EMPIR EURAMET
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METROLOGY FOR BIOMETHANE

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

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With contributions from

INERIS maîtriser le risque pour un développement durable

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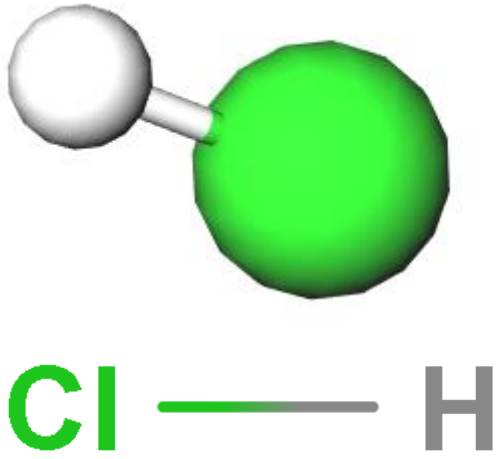
General background: aim

- 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

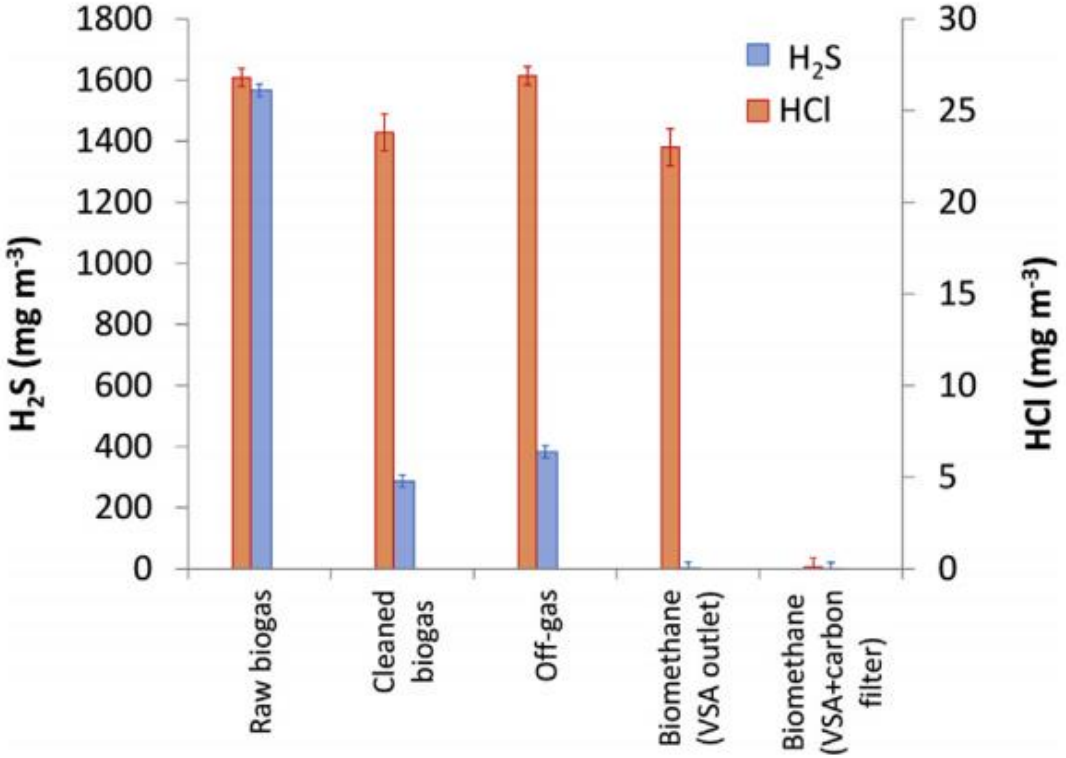


Fig. 2. Concentration of HCl and H_2S in the plant; error bars report standard deviation.

- 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:

Analyte	Target range
HCl	0.5-20 µmol/mol

Source: V. Paolini et al. Characterisation and cleaning of biogas from sewage sludge for biomethane production. *J. Environ. Manag.* 2018, 217: 288-296.

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

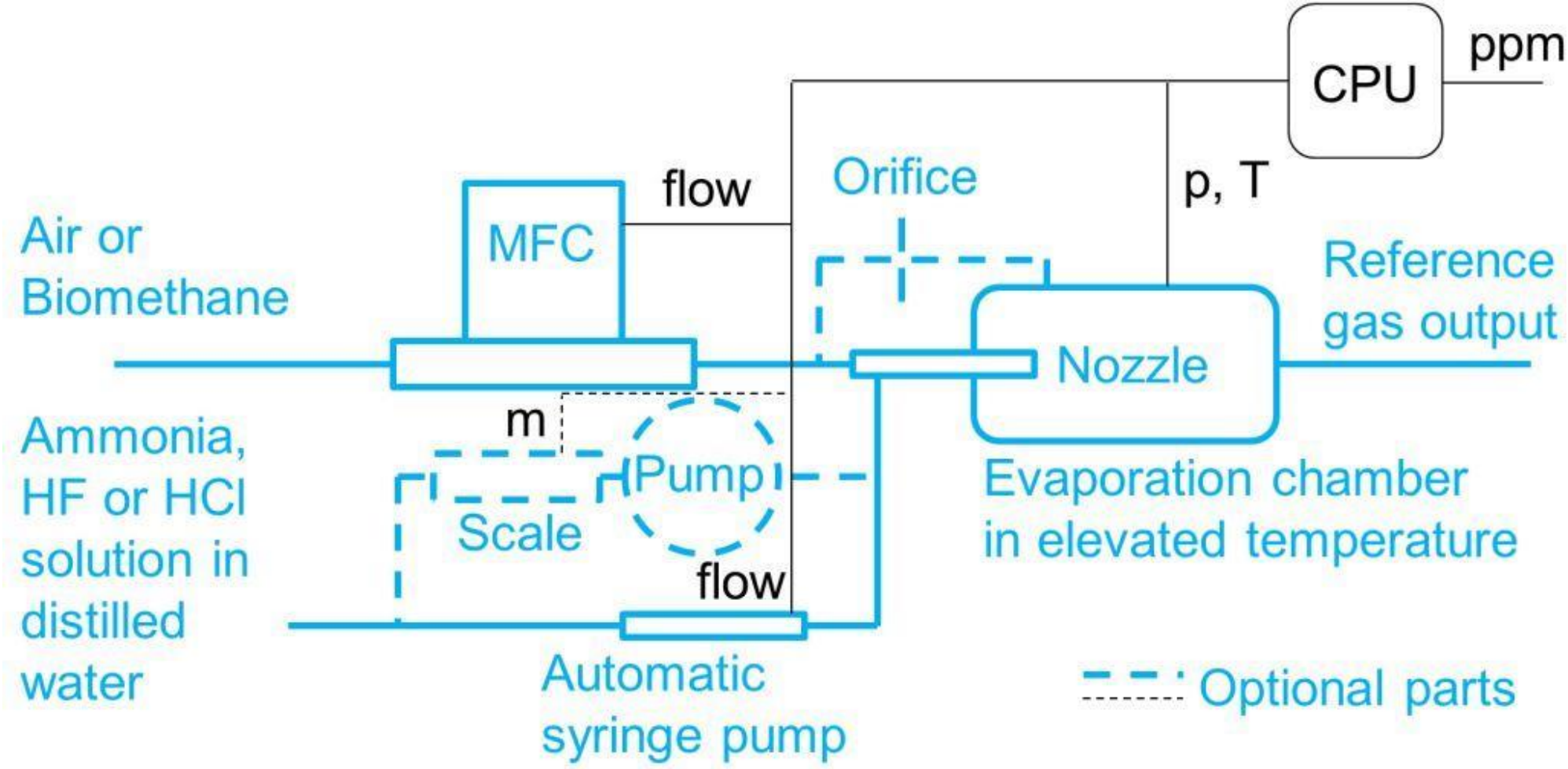
Reference materials: HCl

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



Reference materials: HCl

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

Background: HCl reference materials

Reference materials for HCl in N_2 and HCl in CH_4

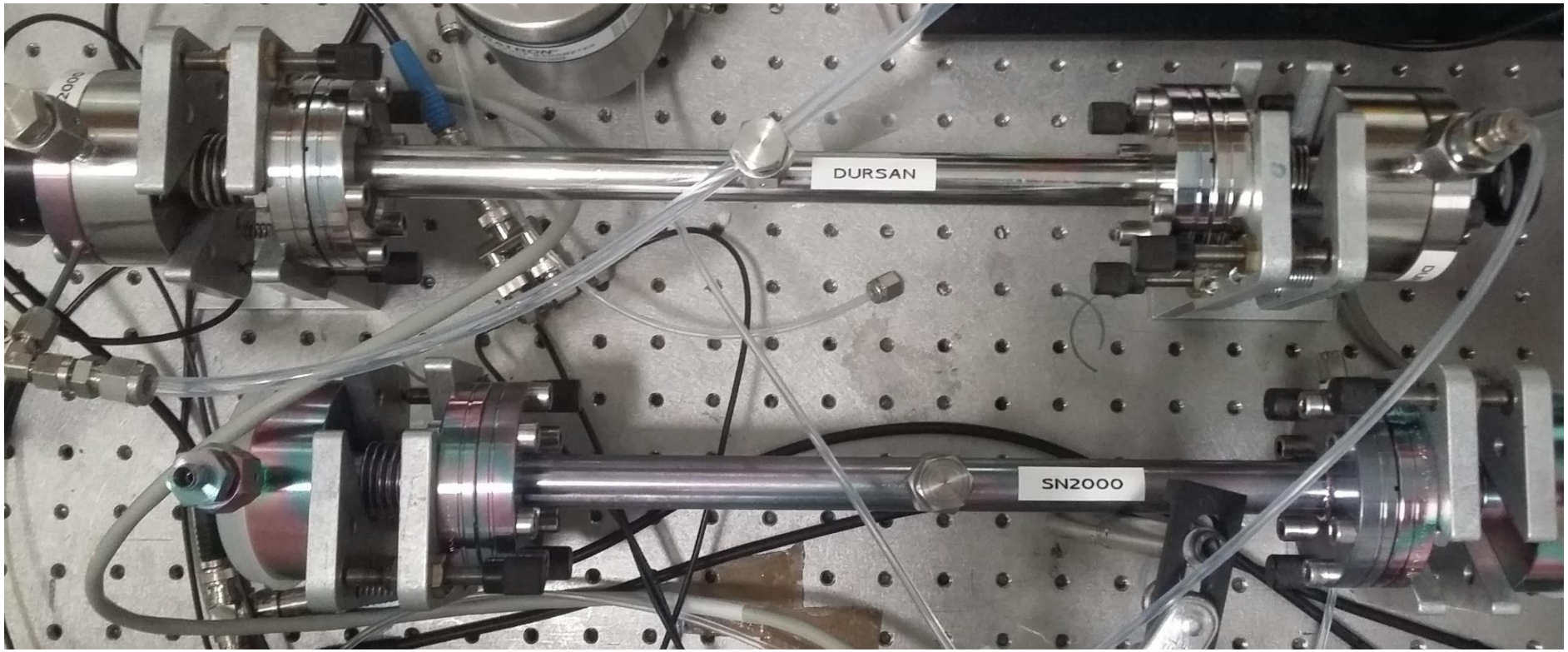
- Dynamic generation using permeation and a magnetic suspension balance
- Cylinder: HCl in N_2 at amount fractions of 3.8-300 µmol/mol (commercial mixtures)
- HCl in CH_4 (10 µmol/mol, commercial mixture)

magnetic suspension balance

HCl permeation tube

Measurement method: HCl

Measurements of HCl using CRDS and OPO light source



HCl in CH_4 analyzed at same wavelength as ICL laser used by PTB

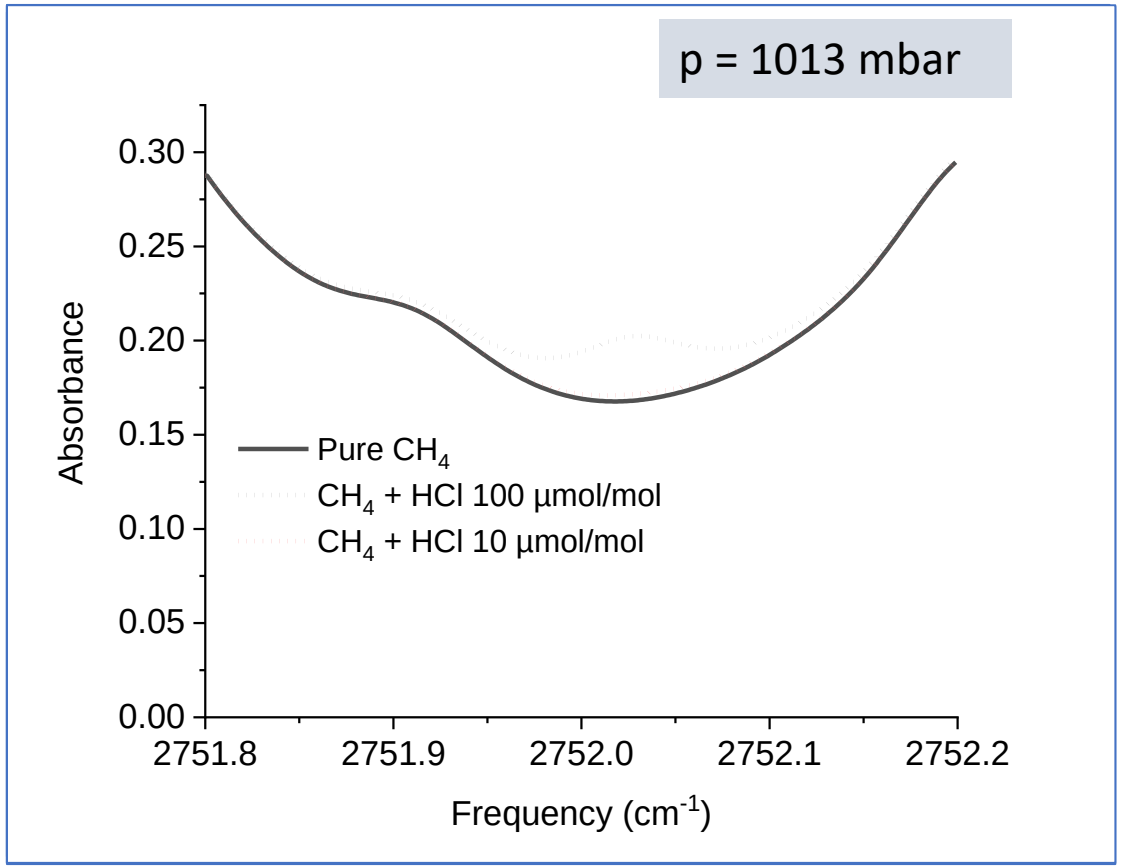
cell pressure 50 mbar.

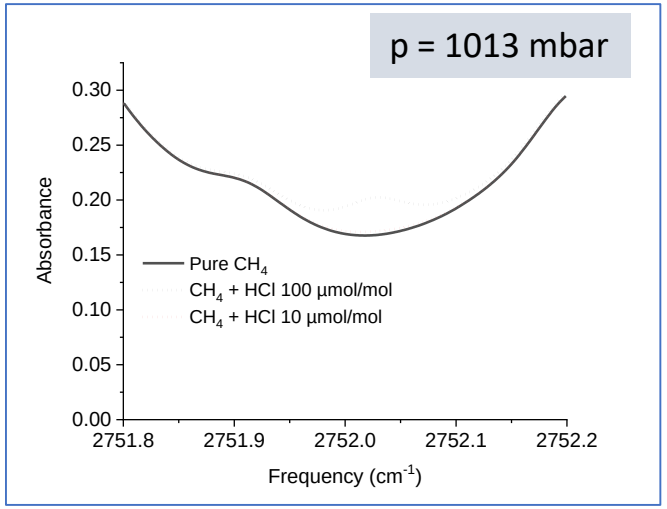
CRDS= cavity Ring Down Spectroscopy
OPO = Optical Parametric Oscillator

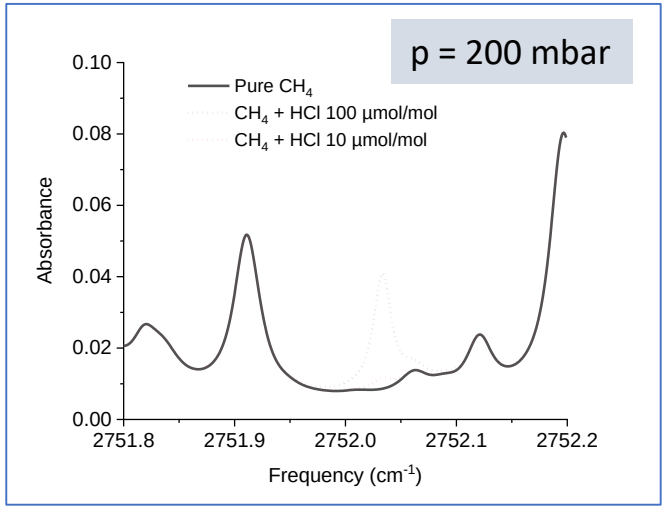
Measurement method: HCl

Effect of pressure on the HCl in CH_4 absorption spectra

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



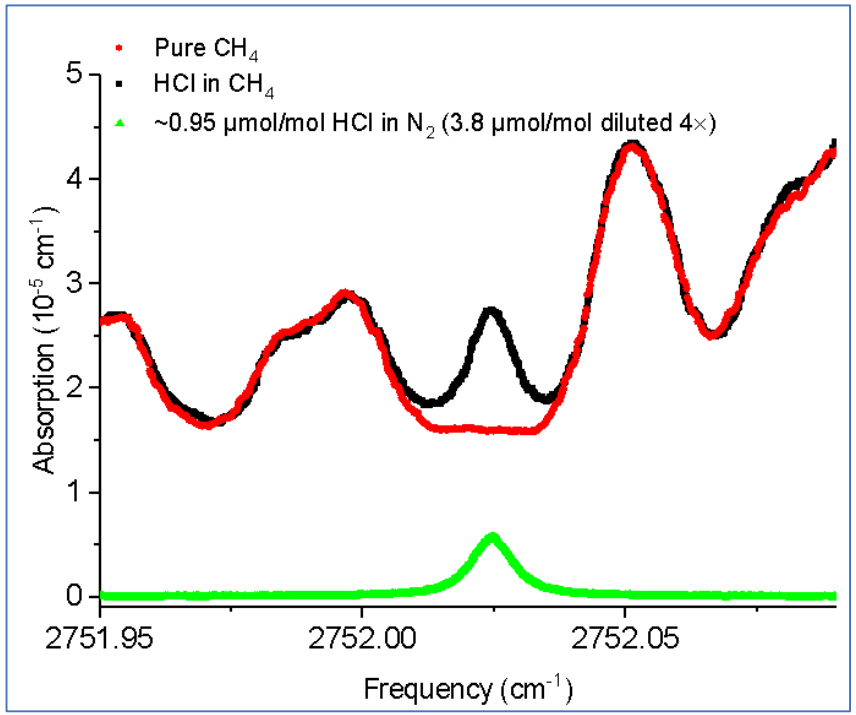




Measurement method: HCl

Measurements of HCl using CRDS and OPO light source

HCl in CH_4 analyzed at wavelength ICL laser (cell pressure 50 mbar).



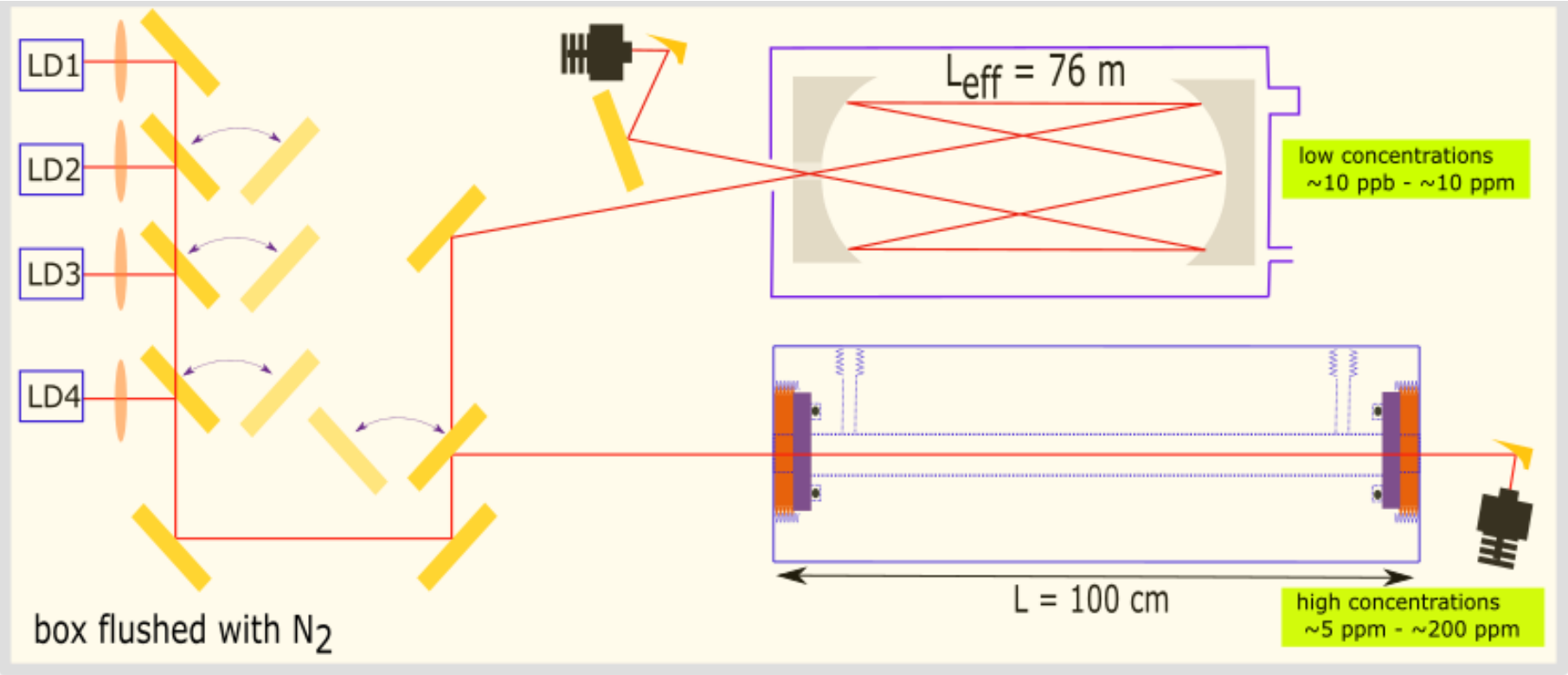
- HCl (~2.5 µmol/mol) in CH_4
- pure CH_4
- HCl in N_2 (0.95 µmol/mol)

CH_4 interference is high (decay time only ~1 µs while in N_2 ~10 µs).

With direct absorption CH_4 interference is expected to be less problematic.

Measurement method: HF & HCl

Design multi-component analyser (HF, HCl, CO, NH_3)



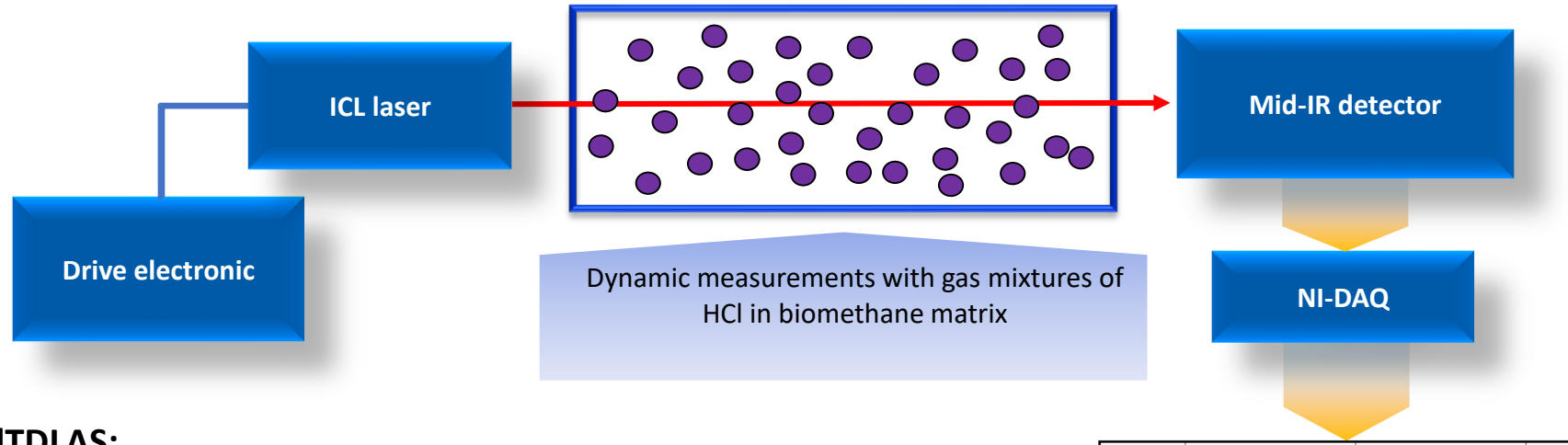
LD1 = DFB laser for HF / LD2 = ICL laser for HCl/ LD3 = QCL laser NH_3 / LD4 = QCL laser for N_2O and CO

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

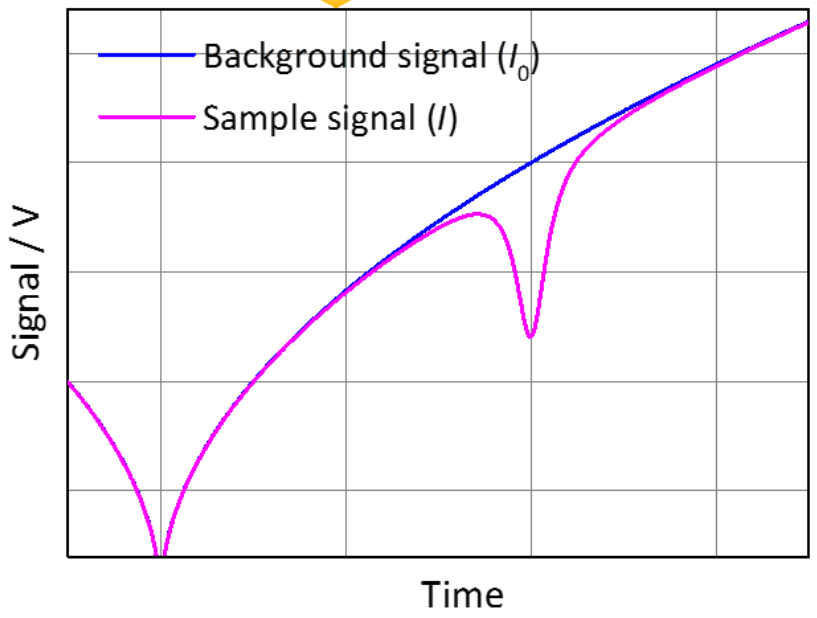
Measurement method: dTDLAS

❑ direct tunable diode laser absorption spectroscopy (dTDLAS)



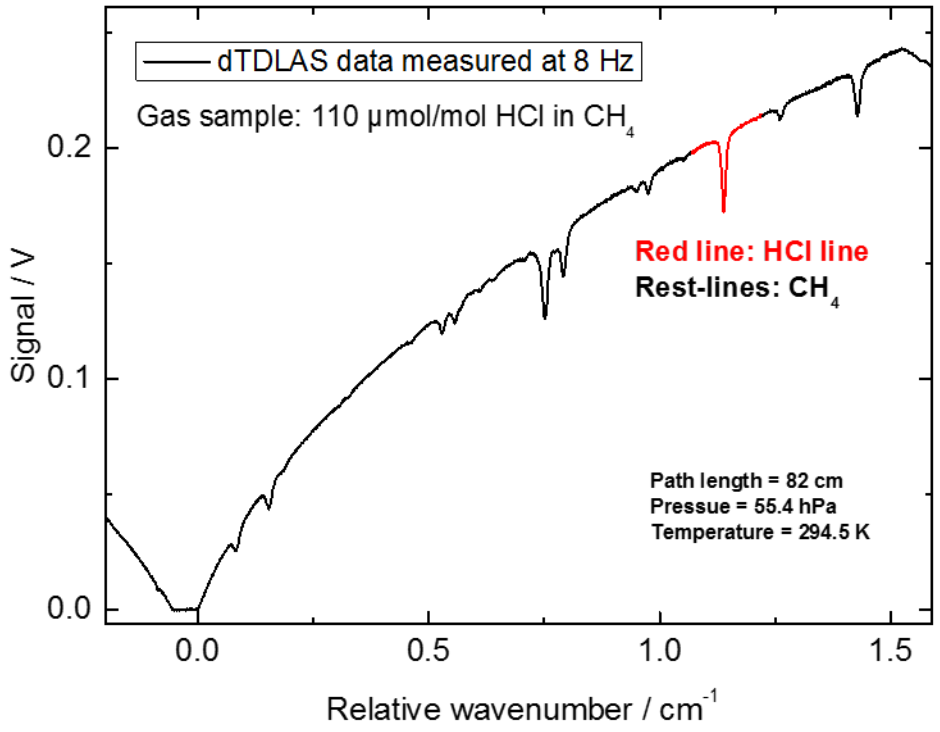
For further reading on dTDLAS:

- B. Buchholz, S Kallweit, V. Ebert, SEALDH-II—An Autonomous, Holistically Controlled, First Principles TDLAS Hygrometer for Field and Airborne Applications: Design–Setup–Accuracy/Stability Stress Test, *Sensors*, *17*, 68 (2017).
- J. A. Nwaboh, S. Persijn, K. Arrhenius, H. Bohlén, O. Werhahn, and V. Ebert, Metrological quantification of CO in biogas using laser absorption spectroscopy and gas chromatography, Meas. Sci. Technol. 29, 095010 (2018)
- J. A. Nwaboh, Z. Qu, O. Werhahn and V. Ebert, Interband cascade laser-based optical transfer standard for atmospheric carbon monoxide measurements, Appl. Opt. 56 E84–93 (2017)

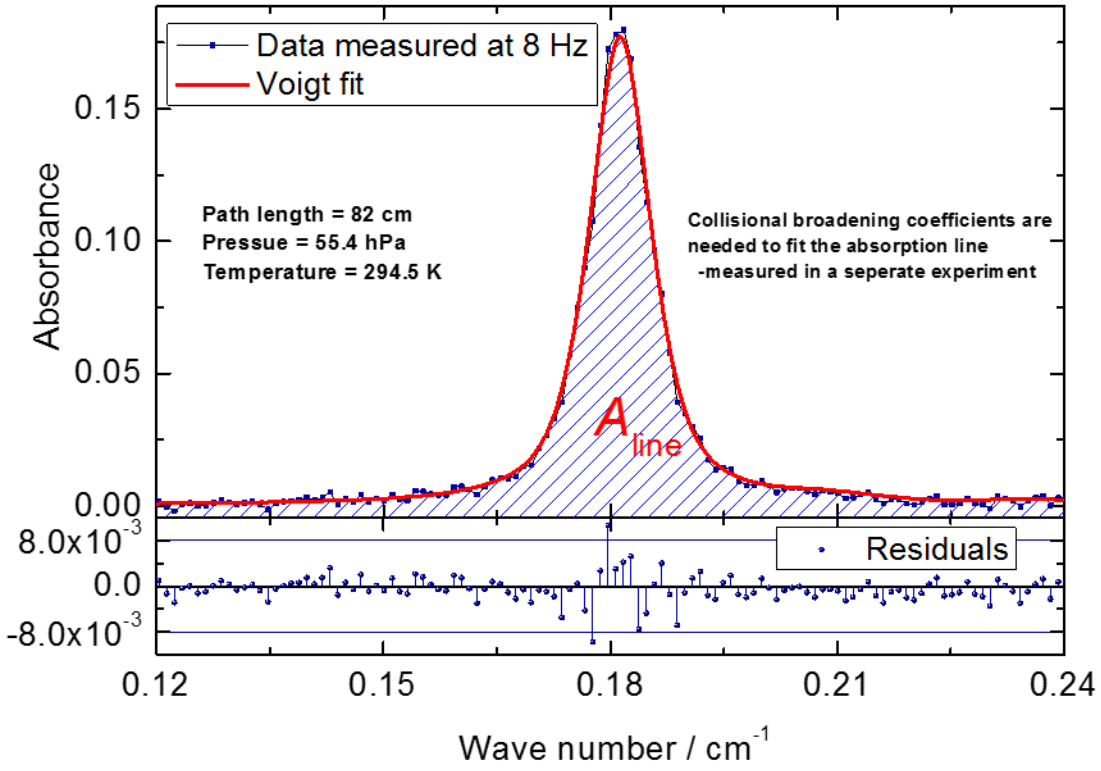


Measurement method: dTDLAS

Typical dTDLAS spectra



Typical absorbance data



- Absolute **(„calibration-free“)** HCl concentration derivation
  - x_{HCl}: SI-traceable, if all input parameters are traceable

references

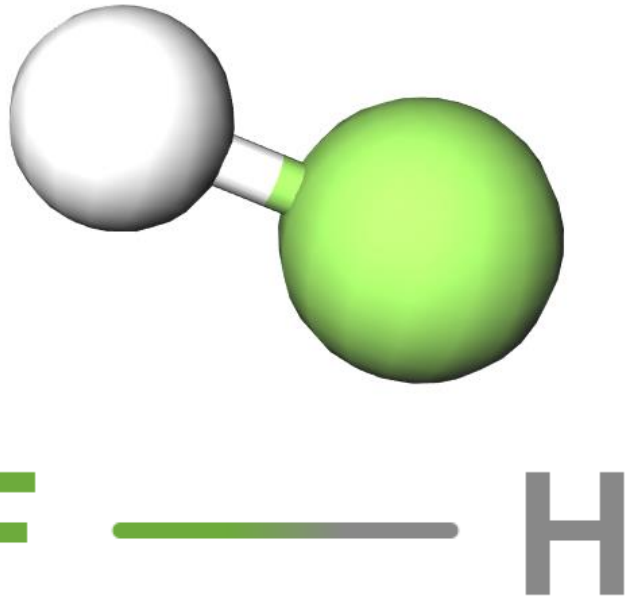
- Werhahn O, Petersen J C (eds.) 2010 TILSAM technical protocol V1_2010-09-29, available from: http://www.euramet.org/fileadmin/docs/projects/934_METCHEM_Interim_Report.pdf
- B. Buchholz, N. Böse and V. Ebert, Absolute validation of a diode laser hygrometer via intercomparison with the German national primary water vapor standard, Appl.Phys. B, vol. 116, 883–899 (2014)

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

    - measurement standards will be based on the permeation method (VSL) and saturation method (VTT)

    - detection will be performed using a suitable spectroscopic technique (CRDS, WMS)

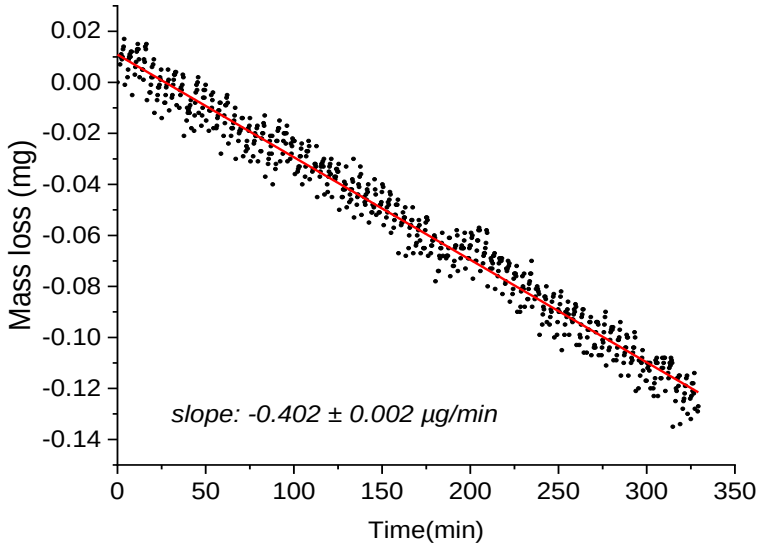
16ENG05: current target range:

Analyte	Target range
HF	500 ppb - 20 ppm

Reference materials: HF

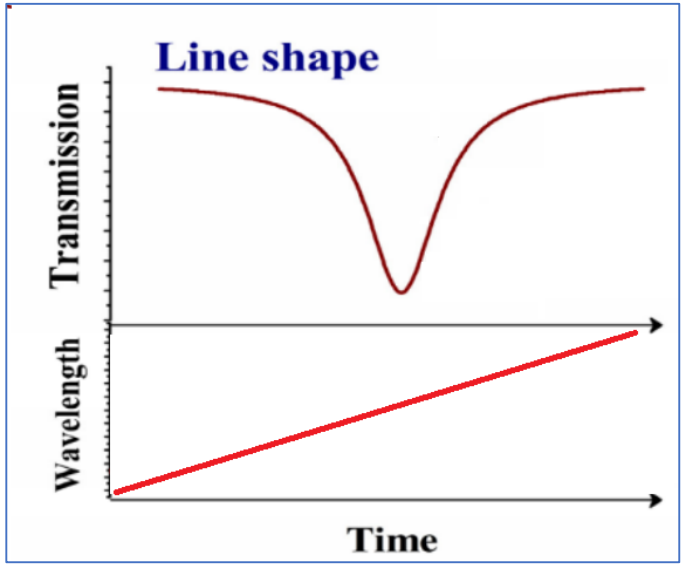
Reference materials for HF in N_2 and HF in CH_4

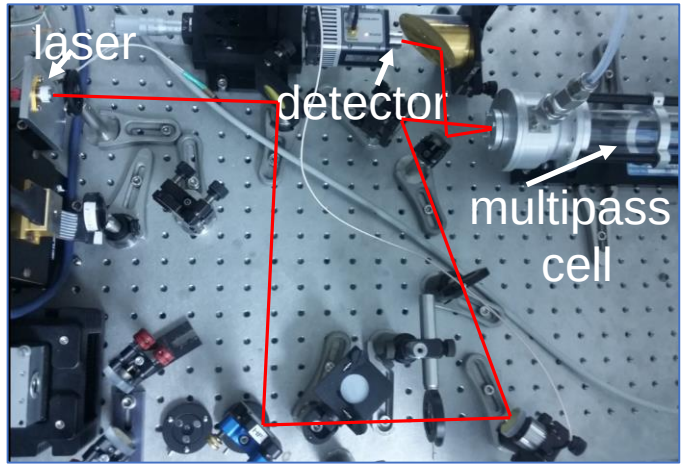
- Dynamic generation using permeation and a magnetic suspension balance (coated). It took >2 days to get a HF signal.
- Cylinder: HF in N_2 (~1.88 ppm). Response time ~20 min.
- Cylinder:10 ppm HF in CH_4



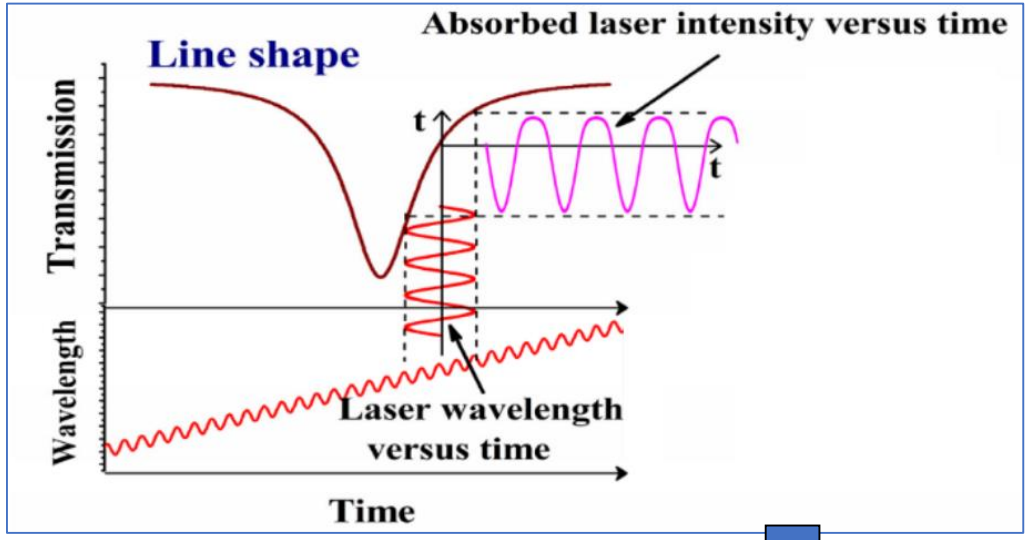
Measurement method: HF

Direct absorption

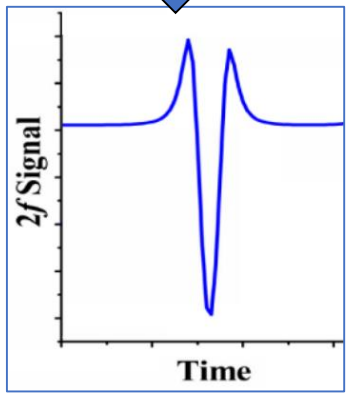




Wavelength modulation



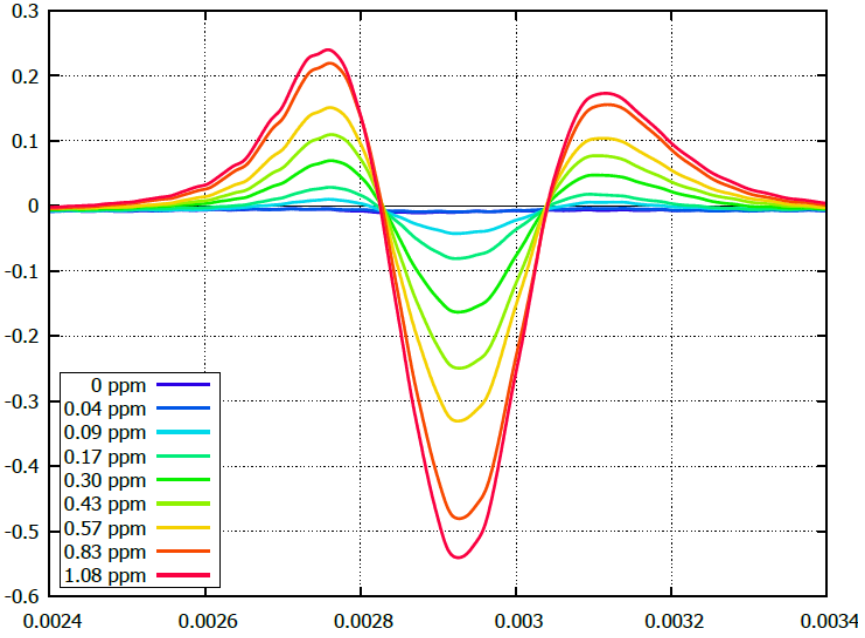
Signal (using phase sensitive detection at 2f)



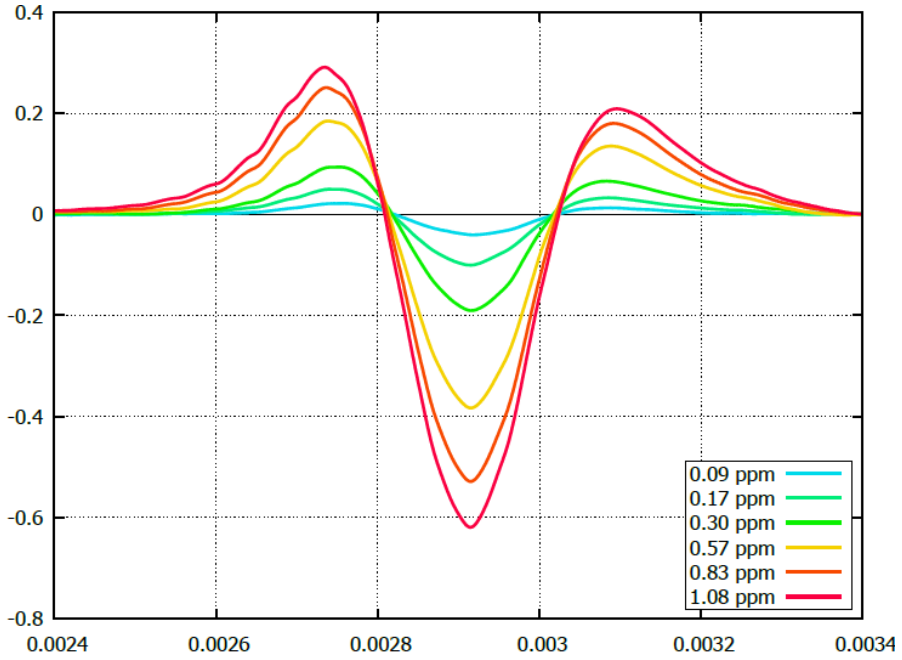
Measurement method: HF

Results for HF in N_2 and HF in CH_4

N_2 matrix



CH_4 matrix
(CH_4 background subtracted)

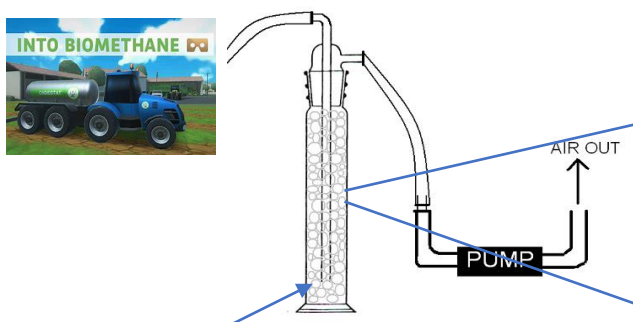


Conclusions:

1. HF in methane can be analyzed in the nmol/mol and lower µmol/mol range
2. Interference by CH_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

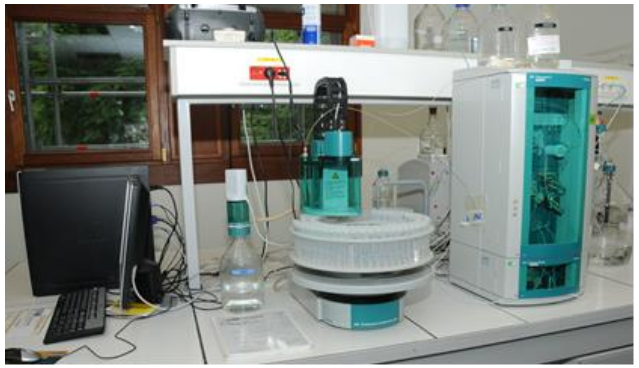
Measurement method: HF, HCl

Development of standardized method for HF and HCl



NaOH 0,1 M absorption solution to trap chloride and fluoride in a biomethane matrix

HCl
NF EN 1911



HF
NF X 43-304

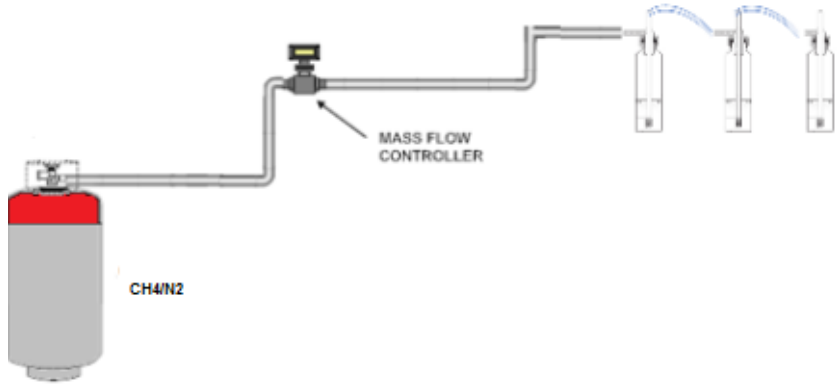
After sampling :

- 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 $\mu S \cdot m^{-1}$)
- ✓ 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
eluent concentration:

time [min]	KOH concentration [mM]	Suppressor current [mA]
0	20	50
16	58	144
19	20	50

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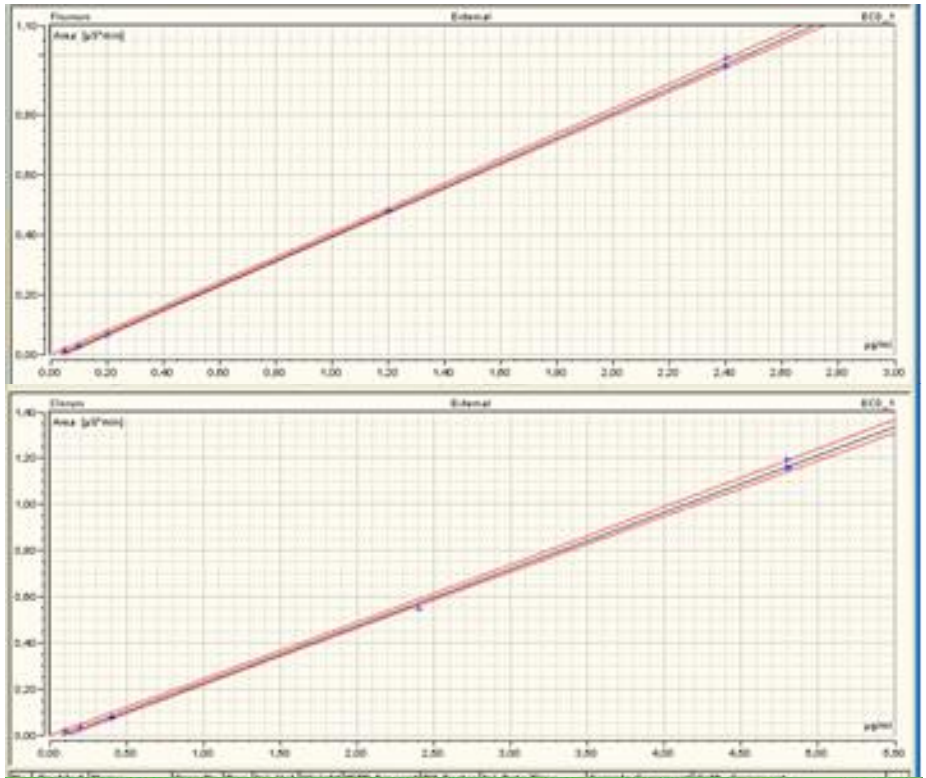
Measurement method: HF, HCl

METROLOGY FOR BIOMETHANE

Example of calibration curve for F- and Cl-



Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	R²	Offset	Slope	Curve
Fluoruro	0LOff	12	3,0452	0,9996	-0,0123	0,4105	0,0000
Cloruro	*0LOff*	*12*	*4,1366*	*0,9992*	*-0,0166*	*0,2462*	*0,0000*
Nitrato	0LOff	12	4,3677	0,9992	-0,0152	0,1061	0,0000
Bromuro	0LOff	12	3,8834	0,9993	-0,0178	0,1395	0,0000
Solfato	0QOff	12	2,1340	0,9998	-0,0123	0,1594	0,0023
Fosfato	0LOff	12	3,2107	0,9995	-0,0153	0,0741	0,0000

Solution analysis (evaluation of possible interference with natural gas)

	Amount µg/ml Fluoride	Amount µg/ml Cloride
test 1	0.97	1.92
test 2	0.97	1.90
test 3	1.08	2.02
test 4	1.05	1.98
test 5	1.04	1.98
average	1.02	1.96
std dev	0.05	0.05

bubbled 30-105 l N2

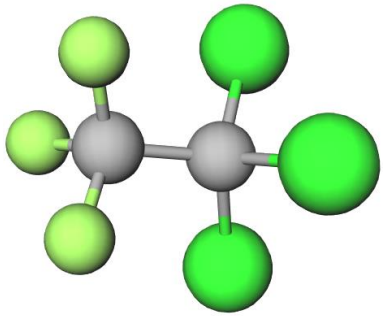
	Amount µg/ml Fluoride	Amount µg/ml Cloride
test 1	0.98	1.93
test 2	0.98	1.92
test 3	1.02	2.02
test 4	1.02	2.02
test 5	1.04	2.05
test 6	1.04	2.05
test 7	1.04	2.01
test 8	1.04	2.00
test 9	1.08	2.14
test 10	1.07	2.13
average	1.03	2.03
std dev	0.03	0.07

bubbled 30-120 l CH4

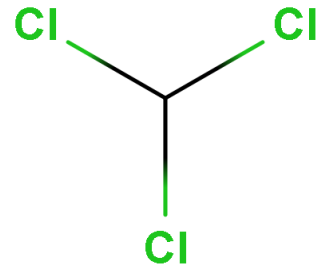
	Amount µg/ml Fluoride	Amount µg/ml Cloride
test 1	1.06	2.01
test 2	1.06	1.99
test 3	1.11	2.08
test 4	1.06	1.98
test 5	1.09	2.03
test 6	1.08	2.04
test 7	1.09	2.06
test 8	1.06	2.00
test 9	1.07	2.01
test 10	1.07	2.03
test 11	1.11	2.09
test 12	1.11	2.11
average	1.08	2.04
std dev	0.02	0.04

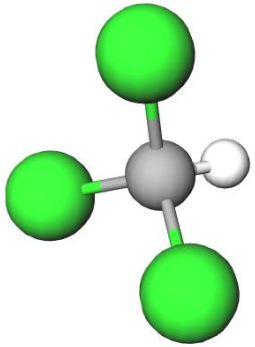
Halogenated VOCs (HVOCs)

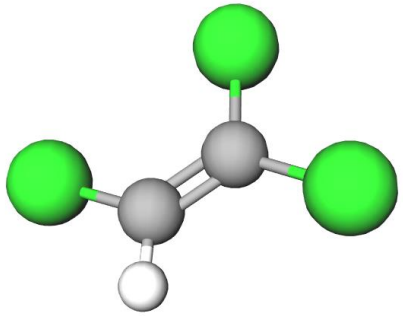
Background



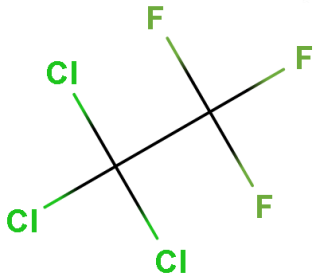
Reference materials

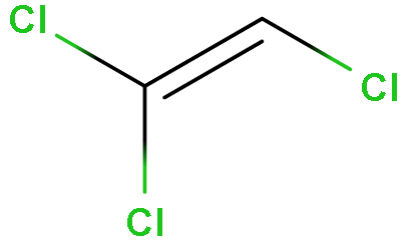






Measurement methods





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)

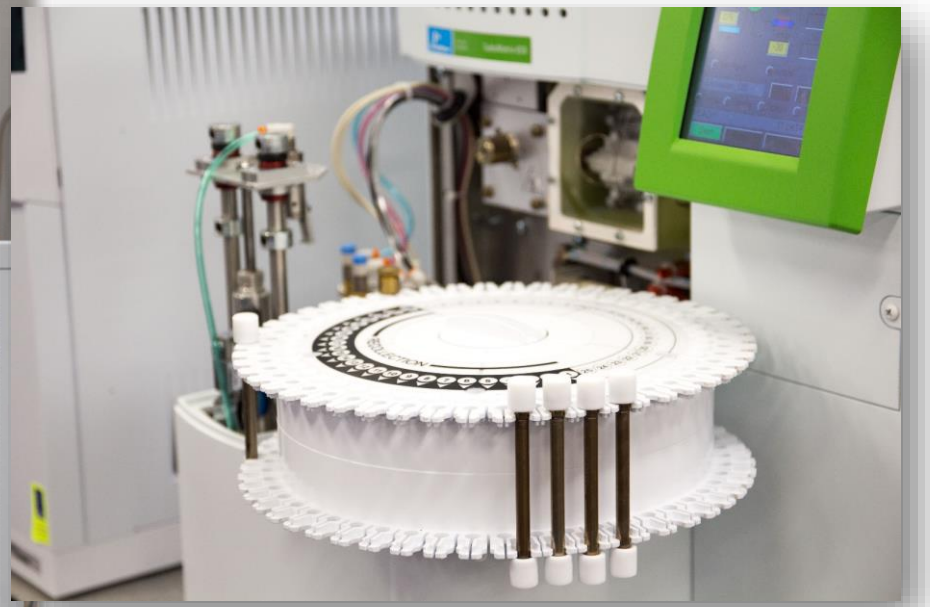
  - The developed methods will be used to validate the gas mixtures prepared

Reference materials: selected HVOCs

Component	Fraction (ppb)	CAS
Chloromethane	50	74-87-3
Dichloromethane	50	75-09-2
cis-1,2-dichloroethane	50	156-59-2
Chloroform	50	67-66-3
Hexane (internal standard)	50	110-54-3
Trichloroethylene	50	79-01-6
1,2-dichloropropane	50	78-87-5
1,1,2-trichloroethane	50	79-00-5
Tetrachloroethylene	50	127-18-4
Trichlorotrifluoroethane (Freon 113)	50	76-13-1
Vinylchloride	50	75-01-4

Measurement method: HVOCs

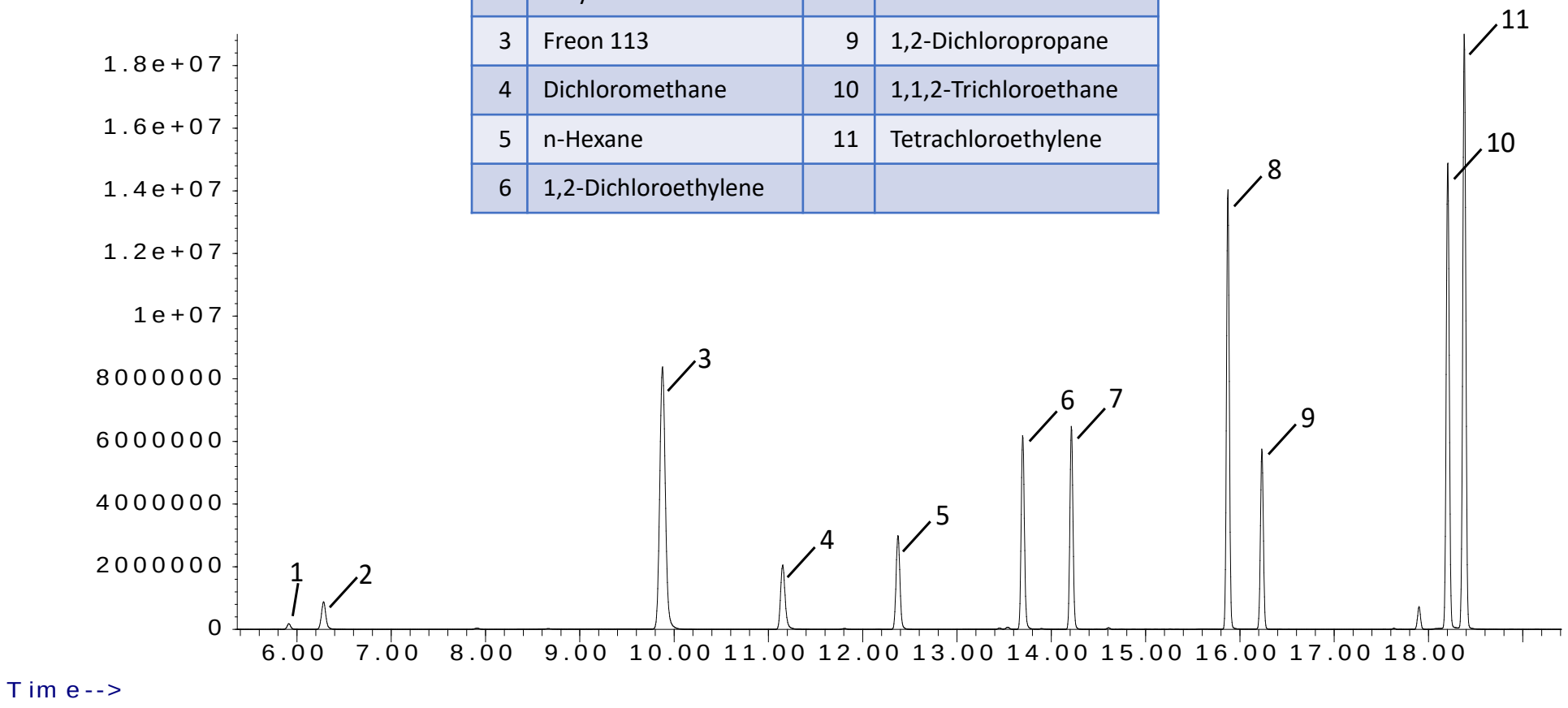
ATD-GC-MSD / FID



Measurement method: HVOCs

Chromatogram using ATD-GC-MSD

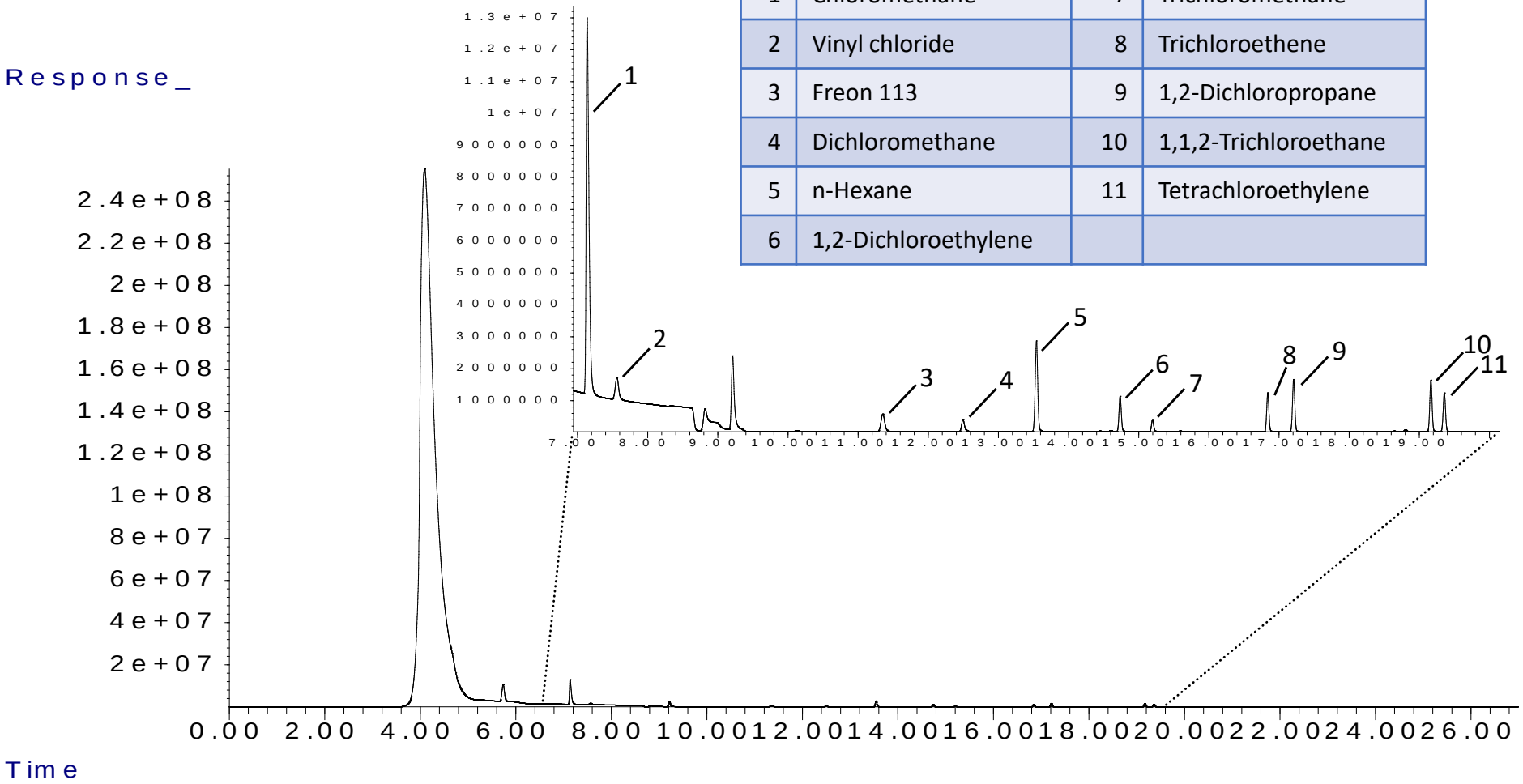
1	Chloromethane	7	Trichloromethane
2	Vinyl chloride	8	Trichloroethene
3	Freon 113	9	1,2-Dichloropropane
4	Dichloromethane	10	1,1,2-Trichloroethane
5	n-Hexane	11	Tetrachloroethylene
6	1,2-Dichloroethylene		



Measurement method: HVOCs

Chromatogram using ATD-GC-FID

1	Chloromethane	7	Trichloromethane
2	Vinyl chloride	8	Trichloroethene
3	Freon 113	9	1,2-Dichloropropane
4	Dichloromethane	10	1,1,2-Trichloroethane
5	n-Hexane	11	Tetrachloroethylene
6	1,2-Dichloroethylene		



Measurement method: HVOCs

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.

	Compound	Stdev (%)
1	Chloromethane	-
2	Vinyl chloride	-
3	Freon 113	0.4
4	Dichloromethane	0.3
5	n-Hexane	0.3
6	1,2-Dichloroethylene	0.5
7	Trichloromethane	0.7
8	Trichloroethene	0.4
9	1,2-Dichloropropane	0.3
10	1,1,2-Trichloroethane	0.4
11	Tetrachloroethylene	0.4

Measurement method: HVOCs

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:

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Iris de Krom (VSL)