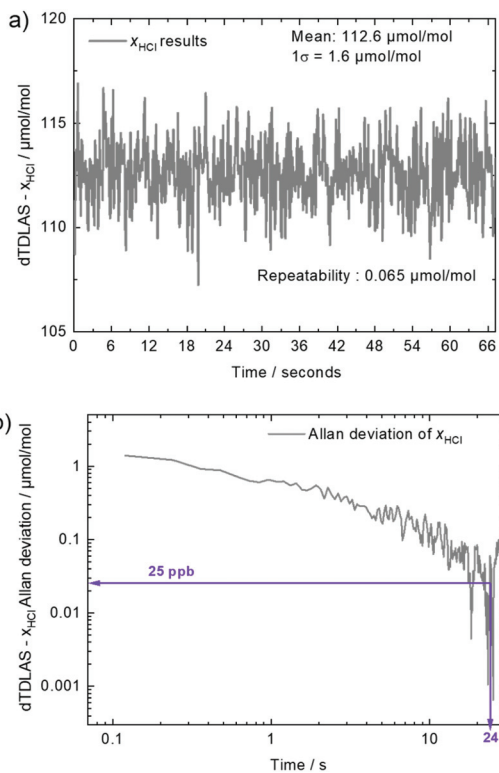


**Fig. 2** (a) Measured dTDLAS HCl-P6 signal as a function of relative wavenumber. (b) Measured absorbance and residuals with respect to a Voigt profile as a function of the wavenumber.

**Table 1** Uncertainty budget for dTDLAS results evaluated similar to the previous work by Nwaboh *et al.*<sup>25</sup>

Parameter	Value	Relative standard uncertainty ( $k = 1$ )/%
Pressure	192.2 hPa	0.20
Temperature	294.6 K	0.10
Path length	0.820 cm	0.24
Line strength <sup>21</sup>	$1.91 \times 10^{-19}$	2.00
	cm per molecule	
Line area	$0.00829 \text{ cm}^{-1}$	1.00
dTDLAS HCl result	$112 \text{ μmol mol}^{-1}$	2.30





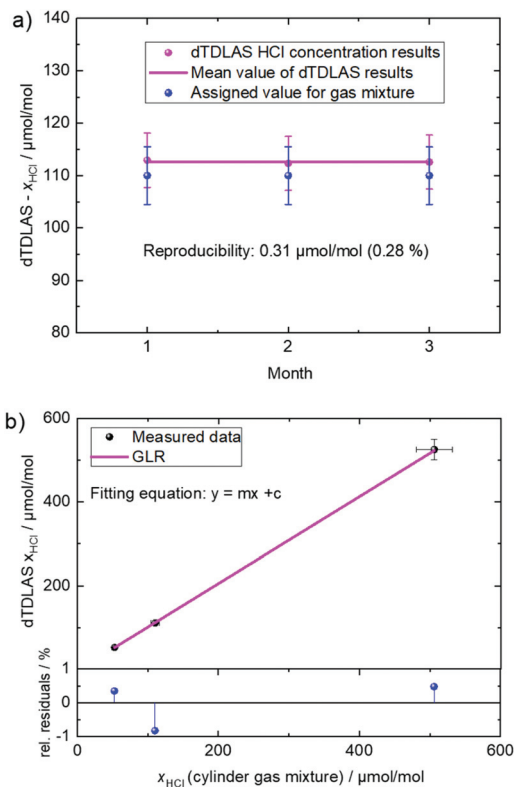
**Fig. 3** (a) dTDLAS- $x_{\text{HCl}}$  results as a function of time. (b) dTDLAS- $x_{\text{HCl}}$  Allan deviation as a function of time.

is larger than the value), demonstrating that there is no offset of the dTDLAS. Therefore, the dTDLAS HCl instrument can perform absolute and calibration free (no pre-calibration of the instrument with a calibration gas mixture) measurements. The HCl amount fraction measurements in biomethane showed good repeatability (e.g., 0.058% at  $112 \mu\text{mol mol}^{-1}$ ), reproducibility (e.g., 0.28% at  $112 \mu\text{mol mol}^{-1}$  for 3 months span), linearity (in the range of  $10\text{--}500 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$ : slope:  $1.038 \pm 0.071$ ) and precision of  $25 \text{ nmol mol}^{-1}$  at a time resolution of 24 s. Direct traceability of the dTDLAS HCl amount fraction results to SI was addressed *via* the traceability of input parameters such as the measured gas pressure and temperature that are traceable to respective PTB standards. The line strength value is traceable to HITRAN<sup>20</sup> entry for HCl form ref. 22 and has been validated (to be fit for purpose) in separate HCl concentration measurements at PTB. A dTDLAS instrument that can deliver gas species amount fraction results that are directly traceable to the SI can be referred to as an “Optical Gas Standard (OGS)”<sup>11,13,15</sup> similar to the Ozone Standard Reference Photometer.<sup>26</sup> To assess compliance with EN 16723-1<sup>3</sup> for HCl in  $\text{CH}_4$  (and biomethane), the dTDLAS HCl instrument can be used.

## 2.2. Calibrated DAS-WMS HCl amount fraction measurements

### 2.2.1. The Laser spectrometer.

At VSL a primary dynamic gas standard and a laser spectrometer combining direct



**Fig. 4** (a) Results of dTDLAS HCl amount of substance fraction measurements performed at month 1, 2 and 3. (b) Plot of dTDLAS  $x_{\text{HCl}}$  results as a function of the values reported for the gas mixtures used. A generalized linear regression is applied to the data (slope:  $1.038 \pm 0.071$ ,  $k = 1$ , intercept:  $(-2.41 \pm 5.57) \mu\text{mol mol}^{-1}$ ).

absorption spectroscopy (DAS) and wavelength modulation spectroscopy (WMS similar to Klein *et al.*<sup>9</sup>) have been developed for the measurement of hydrogen chloride (HCl) at trace levels in various matrices including hydrogen,<sup>27</sup> nitrogen<sup>28</sup> and methane ( $\text{CH}_4$ ).<sup>1</sup> The spectrometer employs a similar ICL laser as employed by PTB (with collimator) to probe the same P6 line centred at  $3633.68 \text{ nm}$  ( $2752.04 \text{ cm}^{-1}$ ) as in section for dTDLAS. This line is not the strongest available HCl absorption line, yet it suffers less from methane spectral interference than other strong HCl absorption lines. Different from section on dTDLAS, wavelength modulation (WMS)<sup>29</sup> was applied to enhance sensitivity, thereby allowing detection of low HCl amount fractions in a methane matrix. The laser is tuned over the absorption line at a rate of 1 kHz. On top of this, a fast 21 kHz modulation to the laser current is applied. The laser beam is coupled into a multi-pass cell (Aerodyne, USA) with an effective path length of 76 m *via* several silver-coated mirrors and the exiting light is focused using a parabolic mirror on a 2-stage Peltier cooled detector (PVI-4TE from VIGO, Poland). The pressure in the cell is maintained at 100 mbar using a combination of a SilcoNert 2000 coated pressure controller and a membrane pump. A lock-in amplifier (model SR830 from Stanford Research Systems, USA) is used to demodulate and extract the second ( $2f$ ) harmonics signal from the detector



signal and the output is acquired using a fast digitizer (Octave digitizer, model OVE-832-009) and GageScope software.

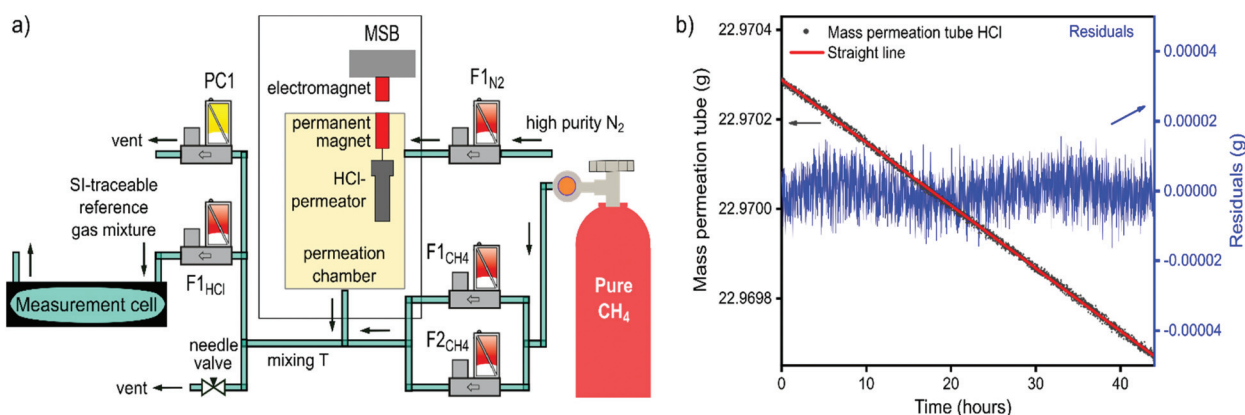
**2.2.2. The permeation system.** To prepare calibration gas mixtures for the spectroscopic measurements, a dynamic-gravimetric preparation method has been developed for generating HCl in methane gas mixtures based on the permeation method as described in ISO 6145-10.<sup>18</sup> A passivated and calibrated magnetic suspension balance (MSB) manufactured by TA instruments performs continuous, accurate mass measurements of a HCl permeator of 99.0% purity (manufacturer Fine Metrology, Italy). The permeation tube is suspended from the micro balance inside the temperature- and pressure-controlled permeation chamber (see Fig. 5a). The permeation chamber is continuously purged with a small, constant flow of high-purity nitrogen (Air Products, BIP+, grade 6.0; volume flow rate  $50 \text{ mL min}^{-1}$ ) and the HCl permeation rate is subsequently determined from the recorded mass loss of the permeation device over time (see Fig. 5b). The prepared calibration gas mixture is then mixed with a variable and much higher dilution flow (up to several  $\text{L min}^{-1}$ ) of high-purity methane (Air Products, grade 5.5) which is regulated by calibrated thermal mass flow controllers according to ISO 6145-7.<sup>30</sup> The composition of the HCl in methane mixture is calculated from the permeation rate as well as the mass flow rates of the carrier  $\text{N}_2$  and dilution gases  $\text{CH}_4$  (in compliance with ISO 6145-10<sup>18</sup> and ISO 6145-7,<sup>30</sup> respectively). Note that the resulting HCl in methane mixture contains also up to a few percent nitrogen. Using this system, HCl in methane amount fractions can be generated at  $\text{nmol mol}^{-1}$  and low  $\mu\text{mol mol}^{-1}$  levels by varying the temperature of the permeation chamber and/or the dilution flow rates. Further, a static gas mixture containing  $10 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$  (Praxair) has been analyzed.

**2.2.3. Results from the validation.** Permeation-based hydrogen chloride calibration gas mixtures in methane were prepared at low  $\mu\text{mol mol}^{-1}$  levels and consecutively measured using the analytical method based on DAS and 2f-WMS (introduced in the first part of this subsection on DAS-WMS). For

line identification and validation close to  $10 \mu\text{mol mol}^{-1}$  HCl, Fig. 6a compares the DAS measurement of a static mixture of  $10 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$  from a cylinder and a  $9.0 \mu\text{mol mol}^{-1}$  HCl in  $\text{N}_2$  mixture prepared using the permeation method. In addition, HITRAN-based simulation of the HCl absorption line in  $\text{CH}_4$  and  $\text{N}_2$  are depicted. We found good agreement when comparing the experimental HCl absorption spectra in  $\text{CH}_4$  as well as in  $\text{N}_2$  with their corresponding simulated spectra from HITRAN,<sup>20</sup> confirming the line strength value (within the associated uncertainty) used in section for dTDLAS.

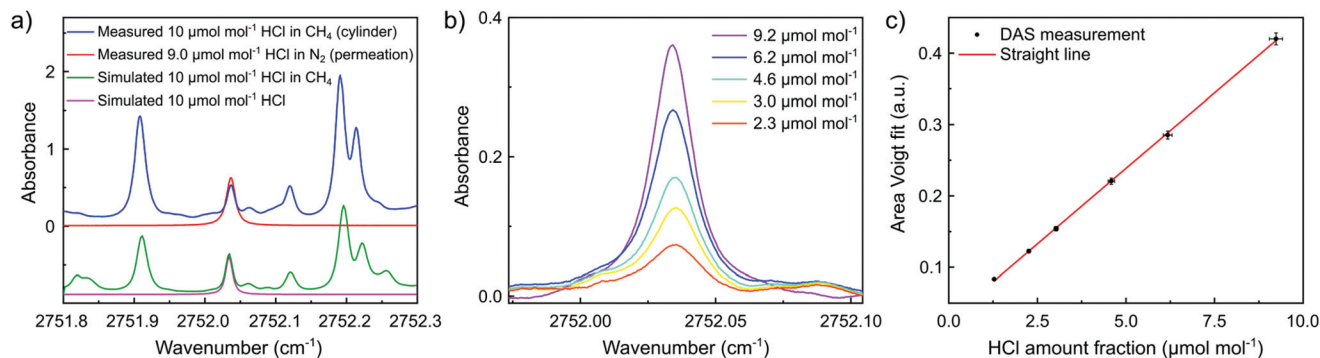
Fig. 6b shows the background subtracted DAS spectra of HCl at different amount-of-substance fractions in  $\text{CH}_4$  generated based on permeation (used to prepare calibration gases for the spectroscopic measurements). The HCl absorption lines were fitted using a simple Voigt profile. The area under the resulting fit was determined and plotted as function of the generated amount of substance fraction (see Fig. 6c, here, straight line: resulting calibration curve for HCl determination different from the analysis method in the dTDLAS subsection). The results show that the response of the instrument follows a straight-line relationship according to Beer-Lambert's law.<sup>31</sup> The obtained straight line meets the consistency requirements of ISO 6143.<sup>32</sup> The slope of the straight line is  $(4.167 \pm 0.096) \times 10^{-2}$  a.u per  $\mu\text{mol}$  per mol and the intercept is  $(2.93 \pm 0.26) \times 10^{-2}$  a.u, where the uncertainties are stated as standard uncertainties. The error bars indicate the expanded uncertainties ( $k = 2$ ). A limit of quantification of  $100 \text{ nmol mol}^{-1}$  was found for the DAS measurement of HCl in  $\text{CH}_4$ . The resulting expanded uncertainty for HCl analysis at  $10 \mu\text{mol mol}^{-1}$  in  $\text{CH}_4$  is 4%.

Enhanced sensitivity and lower detection limits were achieved by using 2f-WMS. Fig. 7a shows the results of 2f-WMS measurements of pure methane,  $0.99 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$ , the matrix-corrected 2f-signals of HCl and its simulated 2f-spectrum based on HITRAN database.<sup>20</sup> The methane matrix causes quite some spectral interference at these low HCl amount fractions but as the  $\text{CH}_4$  background signal is

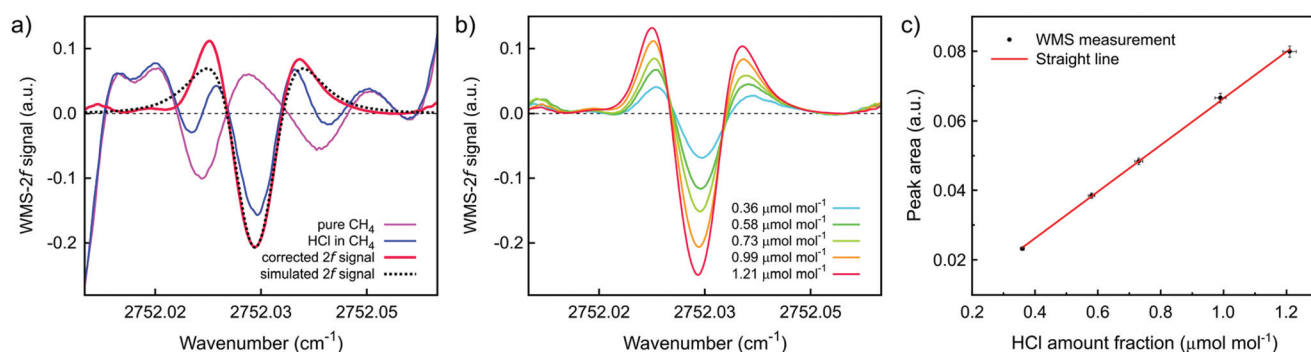


**Fig. 5** (a) Outline of the permeation system used for the dynamic-gravimetric preparation of HCl in methane mixtures. (b) Measurement of the mass of the HCl permeation tube using the MSB. The measured mass loss can be fitted to a linear function (red line), yielding a permeation rate of  $(234.0 \pm 7.5) \text{ ng min}^{-1}$  ( $k = 2$ ) at  $15.6 \text{ }^\circ\text{C}$ . The corresponding residuals (blue, right axis) are also shown.





**Fig. 6** (a) Measured direct absorption spectrum of a static  $10 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$  mixture (blue line) and a permeation-based  $9.0 \mu\text{mol mol}^{-1}$  HCl in  $\text{N}_2$  mixture (blue dots). Measured HCl absorption spectra compared to HITRAN-based simulation of HCl in  $\text{CH}_4$  and  $\text{N}_2$  (red and green, respectively). (b) Background subtracted DAS spectra of HCl in  $\text{CH}_4$  at different amount-of-substance fractions. (c). Dependence of the peak area (Voigt fit) on the HCl amount fraction.



**Fig. 7** (a) WMS-2f signal of pure  $\text{CH}_4$  (magenta),  $0.99 \mu\text{mol mol}^{-1}$  HCl in  $\text{CH}_4$  (blue), and the latter also corrected for the contribution from the  $\text{CH}_4$  matrix (red). Simulated spectrum based on HITRAN database (black). (b) Background-subtracted WMS-2f spectra of HCl in  $\text{CH}_4$  at different amount fractions. (c) Dependence of the peak area on the HCl amount fraction.

very stable this can be easily subtracted. The background-corrected signal shows good agreement with the simulated 2f-spectrum (see Fig. 7a). Fig. 7b depicts the matrix-corrected 2f-WMS spectra of calibration gas mixtures with varying HCl amount fractions in  $\text{CH}_4$  showing the high sensitivity and selectivity of the method, even for such low HCl amount fraction in methane. Using the absolute 2f-area under the curves provides a robust measure of the HCl amount fraction and a good linearity is observed (see Fig. 7c). The obtained straight line meets the requirements of ISO 6143 regarding the goodness-of-fit.<sup>32</sup> The slope of the straight line is  $(6.77 \pm 0.19) \times 10^{-2}$  and the intercept is  $(-1.09 \pm 1.15) \times 10^{-3}$ , where the uncertainties are stated as standard uncertainties. The uncertainty bars plotted denote expanded uncertainties ( $k = 2$ ). A limit of quantification of  $20 \text{ nmol mol}^{-1}$  was found for the 2f-WMS measurement of HCl in  $\text{CH}_4$ . The resulting expanded uncertainty for HCl analysis at  $1.0 \mu\text{mol mol}^{-1}$  in  $\text{CH}_4$  is 4%.

For the analysis of unknown amount fractions of HCl in  $\text{CH}_4$  three main sources of uncertainty can be identified in the measurements:

(1) *Purity of the permeation-based calibration gas:* The most challenging part in the uncertainty budget of permeation is

the purity of the generated gas. Any impurity released by the HCl permeator will affect the observed mass flow rate of permeation and thereby the determined HCl amount fraction. In this study, the purity specification of the manufacturer, *i.e.*, 99.0%, has been taken into account for the uncertainty evaluation of the permeation system. Ongoing work includes further purity analysis of the gas emitted from HCl permeators to minimise the contribution of potential impurities to the standard deviation of the generated calibration gas. The relative uncertainty contribution of the generated HCl amount fractions based on permeation was 3.2% ( $k = 2$ ).

(2) *HCl adsorption:* HCl is highly reactive, reacting rapidly with water and therefore issues exist with the reproducibility of measurements. While both the dynamic gas mixture preparation system and sampling system have been optimized using only SilcoNert 2000 coated materials (*e.g.*, tubings, mass flow controller, pressure controller pressure regulator) the multi-pass measurement cell is made of uncoated aluminium. An optimized cell should be used in case rapid measurements are required. However, measurements of HCl generated by the MSB at amount fractions around  $10 \mu\text{mol mol}^{-1}$  were well reproducible (better than 1%). For similar cylinder measure-



ments a poorer reproducibility was observed probably due to adsorption in the cylinder and pressure reducer. Response times of approximately 30 minutes (using static mixtures) were obtained at volume flow rates of  $0.5 \text{ L min}^{-1}$ . By waiting 30 minutes or more this uncertainty contribution from adsorption issues can thus be reduced but this leads to relatively high gas consumption of at least 15 L.

(3) *Analyzer's (DAS 2f-WMS system) laser and detector instabilities:* Sources contributing to the uncertainty include instability in the laser intensity, laser wavelength and photo-detector. The uncertainty of the analyser has been estimated using the same experimental set-up (cell, electronics, photo-detector and flow system) only with a different laser (QCL) and a stable component ( $\text{N}_2\text{O}$ ). With this set-up a relative expanded uncertainty ( $k = 2$ ) of 0.5% or better has been obtained in the amount fraction determination for a  $\text{N}_2\text{O}$  absorbance mimicking that of to  $10 \mu\text{mol mol}^{-1}$  HCl. As the performance of the ICL laser used for HCl detection is comparable (possibly even better due to the better beam profile and wavelength stability) than the operated QCL laser, the resulting uncertainty will also be of similar magnitude.

In conclusion, to assess compliance with EN 16723-1<sup>3</sup> for the measurement of HCl in  $\text{CH}_4$  both the direct absorption (DAS) as well as wavelength modulation (2f-WMS) method can be used. An advantage of the latter method is that it provides a higher sensitivity and suffers less from optical interference by the  $\text{CH}_4$  matrix. Relative expanded uncertainties of 4% for both the DAS and 2f-WMS method have been achieved for HCl analysis at  $10 \mu\text{mol mol}^{-1}$  (DAS) and  $1.0 \mu\text{mol mol}^{-1}$  in  $\text{CH}_4$  (2f-WMS).

### 2.3. Ion-exchange chromatography

**2.3.1. General.** For ion-exchange chromatography<sup>33</sup> analysis at INERIS and for simplicity, HCl was first collected on an alkali-impregnated quartz fibre filter and the analysis performed according to ISO 21438-2<sup>34</sup> on the determination of inorganic acids by ion chromatography. The method developed has been validated with synthetic biomethane spiked with HCl.<sup>35</sup> This spiking step has been done by using a plastic syringe and different volumes of HCl gas at  $4860 \pm 70$  ppm were injected in the biomethane gas flow. For the four levels, these volumes are from 2 ml up to 95 ml (2 ml, 4 ml, 25 ml and 95 ml, respectively). The uncertainty of the HCl concentration in the standard gas has been calculated by measurement of the repeatability of the analytical method.

The characterization of the method has been carried out by applying two standards, initially published for water matrices, but also largely used for the validation of analytical methods in various matrices:

- the requirements of NF T 90-210<sup>36</sup> for the characterization of the calibration curve, the validation of the limit of quantification, the evaluation of accuracy at various levels of HCl concentrations;
- the requirements of the EN ISO 11352<sup>37</sup> for the evaluation of uncertainties at various levels of HCl concentrations.

**2.3.2. Sampling material.** For gas samples, a gas bottle of HCl at 5000 ppm in nitrogen (Praxair) and a synthetic biomethane supplied by Air Liquide (as indicated in the Table 2 containing a mixture of gases representative of biomethane) were selected. The volume fractions in Table 2 are expressed in %.

Impregnated quartz fiber filters were used to trap HCl from the synthetic biomethane gas. The quartz fiber filter used were from Whatman (QMA: 1851-037). Before being used for the sampling, they were impregnated with 500  $\mu\text{l}$  of a sodium carbonate solution at  $50 \text{ g L}^{-1}$  and disposed into a holder. Two filters were positioned in succession in the holder with the second filter used as a control.

**2.3.3. Sampling method.** A volume of HCl (2 to 95) mL (depending on the amount fraction to be tested) was first collected in a plastic syringe from the HCl gas bottle. The syringe was then connected to a system in line with the synthetic biomethane gas (see Table 2), and the gas samples of HCl injected into the synthetic biomethane gas before the resulting HCl in biomethane mixture is passed through the quartz filters as shown in the Fig. 8.

The sampling was performed at controlled volume flow rates ( $1 \text{ L min}^{-1}$ ) during 30 minutes onto the alkali-impregnated quartz fiber filters. The quartz filters were connected directly to the flow regulator mounted on the gas bottle. A gas counter was connected after the quartz filters to control the flow. This sampling method was used for the evaluation of the limit of quantification (LOQ), the accuracy at different levels of concentrations (amount of substance fractions) of HCl in biomethane and their associated uncertainties.

**2.3.4. Analytical conditions.** For the analysis of the samples, Thermo Scientific ion chromatograph with electro-

**Table 2** Composition of the synthetic biomethane used in this study (as volume fractions)

Compounds	Nominal value (%)
$\text{H}_2$	0.25
$\text{O}_2$	2.00
$\text{N}_2$	4.00
$\text{CO}_2$	5.00
$\text{CH}_4$	88.75



**Fig. 8** Gas mixing device and quartz filter trapping system.



chemical suppression and a conductimetric detector (model ICS 5000+) has been used.

The analytical conditions were:

- Precolumn AG19 4 × 50 mm (Thermo Scientific):  
Particle diameter: 11 μm;  
Functional Group: Alkanol quaternary ammonium;  
Resin: Supermacroporus polyniylbenzyl ammonium cross-linked with divinylbenzene;
- Column Thermo AS19 4 × 250 mm (Thermo Scientific):  
Particle diameter: 7.5 μm;  
Functional Group: Alkanol quaternary ammonium;  
Resin: Supermacroporus polyniylbenzyl ammonium cross-linked with divinylbenzene;
- Flow: 1 L min<sup>-1</sup>;
- Eluant: Using eluant generator from KOH solution at 22%;
- Temperature of the column: 30 °C;
- Injection volume: 25 μl;
- Elution mode: Gradient of eluent concentration (see Table 4);
- Detection: Conductimetric;
- Temperature of the conductimetric cell: 35 °C;
- Electrochemical suppression;  
Suppressor ADRS 600 – 4 mm (Thermo Scientific);  
Suppression current: 112 mA.

**2.3.5. Measurements.** After sampling, the quartz fiber filters were subjected to an aqueous extraction after a sonification step (5 min) at room temperature. This aqueous extraction was proceeded with 20 mL of ultrapure water in a plastic tube of 50 mL. Each filter (the sampling filter and the control) was extracted and analysed individually.

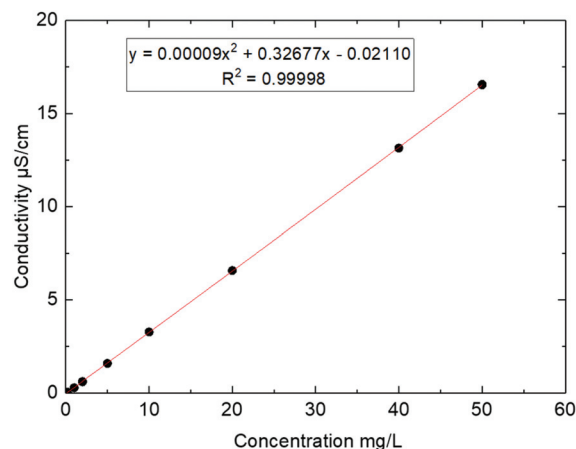
The analysis of the samples was performed on a Thermo Scientific chromatograph with conductimetric detector (model ICS 5000+) after calibration. To perform the calibration, nine standard solutions with different levels of concentration were prepared from liquid solutions of commercial products by successive dilutions in water. The reagents used was chloride at 1 g L<sup>-1</sup> from ChemLab (ref. CL01.0346.0500). The calibration ranges from 2 μg Cl<sup>-</sup> to 1000 μg Cl<sup>-</sup> corresponding to 0.07 mg m<sup>-3</sup> to 34 mg m<sup>-3</sup> (see Table 3). Each calibration was prepared 6 times from independent solutions in conditions of intermediate precision (same person, different day). A second-degree polynomial was used as the calibration model (see Fig. 9). The range was verified according to the French standard NF T 90-210 requirements<sup>36</sup> (maximum acceptable deviation approach), with a coefficient of determination ( $R^2$ ) over 0.999 (see Fig. 9) for HCl for this calibration range.

**Table 3** Low and high concentrations of the calibration range

Compound	Low level	High level
HCl	0.1 mg L <sup>-1</sup>	50 mg L <sup>-1</sup>
	2 μg	1000 μg
	0.07 mg m <sup>-3</sup>	34 mg m <sup>-3</sup>

**Table 4** Gradient of eluent concentration

Time (min)	Events	mM KOH
-7	Stabilization	10
0	Start acquisition	10
10		10
10.01		45
17		45
17.01	End	10



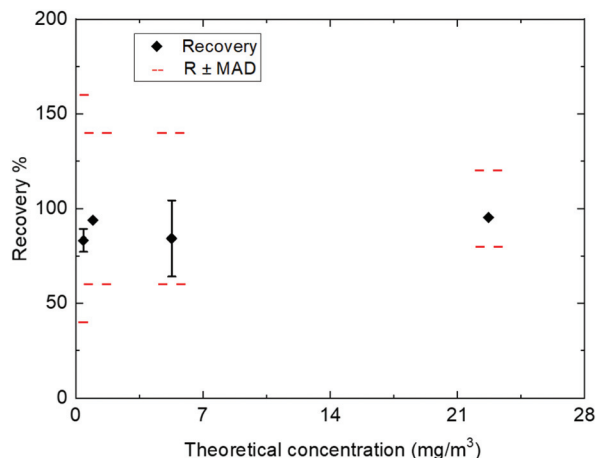
**Fig. 9** Example of a calibration curve for HCl.

**2.3.6. Limit of quantification and accuracy.** The LOQ of the method described was determined according to NFT 90-210,<sup>36</sup> a French standard based on ISO 5725.<sup>38</sup> The LOQ was evaluated within conditions of repeatability with duplicates for the extraction (two samples spiked at the same level of concentration), and inter-day precision by performing 6 series of duplicate extraction on 6 different days. This methodology analyzes trueness and precision of the results for HCl at a concentration close to the supposed limit of quantification. This test ensures that the accuracy (trueness and precision) does not exceed ± 60% of the supposed LOQ. Using this method, a LOQ of 0.1 mg L<sup>-1</sup> (2 μg; 0.07 mg m<sup>-3</sup>) of HCl was validated.

Similarly to the LOQ, the accuracy of the analytical method is evaluated according to NF T 90-210.<sup>36</sup> Tests were performed at 4 levels (see Fig. 10) of concentration including LOQ within conditions of repeatability with duplicates for the sampling and extraction (two samples spiked at the same level of concentration) and inter-day precision by performing 6 series of extraction in duplicates on 6 different days. This methodology analyzes trueness and precision of the results for HCl at the studied concentration. This test ensures that the accuracy (trueness and precision) does not exceed ± 60% of the spiked concentration at the LOQ and 40% for the two intermediate concentrations at LOQ × 2 and 20% of the higher point of the validated range and ±20% of the spiked concentration for the highest concentration at 80% of the higher point of the validated range. The sampling of the biomethane gas spiked by HCl at variable level was performed at controlled flow rates







**Fig. 10** Accuracy profiles at LOQ and at 3 other levels of concentration for HCl. Limits, MAD: Maximum acceptable deviation.

(1 L min<sup>-1</sup>) with exposure time of 30 minutes. As shown in Fig. 10 (depicting accuracy profiles, MAD: maximum acceptable deviation is a criterion on the accuracy), good recoveries between 78% (at the LOQ) to 96% were obtained for HCl. Except at the LOQ, all the recoveries are above 80%.

**2.3.7. Uncertainty evaluation.** The expanded uncertainties (see Table 5) of the measurements were calculated according to the requirements of ISO 11352<sup>37</sup> using the software MUKit Measurement Uncertainty kit developed by SYKE (Finnish Environment Institute). Considering that the measurement uncertainty may vary depending on the concentration range, the uncertainty was estimated separately for at least 3 concentration ranges within the validated range. The determination of uncertainty is based on validation and quality control which represent the within-laboratory reproducibility of the method and the laboratory bias. In ISO 11352, the expanded measurement uncertainty is quantified as the interval comprising the value on the measurand with a probability of about 95%.

It could be noted here that, for the tests at 6.15 mg m<sup>-3</sup> (see Table 5) of HCl trapped on filters, the recoveries obtained on half of the measurements for this series were lower than expected although quality control (ultrapure water spiked with solutions of Cl<sup>-</sup>) were at the expected levels. Therefore, lower overall recoveries and larger uncertainties were obtained for this level of concentration. These observations indicate that a problem might have occurred during the trapping step but as the recoveries and bias were still within the defined range, they were not rejected. Therefore, the recoveries and uncer-

tainty for this level (6.15 mg m<sup>-3</sup>) should be in reality closer to those obtained for the lower and higher level.

### 3. Discussion

The dTDLAS HCl amount fraction results in the (10–500) μmol mol<sup>-1</sup> are reported to be in good agreement with values reported from cylinder-based gas mixtures. The optimal precision of the instrument is 25 nmol mol<sup>-1</sup> at a time resolution (Δt) of 24 s. The agreement of the results demonstrates the capability of the dTDLAS approach as a test method for HCl concentration measurements in biomethane for quality control. The relative uncertainty of the dTDLAS results is in the 2.3% range, *k* = 1. This uncertainty is dominated by the systematic line strength uncertainty of 2%,<sup>20</sup> indicating that, to further reduce the uncertainty (when necessary) of the dTDLAS HCl amount fraction results, focus will be placed on reducing the uncertainty of the line strength value. The good repeatability (0.058%) and reproducibility (0.28%) of the results combined with the detection limit of 25 nmol mol<sup>-1</sup> (Δt = 24 s), further demonstrated the capability of the dTDLAS instrument for HCl quality control measurements in biomethane. Comparing the dTDLAS HCl results in this work (at about 3.6 μm) to the HCl results in Ortwein *et al.*<sup>7</sup> (at about 1.7 μm), the concentration resolution of 0.38 μmol mol<sup>-1</sup> m (calculated using the snapshot precision of 0.46 μmol mol<sup>-1</sup> at Δt = 2 s and path length of 0.82 m) for the dTDLAS results in this work is about 34 times better than the 13 μmol mol<sup>-1</sup> m (note: μmol mol<sup>-1</sup> = ppm) reported in Ortwein *et al.*,<sup>7</sup> indicating the improvement in the dTDLAS HCl results due to a stronger absorption line used in this work at 3.6 μm (fundamental band). This has become possible now, because of the improved mid-infrared interband cascade lasers available nowadays.

Similarly, as for dTDLAS, the calibrated HCl DAS-2f-WMS amount fraction results in the amount of substance fraction range of 0–1.2 μmol mol<sup>-1</sup> were validated by using gas mixtures provided by the dynamic-gravimetric preparation system. The relative expanded uncertainty of the calibrated DAS-2f WMS HCl amount fraction is estimated to be in the order of 4% (*k* = 2), in the same order as the expanded uncertainty of the dTDLAS results of 4.6% (*k* = 2). It should be noted here that the uncertainty of the DAS-WMS results is based on the calibration of the instrument with calibration gases, while that of the dTDLAS results is purely based on the individual input parameters (*e.g.*, gas pressure and temperature, line area and the line strength).

A good recovery (78% to 96%) was achieved for ion exchange chromatography HCl results (range: 0.07 mg m<sup>-3</sup>–34 mg m<sup>-3</sup>), demonstrating the capability of this analytical method for HCl measurements in biomethane. The relative expanded uncertainties for the ion exchange chromatography HCl measurements are in the (10–37) %, *k* = 2. The measurement uncertainty for the ion exchange chromatography measurements depends on the concentration, with the lowest

**Table 5** Summary table of the uncertainties obtained at the various tested levels

Tested level (mg m <sup>-3</sup> )	Relative expanded uncertainty
0.49	37%
0.98	14%
6.15	37%
23.4	10%



Table 6 Summary of measurement methods in this work for HCl analysis in biomethane

Measurement method	Range	Expanded uncertainty achieved/% ( $k = 2$ )	Detection limit/limit of quantification	Key advantage and drawback of method
dTDLAS	10–500 $\mu\text{mol mol}^{-1}$	4.6	25 $\text{nmol mol}^{-1}$ at $\Delta t = 24$ s	Key advantage: Absolute, traceable and calibration-free measurement, capable of performing sampling free <i>in situ</i> analysis. Drawback: Lower optical resolution and hence worse LOD at identical path and time resolution than WMS.
DAS-WMS	0–1.2 $\mu\text{mol mol}^{-1}$	4.0	100 $\text{nmol mol}^{-1}$ (DAS) 20 $\text{nmol mol}^{-1}$ (WMS)	Key advantage: WMS comes with a higher optical resolution than DAS. Drawback: First principles models and calibration-free approach for WMS is much more complicated and metrologically not validated. Higher optical density (OD) resolution requires higher baseline stability which is usually not given and thus forcing the system to be calibrated frequently.
Ion exchange chromatography	0.07–34 $\text{mg m}^{-3}$	10–37	0.07 $\text{mg m}^{-3}$	Key advantage: Trueness of the results with separation of the chloride (no interferences are possible). Drawback: Lab analysis which needs time to obtain the results.

uncertainty (10%) reported for the results at 23.4  $\text{mg m}^{-3}$ . These uncertainties are calculated taken into consideration the within-laboratory reproducibility of the method and the laboratory bias.

For the spectroscopic measurement techniques in this work, compared to those in our previous work on CO (at 4.6  $\mu\text{m}$ ),<sup>13</sup> a complex HCl absorption line selection process (before developing the systems) was required (due to potential interference from absorptions by  $\text{CH}_4$ ) for sensitive and selective measurements, and new high performance interband cascade lasers operated at 3.6  $\mu\text{m}$  have been employed and carefully characterized for the HCl analysis now. Compared to CO, HCl is a very sticky and reactive gas with new challenging properties such as HCl adsorption to the gas cell wall. Therefore, the new spectroscopic systems in the paper have been designed and realized including sampling lines and the single pass gas cell coated with Silconert and Dursan™ to minimize HCl adsorption and to speed up the response time of the instrument for HCl measurements in biomethane. In addition, dTDLAS/QCLAS was used in Nwaboh *et al.*<sup>13</sup> at  $\mu\text{mol mol}^{-1}$  (ppm) levels of CO, while dTDLAS/DAS-WMS containing longer gas cells was employed in this work targeting challenging HCl amount fractions down to the  $\text{nmol mol}^{-1}$  (ppb) levels.

The results presented for the 3 test methods (based on dTDLAS, ICL-2f WMS, ion chromatography), demonstrate that the respective methods can be used for HCl conformity assessment in biomethane with different uncertainties associated to the results depending on the method used. Table 6 holds a summary of the methods presented in this work, concentration ranges, expanded uncertainties, detection limits, key advantages and drawbacks of the respective methods. Using laser spectroscopic and ion chromatography methods offer the possibility of online (*in situ*) analysis and preconcentration procedures to significantly improve the sensitivities of analytical instrumentation, respectively.<sup>39–41</sup> In addition to

biomethane applications, the dTDLAS/DAS-WMS and ion exchange chromatography methods presented in this work have the capabilities to be applied for measurements in other applications such as HCl quality control measurements in clean room environment, atmospheric and industrial emission monitoring. Thus, the spectroscopic systems developed here showed a good potential for possible future commercial applications.

## 4. Conclusions

Three analytical methods (two based on laser spectroscopy and the other based on ion exchange chromatography) have been reported for HCl measurements in biomethane. For the optical techniques, experiments were done in two modes, to evaluate and report the capability of the two modes of operation for HCl concentration measurements in  $\text{CH}_4$  and biomethane. The agreement of the laser spectroscopic (dTDLAS and DAS-2f-WMS) HCl amount fraction results with values reported for gas mixtures demonstrate the capability of laser spectroscopy for accurate and reliable HCl concentration measurements in biomethane, thereby proving the ability of the laser-based methods to be employed as test methods for HCl conformity assessment or quality control measurements in biomethane. For HCl amount of substance fractions in the 0.36–500  $\mu\text{mol mol}^{-1}$ , the expanded uncertainties from the laser spectroscopic measurements are 4.6%,  $k = 2$ . The good recovery demonstrated for the ion exchange chromatographic measurements shows that this typically used analytical method (that is employed to determine the time weighted average mass concentration of sulfuric acid and phosphoric acid in workplace atmospheres, ISO21438-1:2007) can also be used for HCl amount of substance fractions measurements in biomethane (a complex gas matrix) and as a test method for HCl in biomethane quality control. For HCl results in the



range of 0.07–34 mg m<sup>-3</sup>, the expanded uncertainty of the ion exchange chromatography results is currently 37% at the LOQ and 14% at the threshold value of 1 mg m<sup>-3</sup> ( $k = 2$ ). Any of the presented methods can be used for routine analysis, depending on the target uncertainty level required. Laser spectroscopic methods have the added value advantage to have capabilities for both lab and online field routine analysis.

## Author contributions

All co-authors contributed to the work presented in this paper: The dTDLAS part: PTB; the DAS-WMS part: VSL; the Ion exchange chromatography part: INERIS.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The work was supported by the European Metrology Programme for Innovation and Research (EMPIR). The EMPIR initiative is co-funded by the European Union's Horizon 2020 Research and Innovation Programme and the EMPIR Participating States. The authors would also like to acknowledge the support from members of the PTB working group 3.42 (Spectrometric Gas Analysis) on the development of the dTDLAS instrument. PTB and VSL are member of the European Metrology Networks for Energy Gases. PTB is a member of the European Metrology Networks for Climate and Ocean Observation.

## References

- European Metrology Programme for Innovation and Research (EMPIR) project: "Metrology for biomethane", available at: <http://empir.npl.co.uk/biomethane/>.
- J. Li, S. Persijn, I. de Krom, H. Meuzelaar and A. M. H. van der Veen, 19th International Congress of Metrology (CIM2019), 2019, 06002, DOI: 10.1051/metrology/201906002.
- EN 16723-1 Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network. CEN, European Committee for Standardization, Brussels, Belgium, 2016, first edition.
- V. Paolini, F. Petracchini, M. Carnevale, F. Gallucci, M. Perilli, G. Esposito, M. Segreto, L. G. Occulti, D. Scaglione, A. Ianniello and M. Frattoni, *J. Environ. Manage.*, 2018, **217**, 288–296.
- European Biogas Association (EBA) Statistical Report of the European Biogas Association 2018 Brussels Belgium, 2018, available at: [https://www.europeanbiogas.eu/wpcontent/uploads/2019/05/EBA\\_Statistical-Report-2018\\_AbridedPublic\\_web.pdf](https://www.europeanbiogas.eu/wpcontent/uploads/2019/05/EBA_Statistical-Report-2018_AbridedPublic_web.pdf).
- A list of the EU-wide existing best practices for the biogas transport in the natural gas grids REDUBAR WP06 D19/M, available at: [https://ec.europa.eu/energy/intelligent/projects/sites/ieep/projects/files/projects/documents/redubar\\_best\\_practices.pdf](https://ec.europa.eu/energy/intelligent/projects/sites/ieep/projects/files/projects/documents/redubar_best_practices.pdf).
- P. Ortwein, W. Woiwode, S. Fleck, M. Eberhard, T. Kolb, S. Wagner, M. Gisi and V. Ebert, *Exp. Fluids*, 2010, **49**, 961–968.
- B. Buchholz, B. Kühnreich, H. G. J. Smit and V. Ebert, *Appl. Phys. B*, 2013, **110**, 249–262.
- A. Klein, O. Witzel and V. Ebert, *Sensors*, 2014, **14**, 1497–21513.
- A. Pogany, S. Wagner, O. Werhahn and V. Ebert, *Appl. Spectrosc.*, 2015, **69**, 257–268.
- J. A. Nwaboh, Z. Qu, O. Werhahn and V. Ebert, *Appl. Opt.*, 2017, **56**, E84–E93.
- N. Prakash, A. Ramachandran, R. Varma, J. Chen, C. Mazzoleni and K. Du, *Analyst*, 2018, **143**, 3284.
- J. A. Nwaboh, S. Persijn, K. Arrhenius, H. Bohlén, O. Werhahn and V. Ebert, *Meas. Sci. Technol.*, 2018, **29**, 095010.
- J. A. Nwaboh, O. Werhahn and V. Ebert, *Mol. Phys.*, 2014, **112**, 2451–2461.
- B. Buchholz, N. Böse and V. Ebert, *Appl. Phys. B*, 2014, **116**, 883–899.
- M. L. Dawson, V. Perraud, A. Gomez, K. D. Arquero, M. J. Ezell and B. J. Finlayson-Pitts, *Atmos. Meas. Tech.*, 2014, **7**, 2733–2744.
- P. F. Lindgren, *Atmos. Environ., Part A*, 1992, **26**, 43–49.
- ISO 6145-10 Gas analysis – preparation of calibration gas mixtures using dynamic volumetric methods – Part 10: Permeation methods. ISO, International Organization for Standardization, Geneva, Switzerland, 2002, First edition.
- J. Nwaboh, Z. Qu, O. Werhahn and V. Ebert, *Imaging and Applied Optics 2016 LM3G*, 2016, DOI: 10.1364/LACSEA.2016.LM3G.4.
- HITRAN data base, available at: <https://hitran.org/>.
- ISO Guide 98-3 Guide to the Expression of Uncertainty in Measurement, 1. International Organization for Standardization, Geneva, 2008, ISBN 9267101889.
- G. Li, I. E. Gordon, R. J. Le Roy, P. G. Hajigeorgiou, J. A. Coxon, P. F. Bernath and L. S. Rothman, *J. Quant. Spectrosc. Radiat. Transfer*, 2013, **121**, 78–90.
- G. Li, R. E. Asfin, A. V. Domanskaya and V. Ebert, *Mol. Phys.*, 2018, **116**, 3495–3502.
- A. V. Domanskaya, G. Li, H. Tran, M. Gisi and V. Ebert, *J. Quant. Spectrosc. Radiat. Transfer*, 2017, **199**, 71–76.
- J. A. Nwaboh, O. Werhahn, P. Ortwein, D. Schiel and V. Ebert, *Meas. Sci. Technol.*, 2012, **24**, 015202.
- Ozone Standard Reference Photometer (SRP) 2009 available at: <https://www.nist.gov/laboratories/tools-instruments/ozonestandard-reference-photometer>.
- H. Meuzelaar, J. Liu, S. Persijn, J. van Wijk and A. M. H. van der Veen, *Int. J. Hydrogen Energy*, 2020, **45**, 34024.



- 28 EMPIR project: Metrology for Airborne Molecular contaminants II, available at: <http://empir.npl.co.uk/metamcii/>.
- 29 D. D. Arslanov, M. Spunei, A. K. Y. Ngai, S. M. Cristescu, I. D. Lindsay, S. T. Persijn, K. J. Boller and F. J. M. Harren, *Appl. Phys. B*, 2011, **103**, 223–228.
- 30 ISO 6145-7 Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 7: Thermal mass-flow controllers, ISO, International Organization for Standardization, Geneva, Switzerland, 2018, Third edition.
- 31 D. F. Swinehart, *J. Chem. Educ.*, 1962, **39**, 333, DOI: 10.1021/ed039p333.
- 32 ISO 6143 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, ISO, International Organization for Standardization, Geneva, Switzerland, 2001, Second edition.
- 33 M. Shibukawa, A. Taguchi, Y. Suzuki, K. Saitoh, T. Hiaki and T. Yarita, *Analyst*, 2012, **137**, 3154.
- 34 ISO 21438-2 Workplace atmospheres – Determination of inorganic acids by ion chromatography – Part 2: Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid), 2010.
- 35 Validation of an ion chromatography method for the analysis of HCl and HF in biomethane, INERIS report 2019 ref. DRC-20-169395-01916A, available within the documentation of the EMPIR biomethane project at <http://empir.npl.co.uk/biomethane/>.
- 36 NF T 90-210 Water quality – Protocol for the initial method performance assessment in a laboratory, 2018.
- 37 EN ISO 11352 standard Water quality – Estimation of measurement uncertainty based on validation and quality control data, 2013.
- 38 ISO 5725-3 Application of statistics – Accuracy (trueness and precision) of measurement methods and results – Part 3: Intermediate measures of the precision of a standard measurement method, 1994.
- 39 M. Ghysels, G. Durry, N. Amarouche, J. Cousin, L. Joly, E. D. Riviere and L. Beaumont, *Appl. Phys. B*, 2012, **107**, 213–220.
- 40 R. Sur, K. Sun, J. B. Jeffries and R. K. Hanson, *Appl. Phys. B*, 2014, **115**, 9–24.
- 41 M. Novič, M. Guček, J. Turšič, Y. Liu and N. Avdalovic, *J. Chromatogr. A*, 2001, **909**, 289–296.

