NWIP
Analysis of hydrochloric acid (HCl) and and hydrofluoric acid (HF) by Ion Chromatography in biomethane

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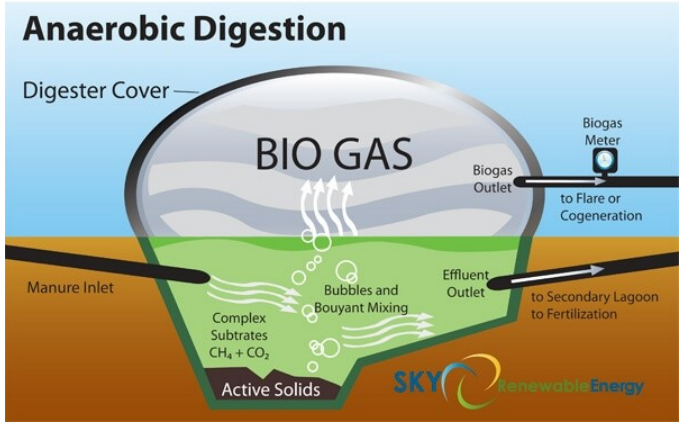
HF and HCl in biomethane



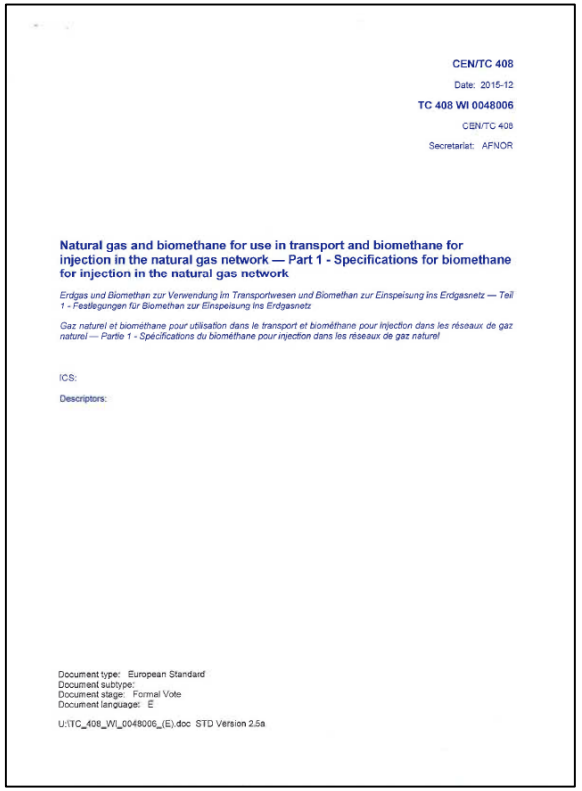
HCl and HF formed by degradation of organochlorine and organofluorine compounds during the anaerobic digestion and the presence of chlorinated agents in the plant for HCl

⇒ Both can lead to risk of

- long term damages due to corrosion
- long term chronic toxicity risk

Reference standard

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/TC 408

Date: 2015-12

TC 408 WI 0048006

CEN/TC 408

Secretariat: AFNOR

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

Erdgas und Biomethan zur Verwendung im Transportwesen und Biomethan zur Einspeisung ins Erdgasnetz — Teil 1 - Festlegungen für Biomethan zur Einspeisung ins Erdgasnetz

Gaz naturel et biométhane pour utilisation dans le transport et biométhane pour injection dans les réseaux de gaz naturel — Partie 1 - Spécifications du biométhane pour injection dans les réseaux de gaz naturel

ICS:

Descriptors:

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Proposed analytical test methods:

- HF : NF X 43-304 ; ISO 15713
- HCl : EN 1911

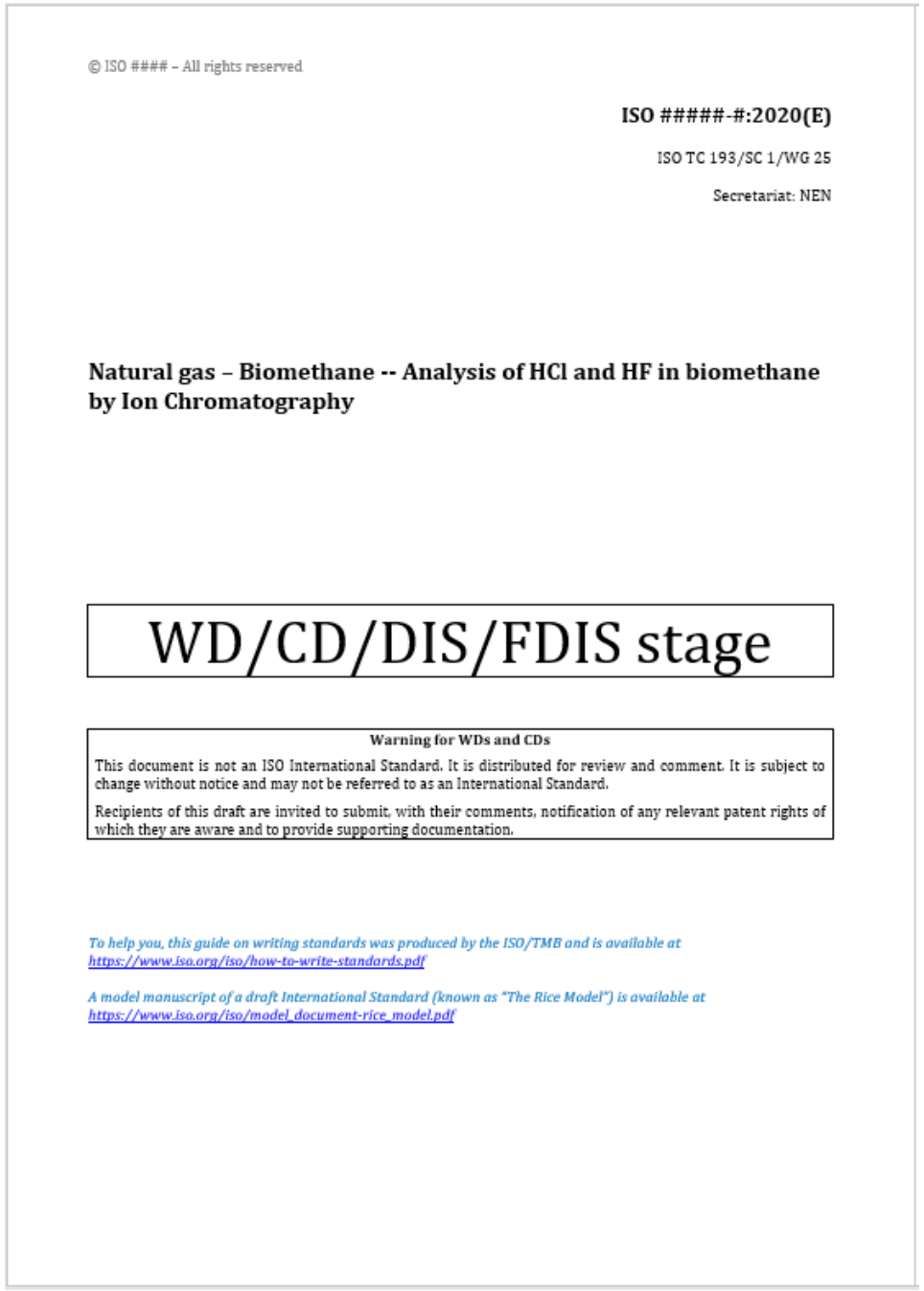
⇒ Not dedicated to biomethane, lack metrological traceability, and have not been demonstrated to be fit-for-purpose

⇒ Objective to deliver dedicated standardised HF and HCl test methods for the standard EN 16723

NWIP

Natural gas –Biomethane- Analysis of HCl and HF in biomethane by Ion Chromatography

- Dynamic generation
- Sampling and sample pre-treatment
- Analysis
- Method performances



ISO #####-#:2020(E)

ISO TC 193/SC 1/WG 25

Secretariat: NEN

Natural gas – Biomethane -- Analysis of HCl and HF in biomethane by Ion Chromatography

WD/CD/DIS/FDIS stage

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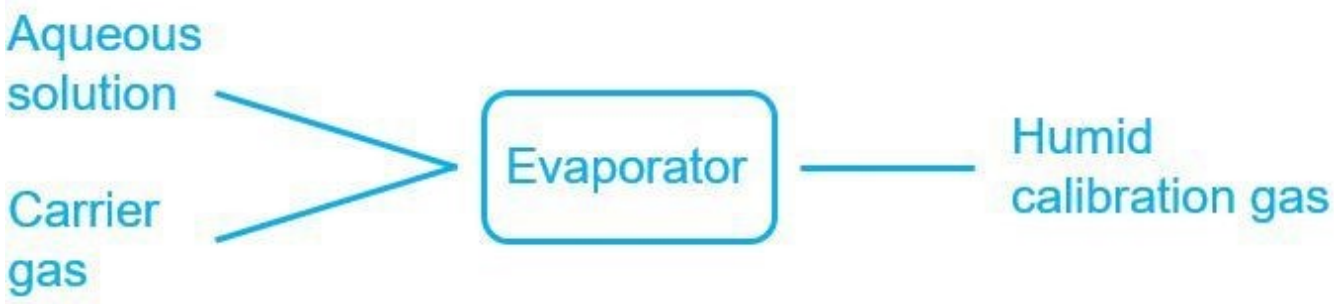
A model manuscript of a draft International Standard (known as "The Rice Model") is available at https://www.iso.org/iso/model_document-rice_model.pdf

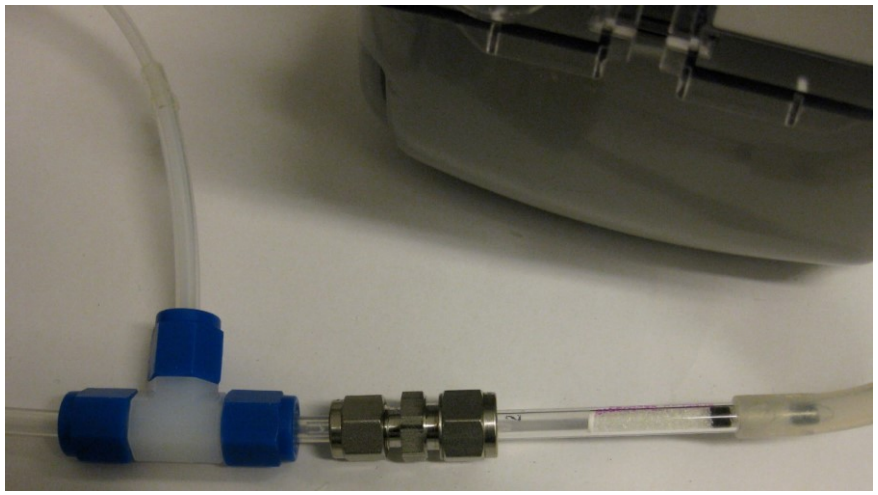
Dynamic generation HCl/HF

- In gaseous form, HCl and HF are reactive chemicals that easily stick to sampling system surfaces.
- To estimate uncertainty caused by this effect on the analysis, dynamic generation method for HCl and/or HF containing reference gas is useable.

Liquid evaporative method → reference gas mixtures with an accurately know concentration of HCl and/or HF.

- Useable in laboratory and field conditions.





Dynamic generation HCl/HF

Concentration of HCl and/or HF in generated gas [µg/m³] is calculated using following equation:

$$c_{gen} = \frac{c_{sol}}{(q_{v,g} + q_{v,w})} \cdot q_{v,sol}$$

c_{sol} concentration of HCl and/or HF in solution [µg/l]

$q_{v,g}$ flow rate of the carrier gas [l/min], e.g. biomethane or methane

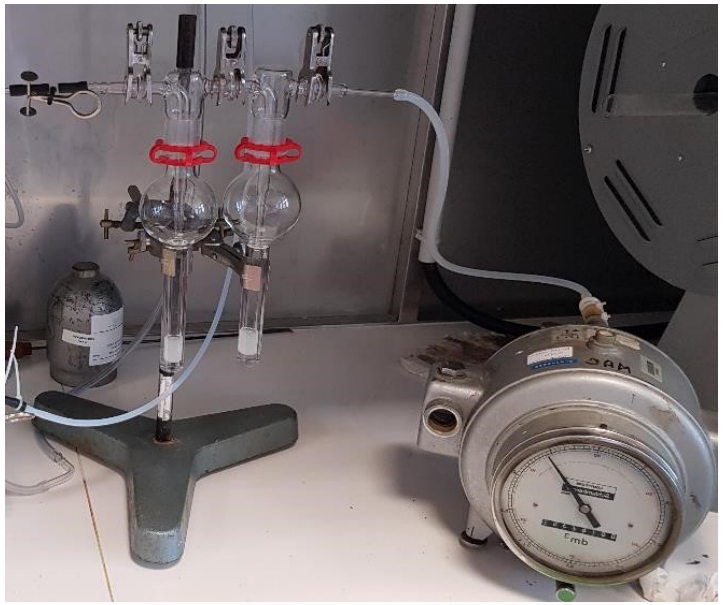
$q_{v,w}$ flow rate of the evaporated water in gas phase [l/min]

$q_{v,sol}$ flow rate of the liquid solution [ml/min]

Sampling and sample pre-treatment

Test with biomethane using impingers such as in EN 1911 (HCl) or NF X 43-304 (HF)

Glass impingers



Use of NaOH 0,01 M absorption solution

PTFE impingers

➔ Good results for HCl but poor recovery for HF (slightly better with PTFE impingers)

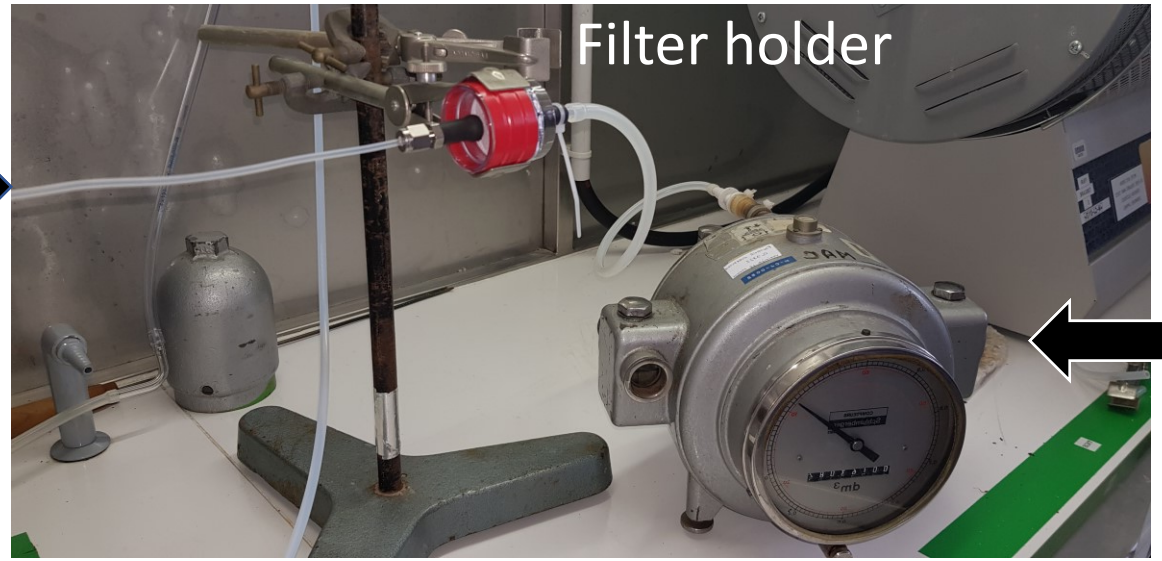
Sampling and sample pre-treatment

➔ Method 1 : use of quartz fiber filter

Sampling

Two filters used: one for sampling and the second as backup to evaluate breakthrough

Biomethane



Pump with controlled volume flow rates set at 1L/min during 30 min

- Quartz filters are impregnated with 500µL of carbonate (Na_2CO_3 at 50 g/L)
- Positionned in series in a holder

Sampling and sample pre-treatment

➔ Method 1 : use of quartz fiber filter

Sample pre-treatment

Filters are put in glass vessel in 20 ml water

Ultrasonication at ambient temperature of the filters in 20 mL water

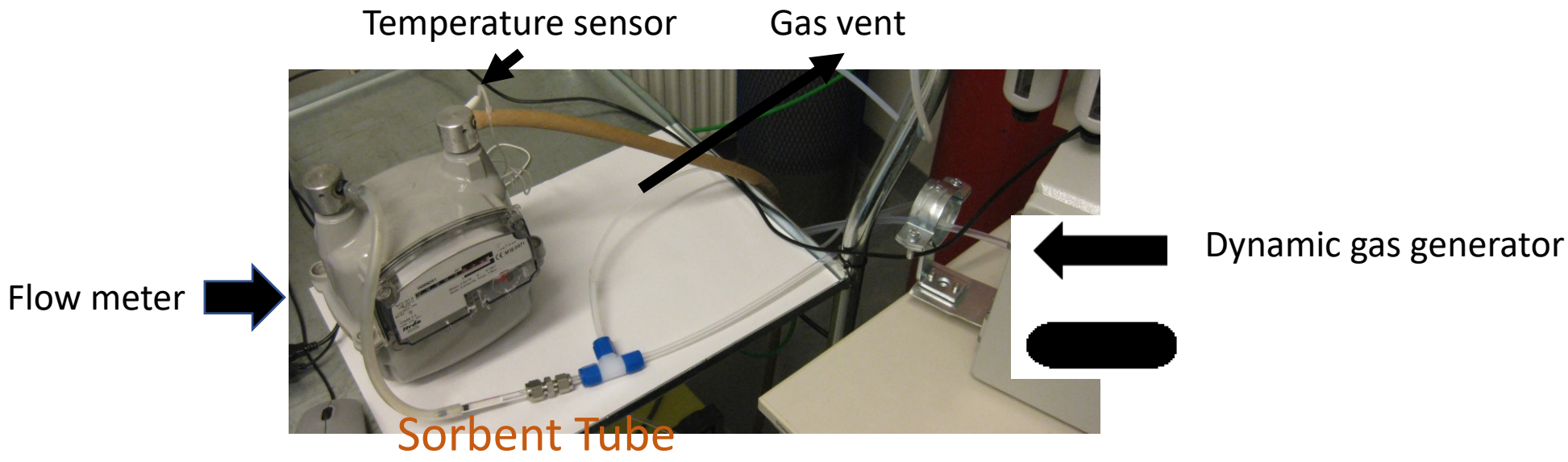
Extracting water is filtered at 0.45 µm with a nylon syringe before injection for the analysis

Sampling and sample pre-treatment

➔ Method 2 : use of cartridges

Sampling

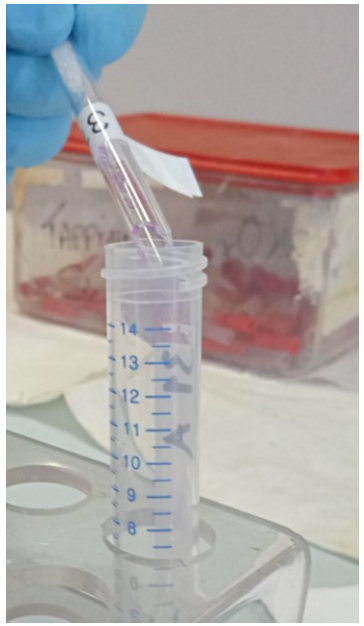
Activated silica gel sorbent tubes, eg commercially available such as ORBO-53 (Supelco)



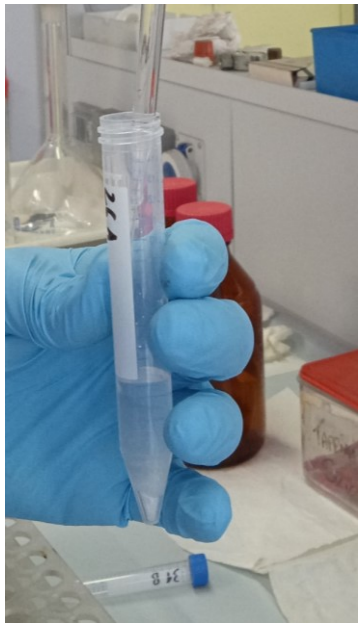
Sampling and sample pre-treatment

➔ Method 1 : use of cartridges

Sample pre-treatment



Silica gel are put in vessel



Add 10 ml of NaHCO3 1.7mM/Na2CO3 1.8mM

Boil 10 min

Add water to 50 ml

Analysis

Analysis of chloride and fluoride by ion-exchange chromatography

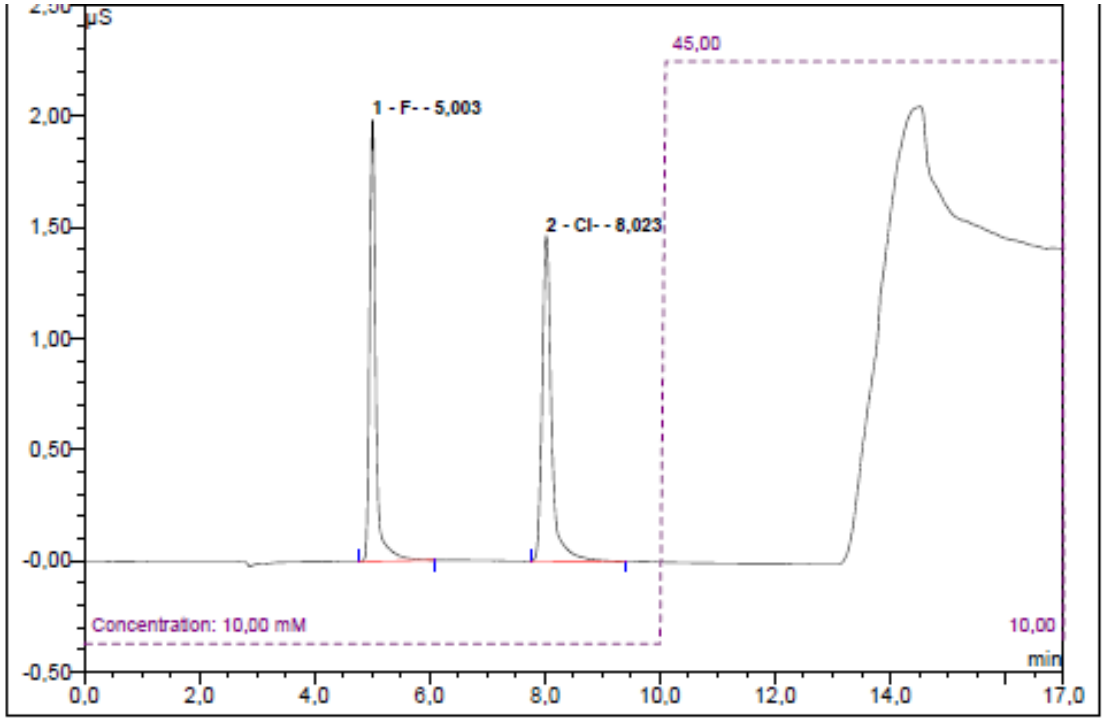
Based on the method described in EN ISO 10304-1- Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate

Analysis

Analysis of chloride and fluoride by ion-exchange chromatography

- Precolumn and Column: AG19 et AS19 4 mm/250 mm (Thermo Scientific);
- Flow: 1 mL/min ;
- Eluant: KOH ;
- Temperature of the column: 30°C ;
- Injection volume: 25 µl ;
- Elution mode : gradient of eluent concentration ;

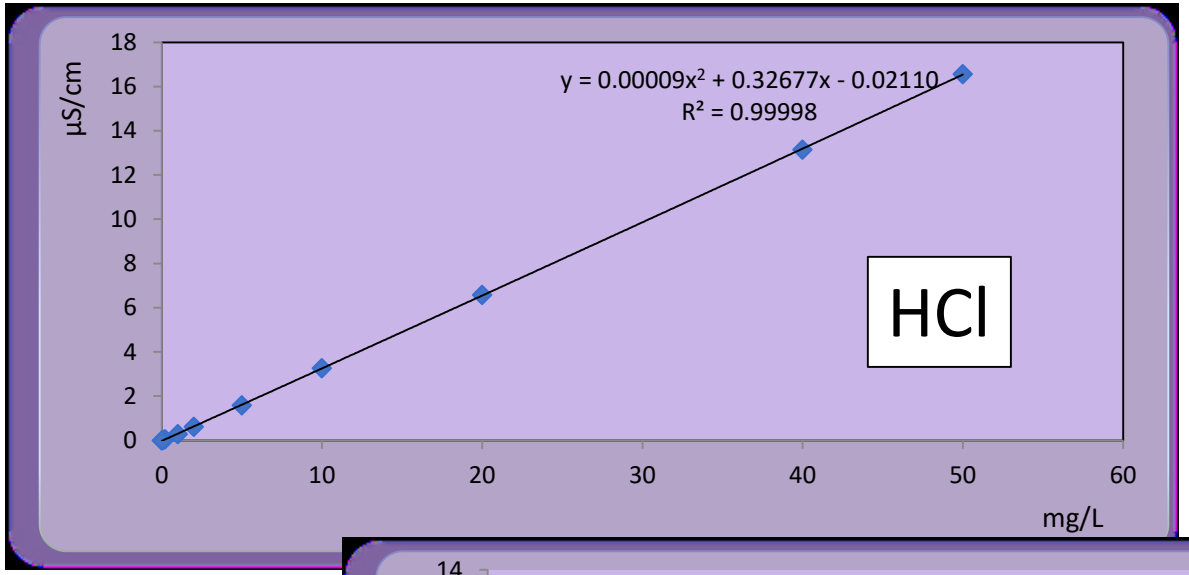
Time (min)	Events	mM KOH
-7	Stabilization	10
0	Start acquisition	10
10		10
1001		45
17		45
1701	End	10

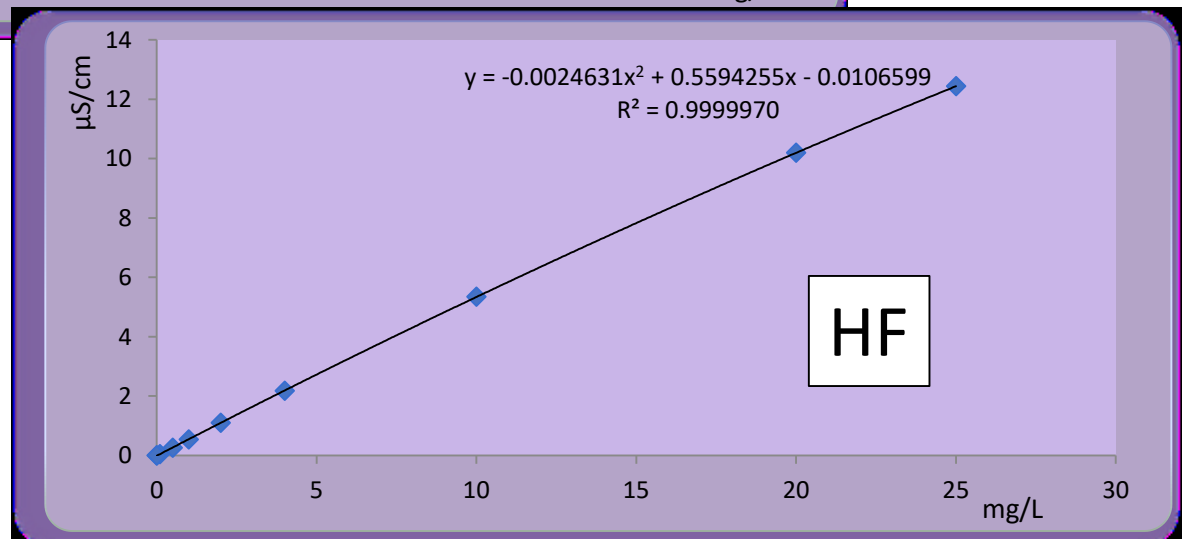


- Detection: conductimetric ;
- Temperature of the conductimetric cell: 35°C ;
- Electrochemical suppression ;
- Suppressor ASRS - 4mm (Thermo Scientific);
- Suppression current: 112 mA ;

Method performances

Calibration curves





Compound	Low level	High level
HCl	0.1 mg/L	50 mg/L
HF	0.1 mg/L	25 mg/L

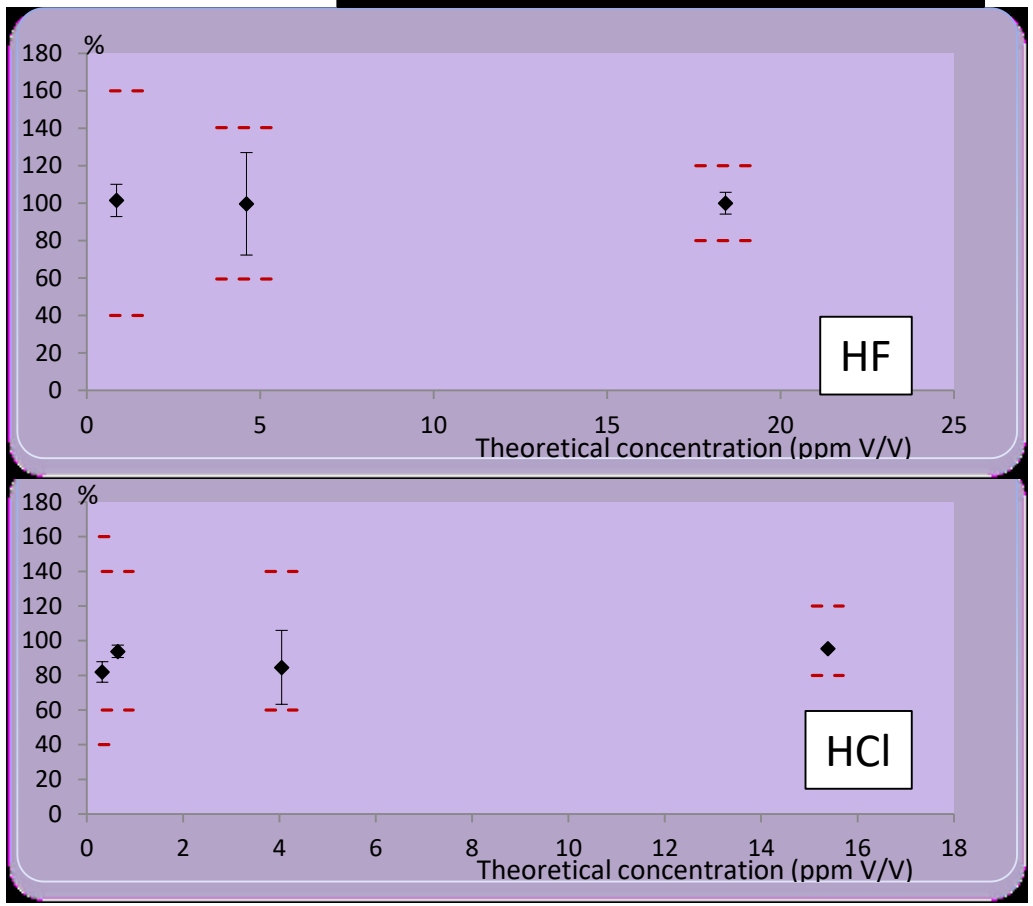
Method performances

Method 1 : use of quartz fiber filter

Limits of quantification

Compound		LOQ
HF	On filter In sample	2 µg/filter 0.71 mg HF/m³
HCl	On filter In sample	2 µg/filter 0.49 mg HCl/m³

Accuracy profiles



Uncertainty measurement

	0.71 mg/m³	3.83 mg/m³	15.3 mg/m³
HF	35%	40%	13%

	0.49 mg/m³	0.98 mg/m³	6.13 mg/m³	23.3 mg/m³
HCl	37%	14%	37%	10%

Method performances

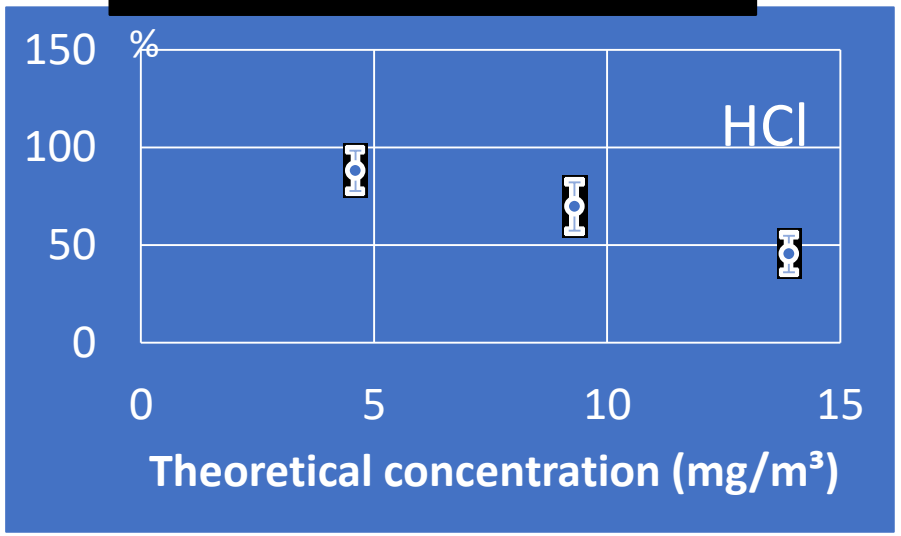
Method 2 : use of cartridges

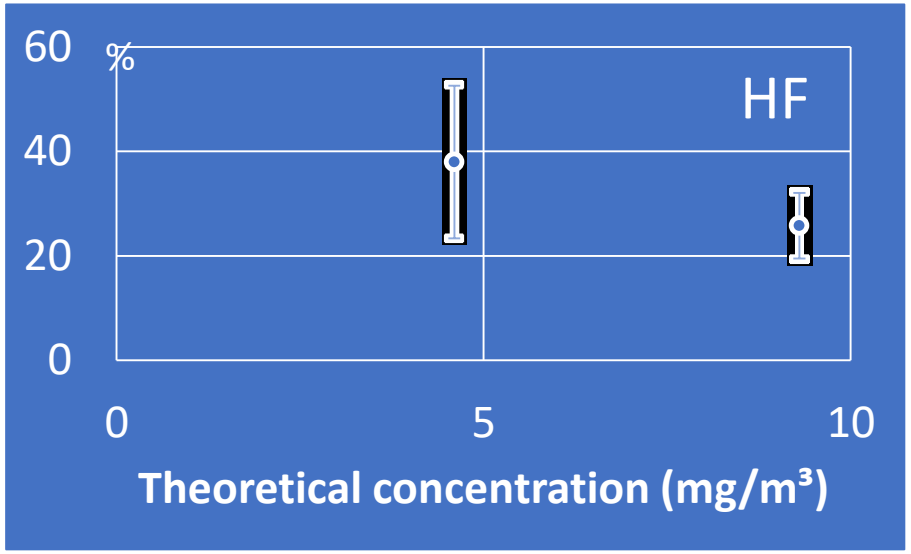
Uncertainty measurement

	4.6 mg/m³	9.3 mg/m³	13.9 mg/m³
HCl	30%	47%	109%

	4.6 mg/m³	9.3 mg/m³
HF	123%	146%

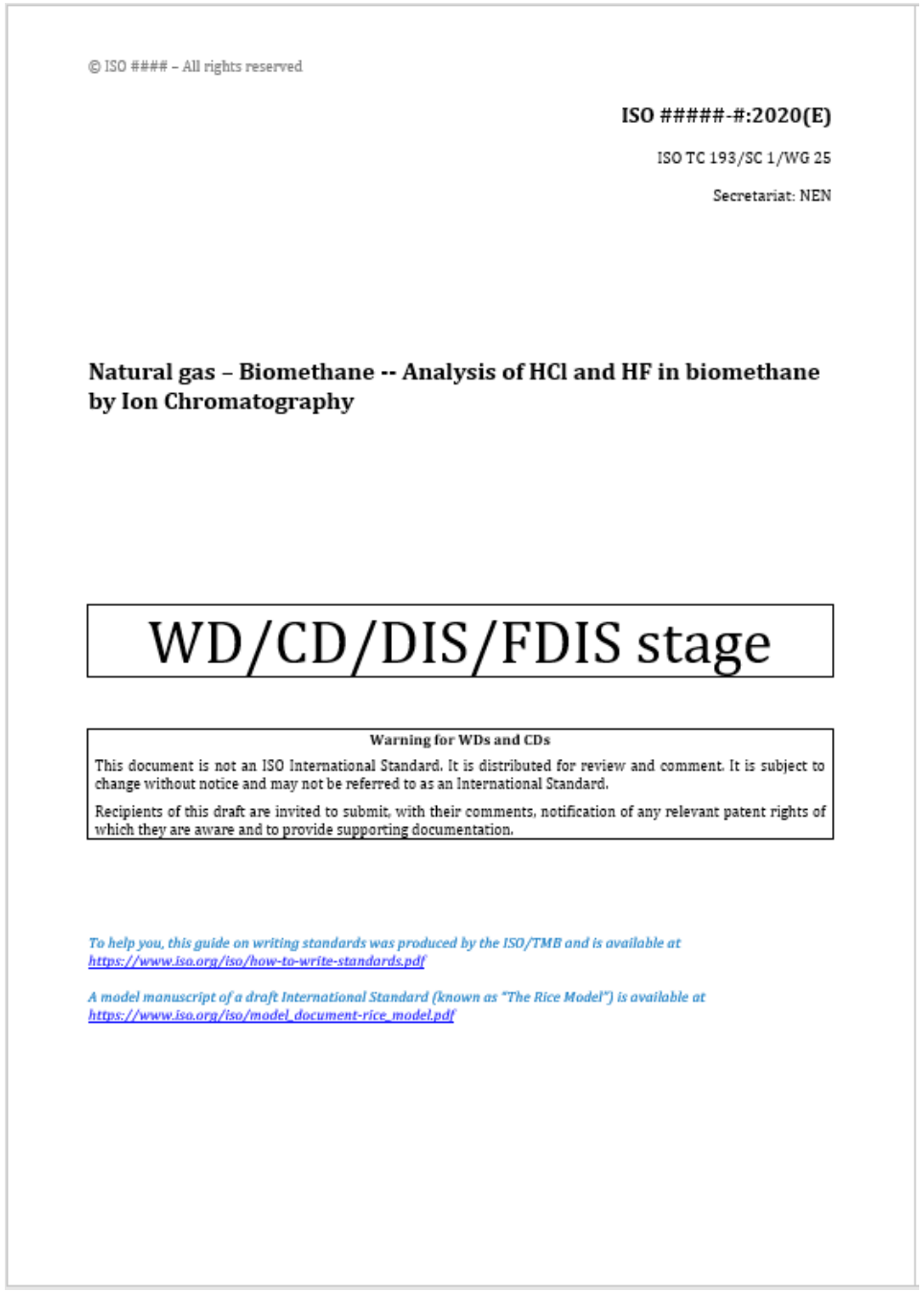
Accuracy profiles





Conclusion

- Experimental work carried out during the projet « metrology for biomethane » enabled to develop specific methods of HCl and HF in biomethane measurement
- First version of NWIP for HCL and HF in biomethane completed
- To be submitted to ISO/TC 193/SC 1/WG 25



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