OIL & GAS

DNV GL's Common practices for the analysis of Biogas

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NEN - Metrology for Biomethane

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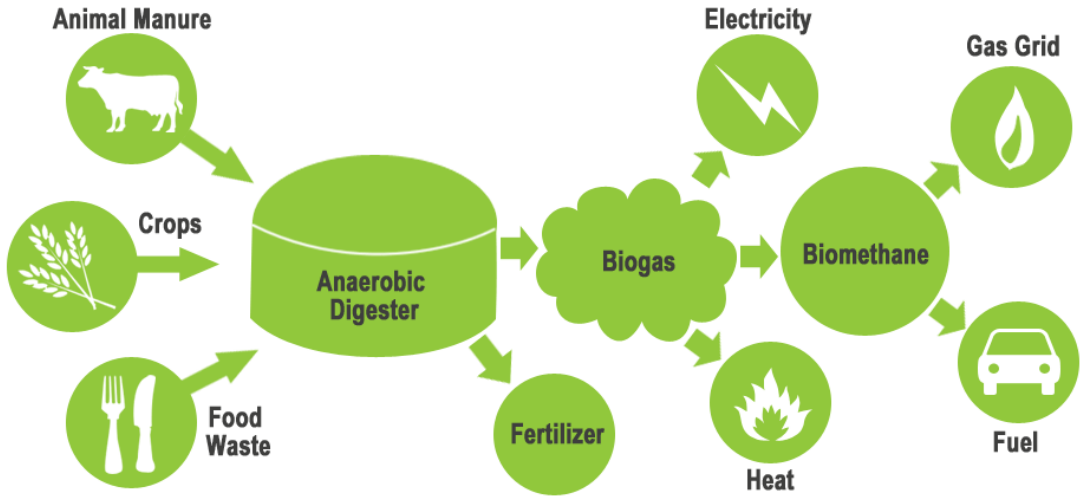
Introduction

- Specification of biogas in the Netherlands
- Composition and physical properties
- Hydrocarbon- and water dewpoint
- Halogenated hydrocarbons
- Silicon’s
- Sulphur components
- Odorant
- Other trace components
- Microbes and particulates
- Solids
- Mobile facilities
- Summary

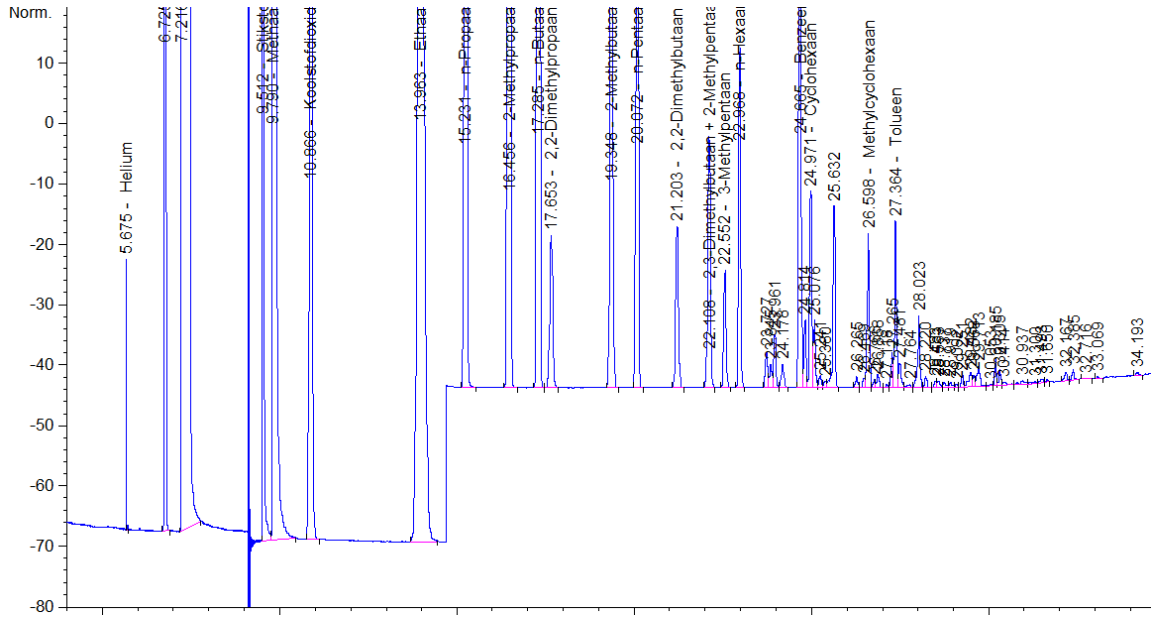
Specification local grids Netherlands (MR Gaskwaliteit 01-01-2019)

Parameter	Min	Max	Unit
Wobbe-index	43.46	44.41	MJ/Nm^3
Hydrocarbons > C1	0	5	mole % (propane equivalents)
Natural gas condensates	0	80	mg/Nm^3 @ –3 °C
Water dewpoint	0	-10	°C @ 8 bar(a)
Oxygen (O_2)	0	0.5	mole %
Hydrogen (H_2)	0	0.5	mole %
Carbon dioxide (CO_2)	0	10.32	mole %
Carbon monoxide (CO)	0	2900	mg/Nm^3
Chlorine (organic)	0	5	mg Cl/Nm^3
Fluorine (organic)	0	5	mg F /Nm^3
Silicon	0	0.1	mg Si/Nm^3
Sulfur (anorganic)	0	5	mg S/Nm^3
Sulfur (organic)	0	6	mg S/Nm^3
THT (odorant)	10	40	mg THT/Nm^3
Total Sulfur (before odorisation)	0	20	mg S/Nm^3
Total Sulfur (after odorisation)	0	31	mg S/Nm^3
Gas temperature	5	20	°C
Particulates > 5 µm	0	100	mg/Nm^3
Pathogenic microbes	0	500	microbes/Nm^3



Composition and physical properties (ISO 6974 and 6976)

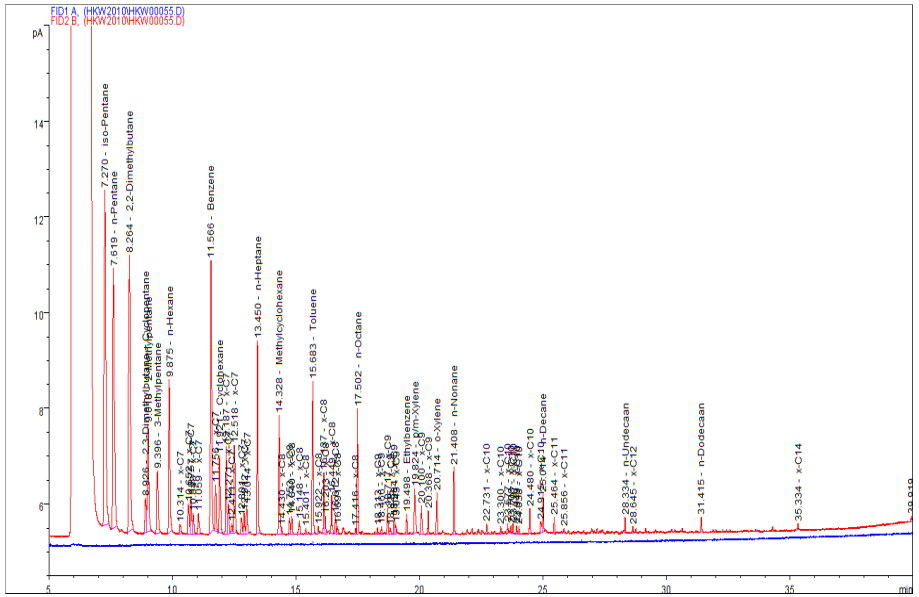
- Gas analysis (ISO 6974, part 3), based on Gas Chromatography (GC).
- Gas analysis is used to determine the quantity and quality of natural gas. The results form the basis to determine the calorific value and other physical properties according to ISO 6976, table 3).
- ISO 17025:2005 accreditation (RvA, scope K103)

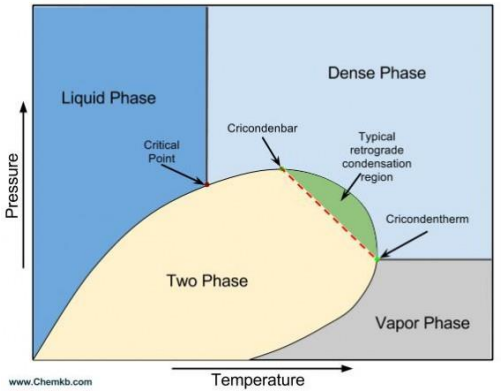


He, H_2, O_2, N_2, CO_2 and C_1 – C_8

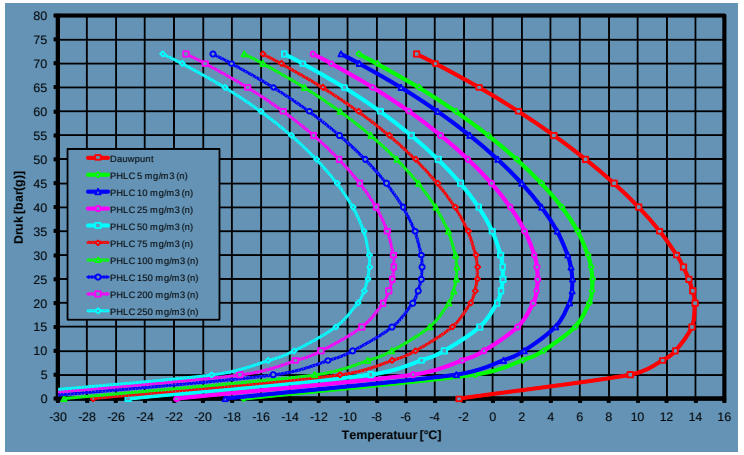
Hydrocarbon liquid content (1)

Hydrocarbon liquid content is calculated, based on compositional data form an extended hydrocarbon analysis according to ISO 6975 (extended hydrocarbon analysis).



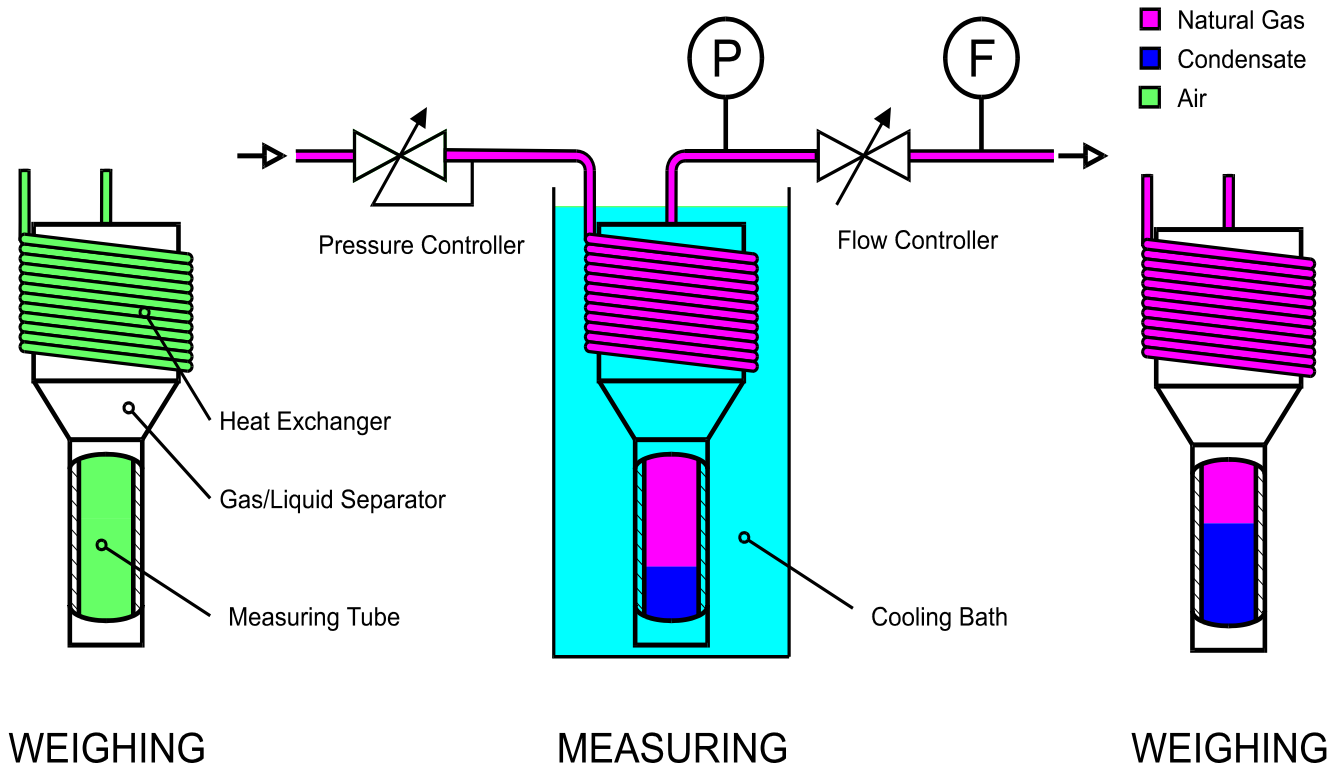


Liquid drop-out curves



Hydrocarbon liquid content (2)

Principle of Manual Method (ISO 6570, part 2)



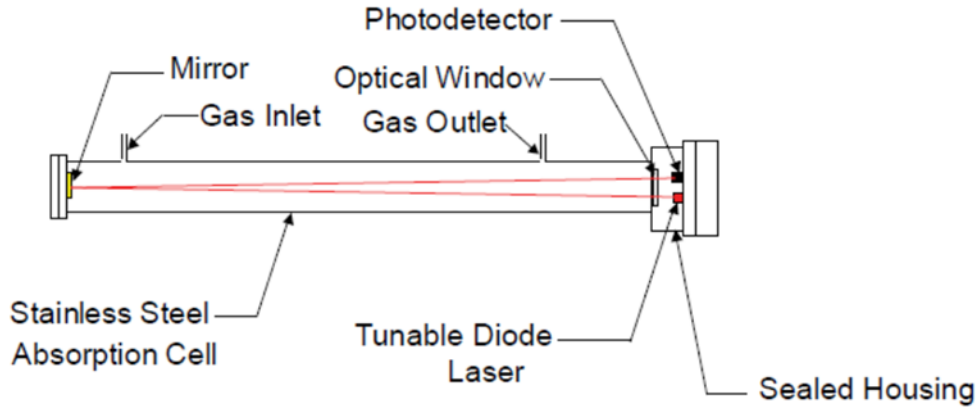
Water dew point (on-line)

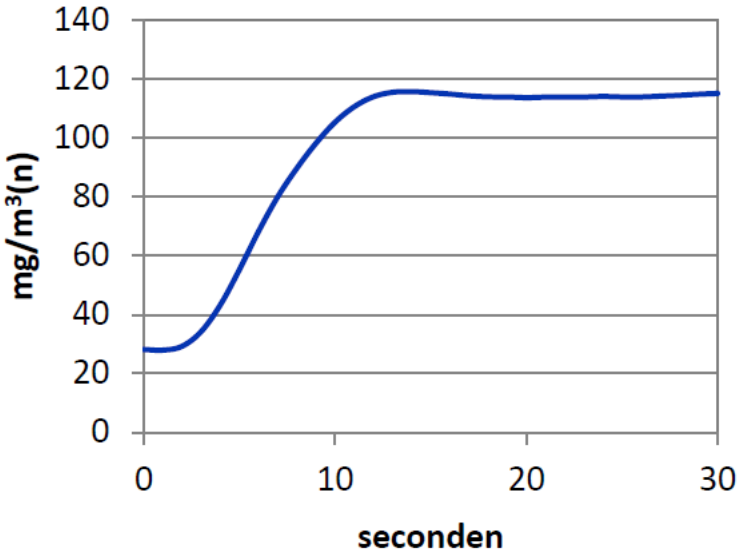
Portable SpectraSensors SS1000 analyser

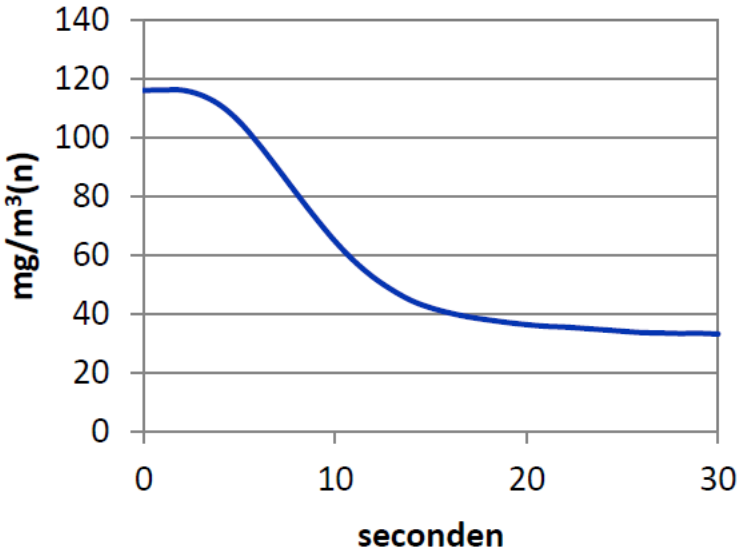
Measurement range 0 – 422 ppm

No calibration needed

Needs pressure to calculate dew point

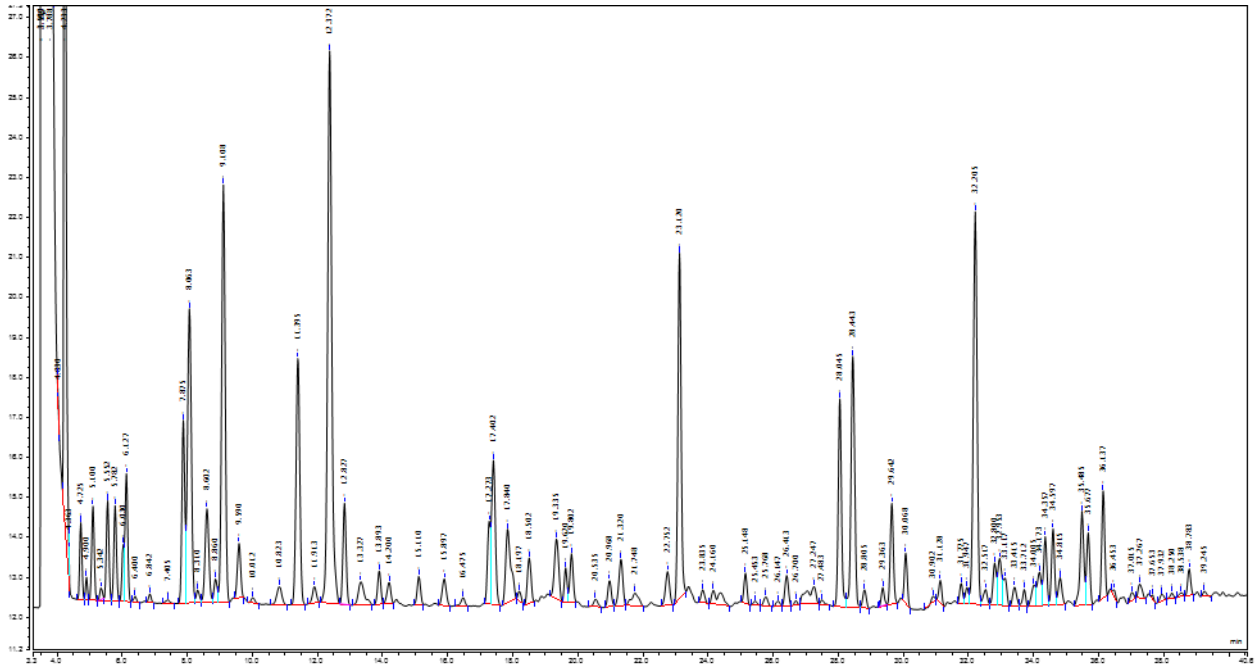






Halogenated hydrocarbons (screening)

Chromatogram of landfill gas



Interscience ISQ GC/MS system

Column OV-1/DB1/CP Sil 5CB

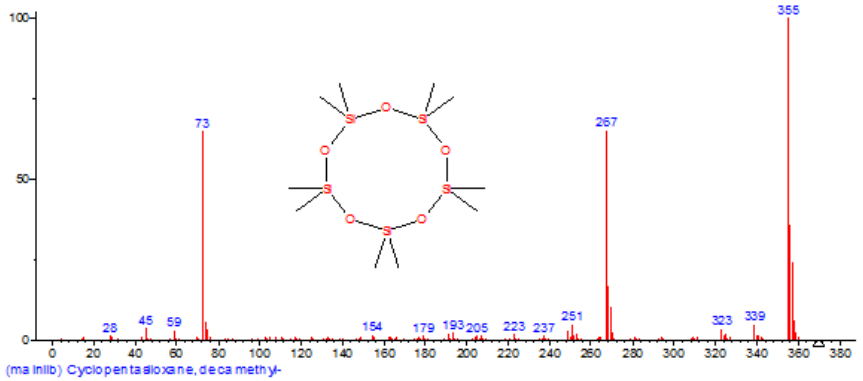
MS and FID in parallel (relative RF's)

scanning 20 – 400 amu

Scotty 104 calibration mixture, 39 components

Silicon's (1)

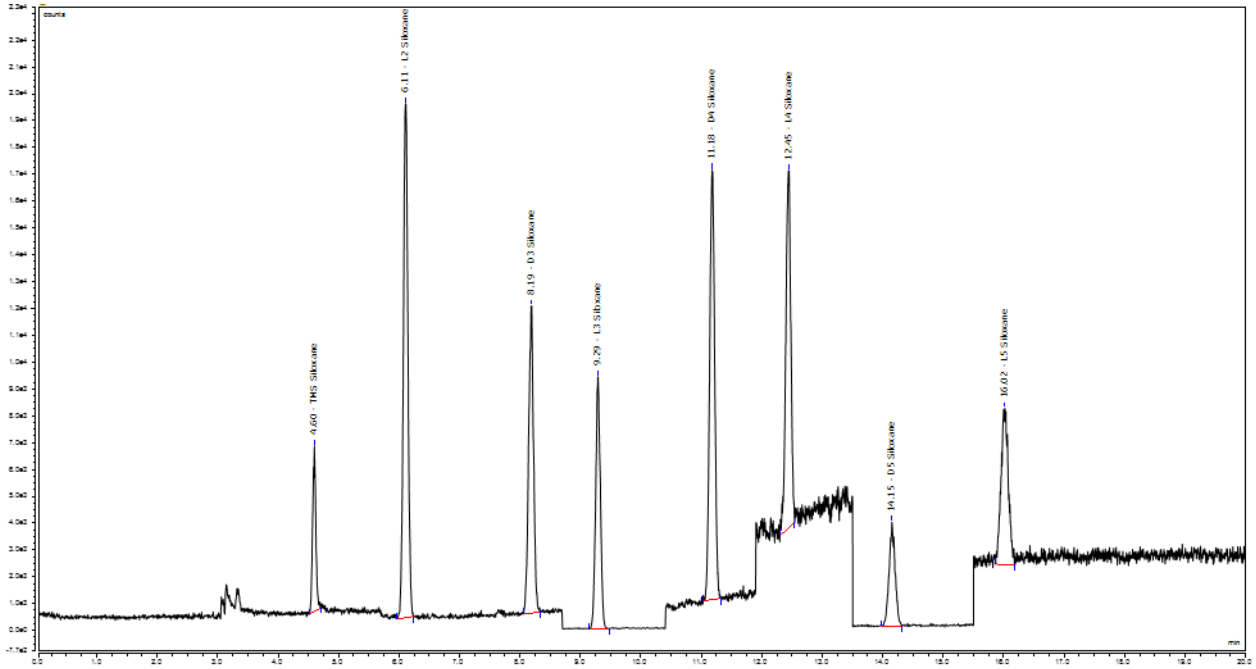
Siloxane	Abrivation	Formula	Boilingpoint	Mol mass	Vapor pressure (25 °C)	SIM Ion
			°C	g/mol	kPa	Amu
Trimethylsilanol	TMS	$C_3H_{10}SiO$	100	90.2	2.13	75
Hexamethyldisiloxane	L2	$C_6H_{18}Si_2O$	100	162.4	4.12	147
Octamethyltrisiloxane	L3	$C_8H_{24}Si_3O_2$	153	236.5	0.52	221
Decamethyltetrasiloxane	L4	$C_{10}H_{30}Si_4O_3$	194	310.7	0.05	207
Dodecamethylpentasiloxane	L5	$C_{12}H_{36}Si_5O_4$	230	384.8	0.009	281
Hexamethylcyclotrisiloxane	D3	$C_6H_{18}Si_3O_3$	134	222.5	1.14	207
Octamethylcyclotetrasiloxane	D4	$C_8H_{24}Si_4O_4$	175	296.6	0.12	281
Decamethylcyclopentasiloxane	D5	$C_{10}H_{30}Si_5O_5$	210	370.8	0.02	355
Dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}Si_6O_6$	245	445.0	0.003	-

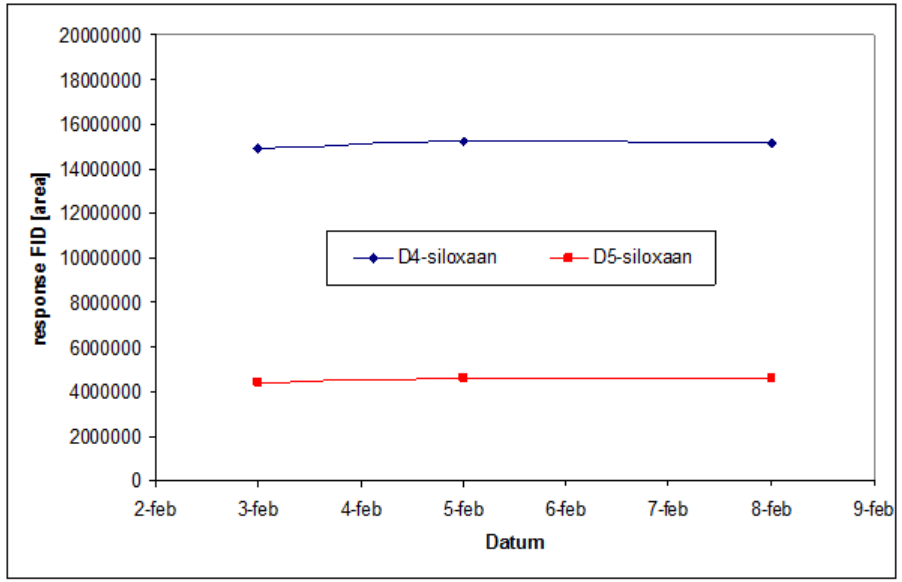


Silicon's (2)

Chromatogram of 20 ppb siloxane mixture SIM-mode

Detection limit < 10 ppb, runtime 20 minutes





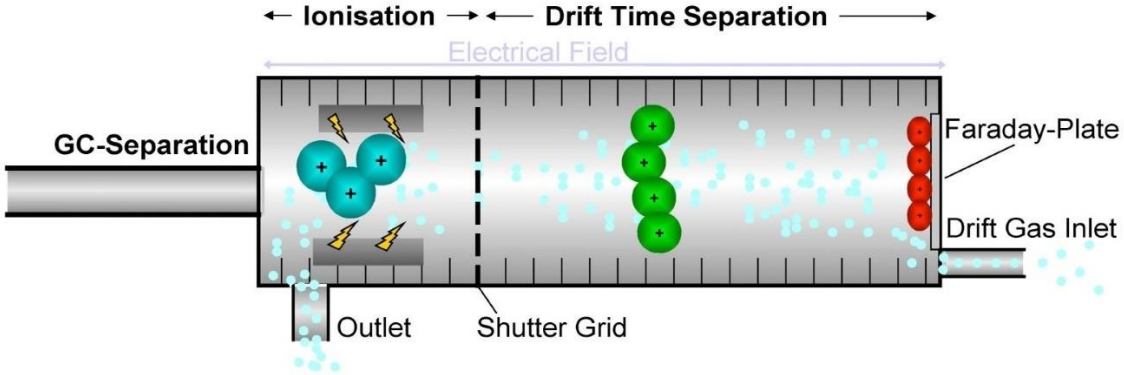
Stability of siloxanes in Tedlar sample bag

Sulfur

Determination of sulfur components according to ISO 19739

- Agilent 6890 with FPD
- Agilent 490 micro GC (TCD & DMD – Differential Mobility Detector)
- Interscience Compact GC with PFPD
- Interscience ISQ GC/MS in SIM mode

New development: IMS - Ion Mobility Detector



Agilent 490 micro GC & GAS Dortmund IMS module

Detection limit approximately 10 ppb, runtime 60 seconds (H_2S and COS)

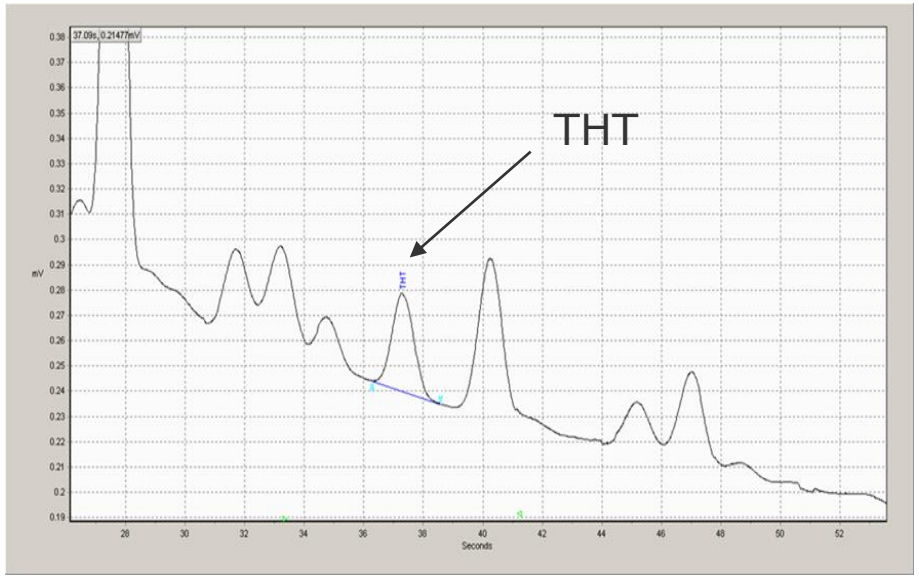
Odorant

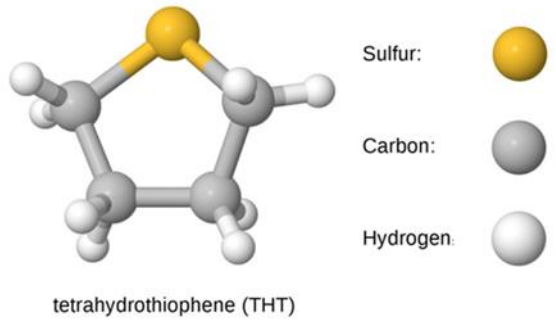
CP-Sil 19 CB, length 6 meter

14% cyanopropyl-phenyl
86% dimethylpolysiloxane

C_4H_8S

Detection limit 4 – 5 mg/m³

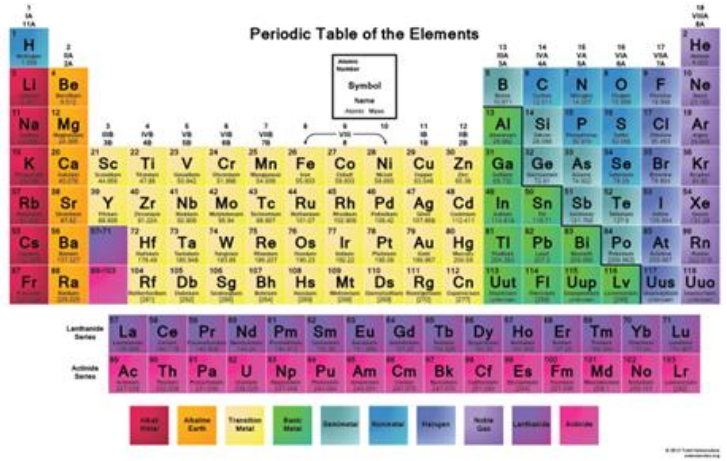


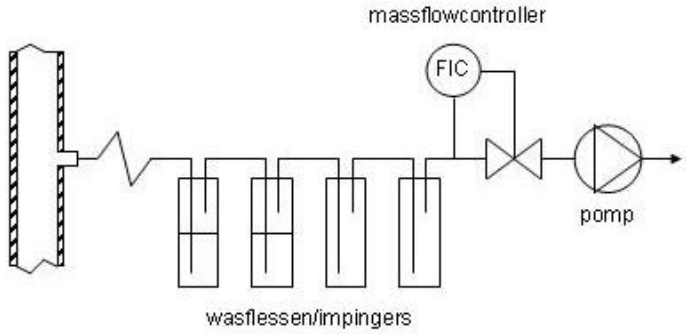


tetrahydrothiophene (THT)

Other trace components

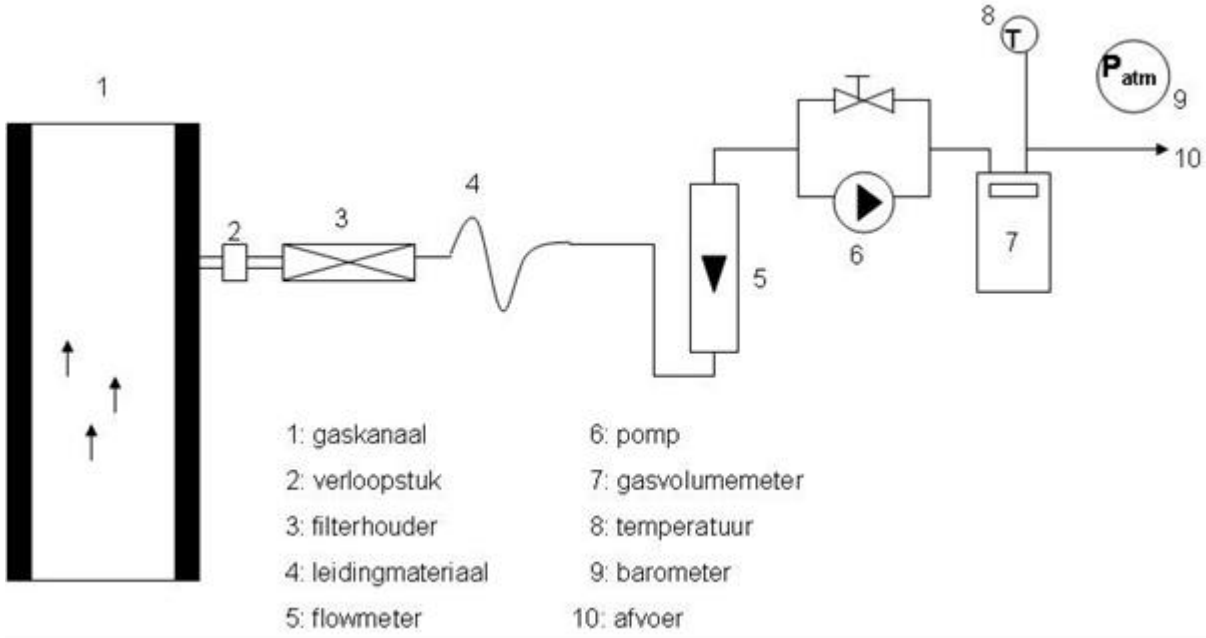
Biogas cannot contain components that will mask the smell of odorant after odorisation. However some trace components like ammonia, aldehydes, ketones and terpenes can influence the sense of odor (Rhinology).





Microbes and particulates

Gas sample volume 100 litres

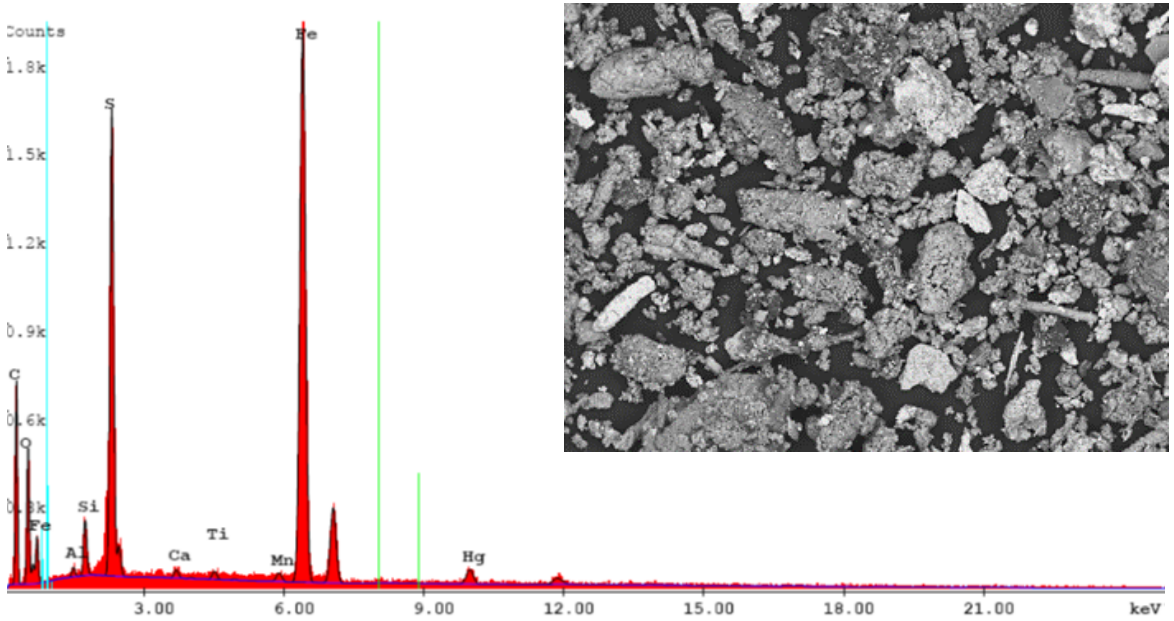


Sampling with 0.2 µm cellulose filter Ø 47mm

Analysis of bacteria and fungi based on RNA/DNA with Quantitative Polymerase chain reaction (Q PCR), outsourced to biolab

Particulate matter (PM) by amount (weight)

Solids (black powder)



Element	Symbol	Weight %
Carbon	C	44.83
Oxygen	O	13.23
Aluminium	Al	0.17
Silicium	Si	1.34
Sulfur	S	8.09
Potassium	K	-
Calcium	Ca	0.31
Titanium	Ti	0.24
Manganese	Mn	0.43
Iron	Fe	25.64
Mercury	Hg	5.71

Scanning Electron Microscope (SEM)
Energy-dispersive X-ray spectroscopy (EDS or EDX)
CHNS-pyrolysis
Particle size distribution

Mobile facilities

Elster-Instromet Encal 3000
Interscience Compact GC
Agilent 490 PRO micro GC (2 & 4 channels)

Main components: H_2, CH_4, N_2, O_2, CO, CO_2
Sulphur components: THT, H_2S, COS and mercaptans

Others: Terpenes and C_2 – C_{12} hydrocarbons

Water dew point (-100 - +20 ^oC) Michell, Easidew

Gas temperature and pressure

Data acquisition and remote access (4G network)

Any questions?

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