Measurement techniques and test methods for measuring fluorine, chlorine and halogenated VOCs contents

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With contributions from
General background: aim

- develop and validate standardised test methods for analysing the contents of trace levels of halogenated VOCs, HF and HCl in biomethane.

- the target ranges for the various components will be established in accordance with the EN 16723 specifications for biomethane.

- reference gas mixtures containing halogenated VOCs and gas mixtures containing HF or HCl will be produced dynamically to validate measurement methods.

- the validation of the method will include (as a minimum) the repeatability, reproducibility, and selectivity of the method.
Hydrogen Chloride (HCl)

Background

Reference materials

Measurement methods
Background: **HCl**

- Example: HCl in biogas from sewage sludge for biomethane production

- High HCl content both related to degradation of organochlorine compounds during the anaerobic digestion and the presence of chlorinated clarifying agents in the plant.

**16ENG05:**

- HCl detection-laser absorption spectroscopy

**current target range:**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Target range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.5-20 µmol/mol</td>
</tr>
</tbody>
</table>

Fig. 2. Concentration of HCl and H$_2$S in the plant; error bars report standard deviation.

Reference materials: HCl

- Reference gases are needed in order to accurately determine concentrations of trace impurities in biomethane.

- Use of methane as a carrier gas instead of commonly used, more inert nitrogen and instrument air.

- Chlorine and Fluorine including gaseous chemicals, especially hydrogen chloride and hydrogen fluoride, are reactive compounds which easily react and adsorb to surfaces.
  
  ⇐ This feature complicates the static mixture preparation in gas cylinders (in particular at low amount fractions).

  ⇐ Dynamic generation enables calibration with decent response time and sufficient accuracy.
Evaporation method for dynamic preparation of gas mixtures containing reactive components

- Gas assisted spraying and following evaporation of a solution with precisely known concentration for the chemical under study

- Continuous control of liquid and gas flows

Reference materials: HCl
Design of evaporation method set-up for the dynamic preparation of gas mixtures containing reactive components such as HF, HCl and ammonia in air and biomethane.
Method properties

❑ Proper materials for the evaporation chamber and other parts in contact with the humid calibration gas
  • Elevated temperatures and high enough gas flow rates in order to minimise adsorption

❑ Pros and cons of the method
  + Flexible change of concentrations in wide concentration and total gas flow ranges
  
  + Good response times (some minutes) even for the most sticky compounds possible
  
  - Multiple components simultaneously: easily increasing uncertainty
  
  - In most cases only binary mixtures possible
  
  - High temperature of evaporator may decompose chemicals

Reference materials: HCl
Background: HCl reference materials

Reference materials for HCl in N$_2$ and HCl in CH$_4$

- Dynamic generation using permeation and a magnetic suspension balance
- Cylinder: HCl in N$_2$ at amount fractions of 3.8-300 µmol/mol (commercial mixtures)
- HCl in CH$_4$ (10 µmol/mol, commercial mixture)
Measurements of HCl using CRDS and OPO light source

HCl in CH₄ analyzed at same wavelength as ICL laser used by PTB cell pressure 50 mbar.

CRDS = cavity Ring Down Spectroscopy
OPO = Optical Parametric Oscillator
Measurement method: HCl

Effect of pressure on the HCl in CH₄ absorption spectra

Selected HCl line together with PTB. At this wavelength ICL laser available (used at PTB and ordered by VSL)
**Measurements method: HCl**

Measurements of HCl using CRDS and OPO light source

HCl in CH₄ analyzed at wavelength ICL laser (cell pressure 50 mbar).

- HCl (~2.5 µmol/mol) in CH₄
- Pure CH₄
- HCl in N₂ (0.95 µmol/mol)

CH₄ interference is high (decay time only ~1 µs while in N₂ ~10 µs).

With direct absorption CH₄ interference is expected to be less problematic.
Measurement method: HF & HCl

Design multi-component analyser (HF, HCl, CO, NH₃)

A ICL laser will be combined with both a multi-pass and a single pass absorption cell.

Design new set-up at VSL. Both direct absorption and WMS
Measurement method: **dTDLAS**

- **direct tunable diode laser absorption spectroscopy (dTDLAS)**

![Diagram](Image)

**For further reading on dTDLAS:**


Measurement method: **dTDLAS**

**Typical dTDLAS spectra**

- Gas sample: 110 μmol/mol HCl in CH₄

  - **Red line:** HCl line
  - **Rest-lines:** CH₄

- Path length = 82 cm
- Pressure = 56.4 hPa
- Temperature = 294.5 K

**Typical absorbance data**

- Path length = 82 cm
- Pressure = 56.4 hPa
- Temperature = 294.5 K

**Absolute ("calibration-free") HCl concentration derivation**

- \( x_{\text{HCl}} \): SI-traceable, if all input parameters are traceable

**References**

Hydrogen fluoride (HF)

Background

Reference materials

Measurement methods
Background: HF

- Currently, no metrologically traceable gas standards for HF content exist due to the corrosive nature of HF
  
  - measurement standard for the HF content in biomethane → based on dynamic gas mixture preparation
    
    o measurement standards will be based on the permeation method (VSL) and saturation method (VTT)
    
    o detection will be performed using a suitable spectroscopic technique (CRDS, WMS)

16ENG05: current target range:

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Target range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>500 ppb - 20 ppm</td>
</tr>
</tbody>
</table>
Reference materials for HF in N₂ and HF in CH₄

- Dynamic generation using permeation and a magnetic suspension balance (coated). It took >2 days to get a HF signal.
- Cylinder: HF in N₂ (~1.88 ppm). Response time ~20 min.
- Cylinder: 10 ppm HF in CH₄
Measurement method: HF

Direct absorption

Wavelength modulation

Signal (using phase sensitive detection at 2f)
Conclusions:
1. HF in methane can be analyzed in the nmol/mol and lower µmol/mol range
2. Interference by CH\textsubscript{4} is relatively low at a cell pressure of 100 mbar
3. HF is very reactive. Response time of the system is reasonable due to use coated materials
Development of standardized method for HF and HCl

Measurement method: HF, HCl

NaOH 0.1 M absorption solution to trap chloride and fluoride in a biomethane matrix

After sampling:
- Analysis of chloride by ion-exchange chromatography
- Analysis of fluoride by ionometry
Measurement method: HF, HCl

Sampling according to EN 1911:2010 (E)

✓ Absorption solution. Chloride-free water of at least grade 2 purity (conductivity less than 100 μS·m⁻¹)

✓ To achieve an efficient absorption, at least two absorbers shall be placed in series

✓ Downstream of these absorbers, an extra empty absorber may be used as a liquid trap and as a protection for the downstream equipment
Measurement method: HF, HCl

Analysis performed by ICS 2500 ion chromatographic system (Dionex) consisting of:

✓ gradient pump (GS50),

✓ a chromatographic oven (LC 25),

✓ electrochemical detector (ED50),

✓ EG50 Eluent Generator with an EluGen EGC-III KOH Cartridge,

✓ ASRS-4-mm Anion Suppressor

✓ Column AS19 4x250 mm

oven temperature  30°C
run time 30 min

<table>
<thead>
<tr>
<th>time [min]</th>
<th>KOH concentration [mM]</th>
<th>Suppressor current [mA]</th>
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<tbody>
<tr>
<td>0</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>16</td>
<td>58</td>
<td>144</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>50</td>
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</table>
Example of calibration curve for F- and Cl-

Solution analysis (evaluation of possible interference with natural gas)

<table>
<thead>
<tr>
<th>Amount µg/ml</th>
<th>Amount µg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>Cloride</td>
</tr>
<tr>
<td>test 1</td>
<td>0.97</td>
</tr>
<tr>
<td>test 2</td>
<td>0.97</td>
</tr>
<tr>
<td>test 3</td>
<td>1.08</td>
</tr>
<tr>
<td>test 4</td>
<td>1.05</td>
</tr>
<tr>
<td>test 5</td>
<td>1.04</td>
</tr>
<tr>
<td>average</td>
<td>1.02</td>
</tr>
<tr>
<td>std dev</td>
<td>0.05</td>
</tr>
</tbody>
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</tr>
<tr>
<td>test 3</td>
<td>1.02</td>
</tr>
<tr>
<td>test 4</td>
<td>1.02</td>
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<td>1.04</td>
</tr>
<tr>
<td>test 6</td>
<td>1.04</td>
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<td>test 7</td>
<td>1.04</td>
</tr>
<tr>
<td>test 8</td>
<td>1.04</td>
</tr>
<tr>
<td>test 9</td>
<td>1.08</td>
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<tr>
<td>test 10</td>
<td>1.07</td>
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<tr>
<td>average</td>
<td>1.03</td>
</tr>
<tr>
<td>std dev</td>
<td>0.03</td>
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</table>

<table>
<thead>
<tr>
<th>Amount µg/ml</th>
<th>Amount µg/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>Cloride</td>
</tr>
<tr>
<td>test 1</td>
<td>1.06</td>
</tr>
<tr>
<td>test 2</td>
<td>1.06</td>
</tr>
<tr>
<td>test 3</td>
<td>1.11</td>
</tr>
<tr>
<td>test 4</td>
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<td>test 5</td>
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<td>average</td>
<td>1.08</td>
</tr>
<tr>
<td>std dev</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Measurement method: HF, HCl
Halogenated VOCs (HVOCs)

Background

Reference materials

Measurement methods
Background: HVOCs

- develop measurement standards for halogenated VOCs with a set of 10 frequently-occurring components in biomethane and upgraded biogas

- assess the stability of the measurement standards for 24 months.

  - The analytical method to be set up is based on the work undertaken by INERIS and RISE in EMRP JRP ENG54. The aim is to develop measurement standards with a relative expanded uncertainty of less than 3%.

Analytical method development:

- VSL with support from RISE and INERIS set up a high-accuracy analytical method with a < 3 % uncertainty, using Thermal Desorption Gas Chromatography with a flame ionization detector (TD-GC-FID) and Thermal Desorption Gas Chromatography/Mass Spectrometry (TD-GC-MS)

  - The developed methods will be used to validate the gas mixtures prepared
# Reference materials: selected HVOCs

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction (ppb)</th>
<th>CAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>50</td>
<td>74-87-3</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>50</td>
<td>75-09-2</td>
</tr>
<tr>
<td>cis-1,2-dichloroethane</td>
<td>50</td>
<td>156-59-2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>50</td>
<td>67-66-3</td>
</tr>
<tr>
<td>Hexane (internal standard)</td>
<td>50</td>
<td>110-54-3</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>50</td>
<td>79-01-6</td>
</tr>
<tr>
<td>1,2-dichloropropane</td>
<td>50</td>
<td>78-87-5</td>
</tr>
<tr>
<td>1,1,2-trichloroethane</td>
<td>50</td>
<td>79-00-5</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>50</td>
<td>127-18-4</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane (Freon 113)</td>
<td>50</td>
<td>76-13-1</td>
</tr>
<tr>
<td>Vinylchloride</td>
<td>50</td>
<td>75-01-4</td>
</tr>
</tbody>
</table>
Measurement method: HVOCs

ATD-GC-MSD / FID
Measurement method: HVOCs

Chromatogram using ATD-GC-MSD

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chloromethane</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>Vinyl chloride</td>
<td>8.00</td>
</tr>
<tr>
<td>3</td>
<td>Freon 113</td>
<td>9.00</td>
</tr>
<tr>
<td>4</td>
<td>Dichloromethane</td>
<td>10.00</td>
</tr>
<tr>
<td>5</td>
<td>n-Hexane</td>
<td>11.00</td>
</tr>
<tr>
<td>6</td>
<td>1,2-Dichloroethylene</td>
<td>12.00</td>
</tr>
<tr>
<td>7</td>
<td>Trichloromethane</td>
<td>13.00</td>
</tr>
<tr>
<td>8</td>
<td>Trichloroethene</td>
<td>14.00</td>
</tr>
<tr>
<td>9</td>
<td>1,2-Dichloropropane</td>
<td>15.00</td>
</tr>
<tr>
<td>10</td>
<td>1,1,2-Trichloroethane</td>
<td>16.00</td>
</tr>
<tr>
<td>11</td>
<td>Tetrachloroethylene</td>
<td>17.00</td>
</tr>
</tbody>
</table>
Measurement method: HVOCs

Chromatogram using ATD-GC-FID

<table>
<thead>
<tr>
<th>1</th>
<th>Chloromethane</th>
<th>7</th>
<th>Trichloromethane</th>
</tr>
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<tr>
<td>2</td>
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<td>3</td>
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<td>11</td>
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</tr>
<tr>
<td>6</td>
<td>1,2-Dichloroethylene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Performance of developed methods for halogenated VOC standards

- Repeatability ATD-GC-FID method

- The **chloromethane** peak is overlapping with something else in the FID chromatogram

- The **vinyl chloride** peak is not always visible in the FID chromatogram

- For **chloromethane** and **vinyl chloride** MSD is the preferred detection method. However the repeatability has yet to be determined.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stdev (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloromethane</td>
<td>-</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>-</td>
</tr>
<tr>
<td>Freon 113</td>
<td>0.4</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>0.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.3</td>
</tr>
<tr>
<td>1,2-Dichloroethylene</td>
<td>0.5</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>0.7</td>
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<tr>
<td>Trichloroethene</td>
<td>0.4</td>
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<tr>
<td>1,2-Dichloropropane</td>
<td>0.3</td>
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<tr>
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<td>0.4</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Stability testing of halogenated VOC standards

- Using the developed and validated method, VSL will assess the stability of the biomethane mixtures containing the 10 halogenated hydrocarbons. The stability will be tested every 6 months for 24 months.
  
  • First measurements performed in 2018: 18 July, 29 August, 16 October
    (encouraging preliminary results)
  
  • Next measurements: April 2019 and October 2019

Final output (VSL, RISE and INERIS): ‘Report on the improved stability (2-3 years for static standards) of the measurement standards, a validated calibration method for the measurement of halogenated VOCs content in biomethane and a relative expanded uncertainty of 3 %’.
Thanks for your attention!

Acknowledgement:

Partners ISSI and INERIS

Iris de Krom (VSL)