Improving biomethane quality infrastructure: A traceable international comparison of siloxane and total silicon measurement capabilities

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Siloxanes in Biomethane

Biomethane is a “gas comprising principally methane, obtained from either upgrading of biogas or methanation of biosyngas”².

Siloxanes in Biomethane

- Silicon-based impurities are introduced into the gas stream when transitioning from natural gas to biomethane.

- In the form of **linear and cyclic siloxanes**, silicon-based impurities form **damaging solid silicon oxides** upon combustion.
Siloxanes in Biomethane

- Siloxanes cause **damage at very low amount fractions**, presenting **analytical limitations** for these types of measurement.

- The **accurate measurement** of silicon-based impurities is essential to **limit the damage** to existing gas infrastructure.

courtesy of P. Griffin, Severn Trent Water, UK
Siloxanes in Biomethane

EC Mandate M/475
- 20% of energy from **renewable** sources
- 10% of transport from **biofuels**

TC 408 (biomethane)
- **EN 16723-1** (grid injection)
- **EN 16723-2** (automotive)

- National biomethane quality standardisation
Siloxanes in Biomethane

• The UK biomethane industry has been driven by several Ofgem led initiatives, alongside BEIS, HSE, UNC and independent support schemes.

• The Gas Safety (Management) Regulations (GS(M)R) 1996 outline ‘impurities’, while EN 16723 limits the value of silicon to < 0.3 to 1 mg m⁻³.
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Support for Impact Project

• This EMPIR Support for Impact Project (SIP) addresses the measurement challenges posed by the biomethane impurity thresholds in EN 16723.

• The project compares silicon and sulphur measurement capabilities through traceable comparisons.
Aim: To evaluate the measurement capabilities of silicon-containing compounds in methane gas standards by a round robin test.

Partners:

NPL
National Physical Laboratory

VSL

PAUL SCHERRER INSTITUT
PSI
The National Physical Laboratory has successfully established novel methods for high accuracy preparation and analysis of traceable reference gas mixtures containing siloxanes (L2, D4 and D5) in methane.
Support for Impact Project
Support for Impact Project

VSL

gti

SGS

DNV-GL

NPL

Paul Scherrer Institut

GAS

kiwa

enagas
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Standard Preparation and Validation

- Gas standards prepared to a total silicon mass fraction of \(1.5 \text{ mg/m}^3\) via multi-stage dilution
Standard Preparation and Validation

- Mixtures were prepared from liquid siloxanes:
  - Hexamethyldisiloxane – L2 Siloxane
  - Octamethylcyclotetrasiloxane – D4 Siloxane
  - Decamethylcyclopentasiloxane – D5 Siloxane
The gas mixtures were prepared by NPL in accordance with ISO 6142-1\(^3\) (gravimetric method) in high-pressure passivated cylinders.

Bespoke custom made ‘micro-loops’ used to prepare a ‘parent’ mixture from pure liquid siloxanes, which is diluted to the amount-of-substance fractions.

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Standard Preparation and Validation

- The comparison mixtures were assigned a value in accordance with ISO 6143\textsuperscript{4} using a \textbf{direct comparison method}.

- A Gas Chromatograph system fitted with a \textbf{Flame Ionisation Detector} and a \textbf{Mass Selective Detector} was used at NPL to determine amount fractions.

\textsuperscript{4} - International Organization for Standardization, “ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”
Standard Preparation and Validation

FID
Standard Preparation and Validation
Standard Preparation and Validation

FID

D5
8.119 min.

MS

D5(MS)
8.172 min.
Standard Preparation and Validation

- The re-verification of comparison mixtures returned to NPL has indicated stability in L2, D4 and D5 siloxanes amount fractions.

- Siloxanes have exhibited homogeneity and stability challenges with certain cylinder passivation in previous projects.\(^5\)

- Adsorption in sample lines may lead to unstable measurements.

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\(^5\) EMPIR 16ENG05 Metrology for Biomethane, Deliverable D1, NPL and VSL
Summary of Comparison

- A variety of distinct Gas Chromatograph systems were applied to the siloxane gas standards analysis across the 9 participants (including NPL).
Summary of Comparison

- A wide range of separation techniques and calibration standards were used.

- All participants reported their measured amount or mass fractions along with their expanded uncertainties and method descriptions.
Summary of Comparison

Reported amount fractions for D5 Siloxane

[Graph showing deviation from reference amount fraction in µmol for various laboratories]
Summary of Comparison

Reported amount fractions for D4 Siloxane

![Graph showing deviation from reference amount fraction / µmol for different laboratories.](image)
Summary of Comparison

Reported amount fractions for L2 Siloxane

![Graph showing deviation from reference amount fraction / μmol for different laboratories.](image)
Summary of Comparison

Reported mass fractions for Total Silicon

![Graph showing deviations from reference mass fraction for various laboratories.](image-url)
Summary of Comparison

- In accordance with ISO 13528\(^6\), the performance of the laboratories have been evaluated using z-scores and \( E_n \)-scores:

\[ z = \frac{x - X}{\hat{\sigma}} \quad \quad \quad E_n = \frac{x - X}{\sqrt{U_{lab}^2 + U_{ref}^2}} \]

- An evaluation has also been carried out using zeta scores (\( \zeta \)):

\[ \zeta = \frac{x - X}{\sqrt{u_{lab}^2 + u_{ref}^2}} \]

- Where \( x \) is the participant's result; \( X \) is the NPL assigned value; \( \hat{\sigma} \) is the standard deviation for proficiency assessment; \( U \) is the expanded uncertainty and \( u \) is the standard uncertainty.

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**Summary of Comparison**

**Results for D5 Siloxane**

| z | ≤ 2 is Satisfactory | 2 < |z| < 3 is Questionable | |z| ≥ 3 is Unsatisfactory |
|---|---|---|---|
| Participant code | L09 | L02 | L08 | L04 | L07 | L06 | L01 | L05 | L03 |

![Graph showing zeta-score comparisons for different participants.](Image)
Summary of Comparison

Results for D4 Siloxane

|z| ≤ 2 is Satisfactory  
2 < |z| < 3 is Questionable  
|z| ≥ 3 is Unsatisfactory
Summary of Comparison

Results for L2 Siloxane

| $z$ | $\leq 2$ is Satisfactory | $2 < |z| < 3$ is Questionable | $|z| \geq 3$ is Unsatisfactory |

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Summary of Comparison

Sulphur Round Robin

Aim: To evaluate the measurement capability of industrial laboratories performing measurement of sulphur-containing compounds and total sulphur concentration in biogas and/or biomethane gas standards by organising a round robin test.

Partners:
This work was supported by the UK government’s Department for Business, Energy and Industrial Strategy (BEIS)

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