



**Dutch
Metrology
Institute**

**METROLOGY FOR
BIOMETHANE**

Biomethane conformity assessment

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Workshop on conformity assessment of biomethane

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Motivation of our work

- Urgent need to diversify the supply of natural gas
 - Environmental (carbon dioxide emission reduction)
 - Economical (EU resources for natural gas are declining)
 - Geopolitical (lesser dependence on imported gas)
- Biomethane and upgraded biogas need to fulfil certain criteria to be compatible with appliances of end users (households, industry)
- Demonstrating compatibility requires
 - Setting criteria
 - Reliable measurement methods
 - Measurement standards and certified reference materials
 - Laboratories with competence in determining properties of biomethane and biogas
 - Conformity assessment



Terminology - biogas and biomethane

Terms related to biogas and biomethane [taken from EN 16723-1:2016]

3.1 biogas

gas, comprising principally methane and carbon dioxide, obtained from the anaerobic digestion of biomass

3.2 biomass

biological material from living, or recently living organisms, typically this may be plants or plant-derived materials

3.3 biomethane

gas comprising principally methane, obtained from either upgrading of biogas or methanation of bio-syngas

3.4 bio-syngas

gas, comprising principally carbon monoxide and hydrogen, obtained from gasification of biomass

3.13 syngas

gas, comprising principally of carbon monoxide and hydrogen, obtained from gasification of fossil fuel

3.14 upgrading of biogas

removal of carbon dioxide and contaminants from biogas

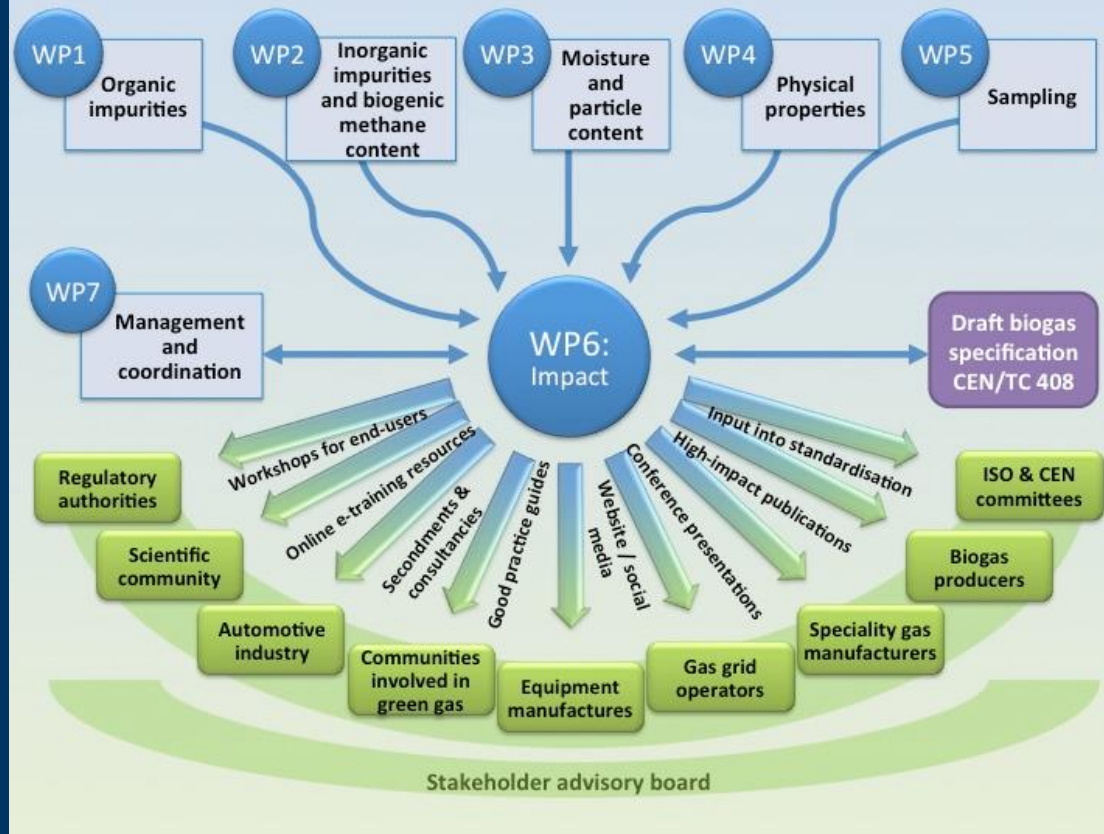
Specifications EN 16723

Parameter	EN 16723-1	EN 16723-2	Notes
Silicon conc.	≤ 0.3 to 1 mg/m^3	$\leq 0.5 \text{ mg/m}^3$	
Hydrogen fraction	See EN 16726	$\leq 2 \%$	
Hydrocarbon dewpoint	See EN 16726	$\leq -2 \text{ }^\circ\text{C}$	
Oxygen fraction	See EN 16726	$\leq 1 \%$	
Sulphur content	$\leq 20 \text{ mg/m}^3$	$\leq 5 \text{ mg/m}^3$	
Methane number	See EN 16726	≥ 65 (80 for high grade)	
Compressor oil content	“de deminis”	“de deminis”	
Dust impurities	“de deminis”	$\leq 10 \text{ mg/L}$	
Amines content	$\leq 10 \text{ mg/m}^3$	$\leq 10 \text{ mg/m}^3$	
Water dewpoint	See EN 16726	$\leq -10 \text{ }^\circ\text{C}$	Class A
Chloride conc.	“de deminis”		
Fluoride conc.	“de deminis”		
Carbon monoxide fraction	$\leq 0.1 \%$		
Ammonia conc.	$\leq 10 \text{ mg/m}^3$		



METROLOGY for BIOGAS

2014 - 2017

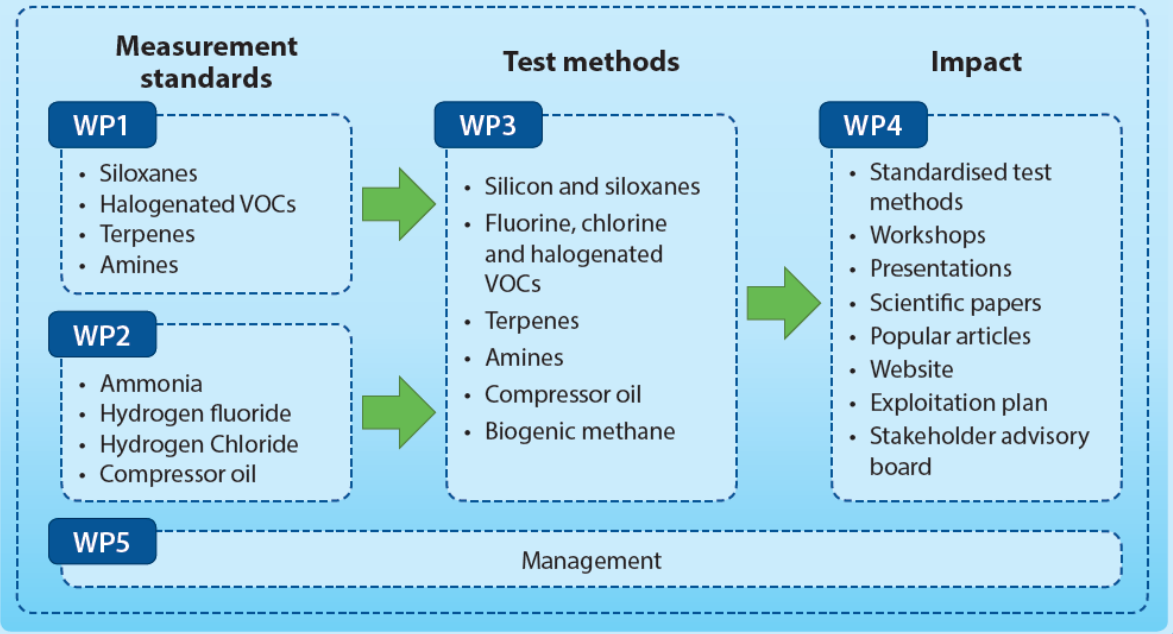


METROLOGY FOR BIOMETHANE

2017 - 2020

Objectives

- To develop robust, standardised test methods, and develop both novel and improved reference standards to meet urgent industry needs.

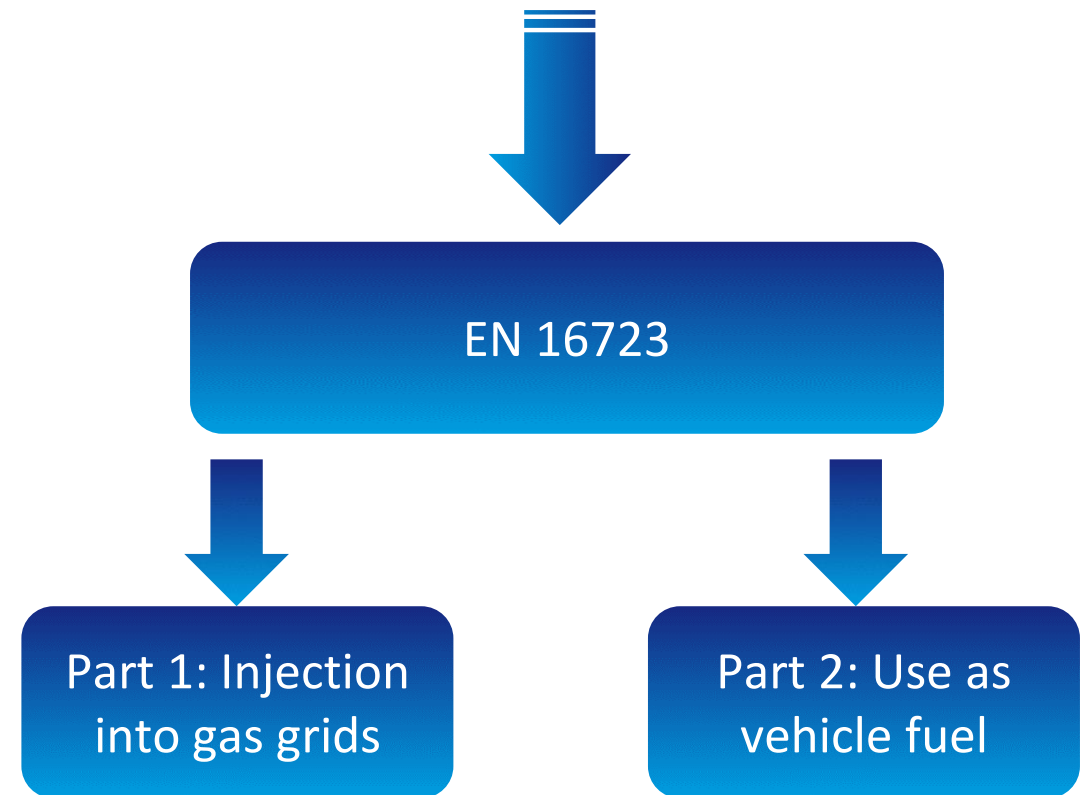


To develop and validate methods for determining the contents of key impurities, moisture, particulates, calorific value, and density in biogas:

- novel methods for the measurement of the contents of key trace-level impurities in biogas and biomethane namely: **total silicon** and **siloxanes**, **sulphur-containing compounds**, aromatic hydrocarbons, **halogenated hydrocarbons**, **ammonia**, hydrogen cyanide, **hydrogen chloride** and **carbon monoxide**;
- capabilities for the measurement of the **particulate content** and **water content** / dew point of biogas and biomethane;
- methods for the measurement of the **calorific value**, **heat capacity**, and **density** of biogas and biomethane;
- traceable method for determining the **fraction biomethane** in samples of blended biomethane and natural gas;
- robust methods for **sampling** biogas and biomethane.

EMRP ENG54 Metrology for biogas (2014 – 2017)

<http://projects.npl.co.uk/metrology-for-biogas/>



Metrology for biogas – results

- Project has developed
 - calibration methods and measurement standards for key impurities in biomethane and biogas
 - Method for water dewpoint measurement
 - Method for particulate concentration
 - Methods for direct calorific value and density measurement
 - Sampling methods
- Project has demonstrated some issues with commonly used equations-of-state (GERG-2008, AGA8) in relation to biogas
- More work is needed on some of the measurement standards (such as silicon, halogens) and for developing test methods



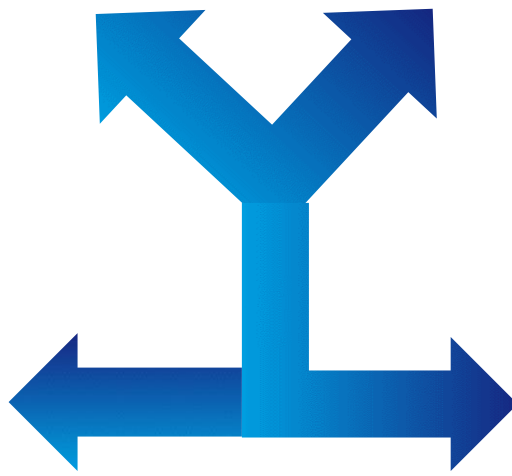
Metrology for biomethane – objectives

DEVELOP MEASUREMENT STANDARDS FOR

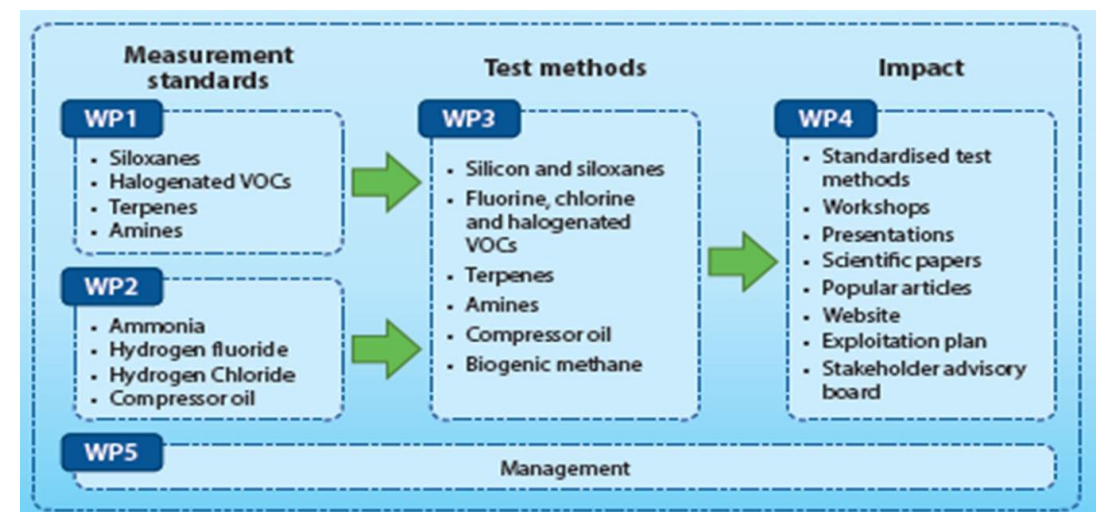
- Siloxanes
- Halogenated VOCs
- Terpenes
- Amines
- Ammonia
- Hydrogen fluoride
- Hydrogen chloride
- Compressor oil

DEVELOP CALIBRATION METHODS FOR

- Total silicon and siloxanes
- Fluorine, chlorine and halogenated VOCs
- Terpenes
- Amines
- Ammonia
- Compressor oil
- Biogenic methane

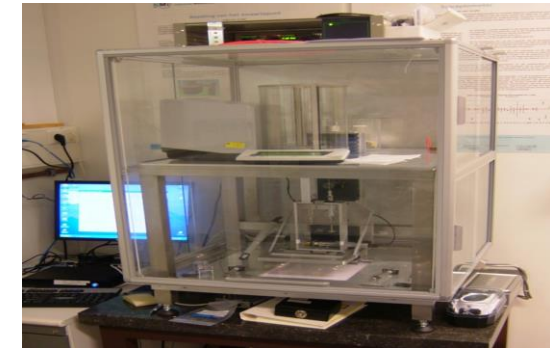
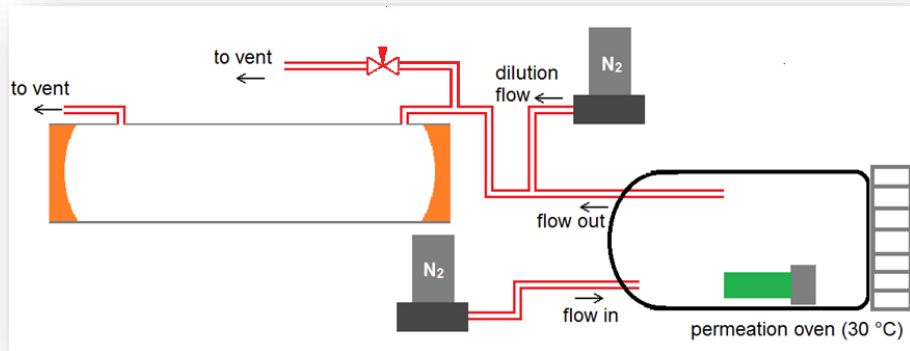


Support **ISO/TC193/SC1/WG25** Biomethane



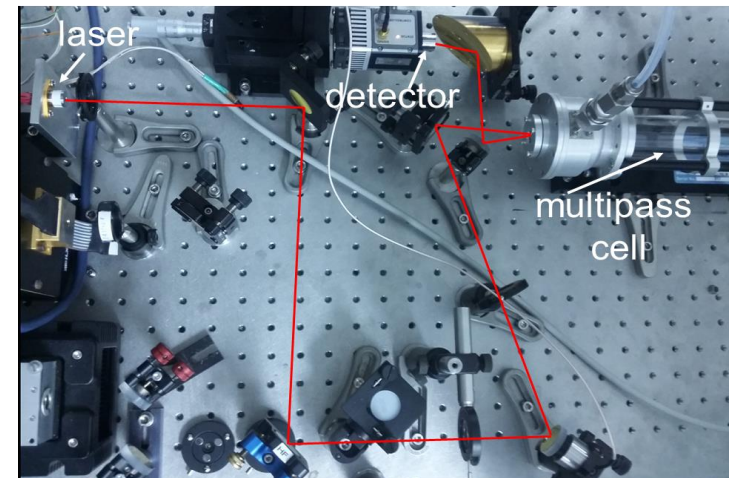
Development of measurement standards

- ❑ Gravimetrically (ISO 6142-1: 2015)
- ❑ Dynamically (ISO 6145)
 - Continuous injection (part IV)
 - Diffusion (part VIII)
 - Permeation (part X)
 - Others



Development of calibration methods

- ❑ Total silicon and siloxanes
 - ICP-MS, GC-ICP-MS, TD-ICP-MS, TD-GC-MS, TDT-GC-FTIR
- ❑ Total fluorine, chlorine and halogenated VOCs
 - CRDS, Laser absorption spectroscopic system, GC-MS, GC-FID
- ❑ Ammonia
 - micro-GC, CEAS, OFCEAS, UV Spectrometer-based, IC
- ❑ Terpenes
 - TD-GC-MS/FID, micro-GC-TCD, TDS-GC-MS
- ❑ Amines
 - (TD)GC-MS, (TD)GC-FID
- ❑ Compressor oil
 - TD-GC/FTIR, GC-FID, GC-MS
- ❑ Biogenic methane content
 - ^{14}C method (using AMS technique)



Test online and offline sampling and analytical methods

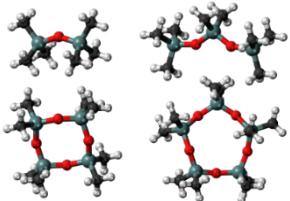
WP1 Measurement standards for VOCs

WP1 Tasks





Work will fully develop measurement infrastructure in order to support the requirements of EN16723

- Task 1.1: Improved stability of siloxane measurement standards
- Task 1.2: Improved stability of halogenated VOC standards
- Task 1.3: Measurement standards for terpenes
- Task 1.4: Measurement standards for amines

Siloxanes







Halogenated VOCs

halogen	molecule	structure	model
fluorine	F ₂	$\text{F}-\text{F}$ 142 pm	
chlorine	Cl ₂	$\text{Cl}-\text{Cl}$ 199 pm	
bromine	Br ₂	$\text{Br}-\text{Br}$ 228 pm	
iodine	I ₂	$\text{I}-\text{I}$ 268 pm	
astatine	At ₂		

Terpenes



Amines

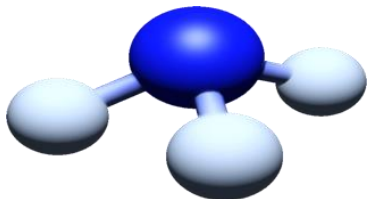
AMMONIA	PRIMARY AMINE	SECONDARY AMINE	TERTIARY AMINE
$\text{H}-\text{N}-\text{H}$ 	$\text{R}-\text{N}-\text{H}$ 	$\text{R}-\text{N}-\text{R}'$ 	$\text{R}-\text{N}-\text{R}''$ 
NH ₃	CH ₃ -NH ₂	CH ₃ -NH-CH ₃	CH ₃ -N(CH ₃) ₂

WP2 Tasks

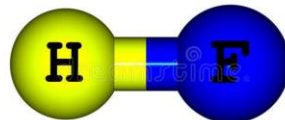
Work will fully develop measurement infrastructure in order to support the requirements of EN16723

- Task 2.1: Improved stability of ammonia standards
- Task 2.2: Measurement standards for HF
- Task 2.3: Measurement standards for HCl
- Task 2.4: Methods for the measurement of compressor oil content

ammonia



HF



HCl



Compressor oil



WP3: Standardised test methods for biomethane

WP3 Tasks

This WP will deliver 7 Seven New Work Item Proposals (NWIPs) for novel validated test methods, based on existing calibration methods, for the **regular conformity assessment of biomethane**:

- Task 3.1: Test method for total silicon and siloxanes
- Task 3.2: Test method for total fluorine, chlorine and halogenated VOCs
- Task 3.3: Test method for ammonia
- Task 3.4: Test method for terpenes
- Task 3.5: Test method for the determination of compressor oil carryover
- Task 3.6: Test method for amines
- Task 3.7: Test method for biogenic methane content (based on ^{14}C)

Goals of this workshop

The aim of the workshop is to collect ideas for the development of standardised test methods in support of EN16723.

- Learn from experts in relevant fields
- Present results obtained within EMPIR 16ENG05 Biomethane consortium and those established metrology infrastructure for biogas and biomethane conformity assessment
- If possible, preselect measurement methods for standardisation
- Discuss with audience and get feedback/ recommendations to further shape the 16ENG05 Biomethane project and ISO/TC193/SC1/WG25 Biomethane



EMPIR 16ENG05 consortium and stakeholders



EMPIR 16ENG05 Metrology for biomethane (2017 - 2020) project website

<http://empir.npl.co.uk/biomethane/>

Project stakeholders' committee now consists of 32 members and is still open to future stakeholders/ collaborators



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EMPIR



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*Thank you for your attention!
Questions?*



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EMPIR 16ENG05 Metrology for biomethane

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