Metrology for biomethane

Measurement techniques and test methods for measuring ammonia content

Lucy Culleton (NPL)

Workshop on conformity assessment of biomethane, Delft, 25th January 2019
## Ammonia within EN16723

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EN 16723-1</th>
<th>EN 16723-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon concentration</td>
<td>≤ 0.3 to 1 mg/m³</td>
<td>≤ 0.5 mg/m³</td>
</tr>
<tr>
<td>Hydrogen fraction</td>
<td>See EN 16726</td>
<td>≤ 2 %</td>
</tr>
<tr>
<td>Hydrocarbon dew point</td>
<td>See EN 16726</td>
<td>≤ -2 °C</td>
</tr>
<tr>
<td>Oxygen fraction</td>
<td>See EN 16726</td>
<td>≤ 1 %</td>
</tr>
<tr>
<td>Sulphur concentration</td>
<td>≤ 20 mg/m³</td>
<td>≤ 5 mg/m³</td>
</tr>
<tr>
<td>Methane number</td>
<td>See EN 16726</td>
<td>≥ 65 (80 for high grade)</td>
</tr>
<tr>
<td>Compressor oil content</td>
<td>“de minimis”</td>
<td>“de minimis”</td>
</tr>
<tr>
<td>Dust impurities</td>
<td>“de minimis”</td>
<td>≤ 10 mg/L</td>
</tr>
<tr>
<td>Amines content</td>
<td>≤ 10 mg/m³</td>
<td>≤ 10 mg/m³</td>
</tr>
<tr>
<td>Water dew point</td>
<td>See EN 16726</td>
<td>≤ -10 °C</td>
</tr>
<tr>
<td>Chloride concentration</td>
<td>“de minimis”</td>
<td></td>
</tr>
<tr>
<td>Fluoride concentration</td>
<td>“de minimis”</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide fraction</td>
<td>≤ 0.1 %</td>
<td></td>
</tr>
<tr>
<td>Ammonia concentration</td>
<td>≤ 10 mg/m³</td>
<td></td>
</tr>
</tbody>
</table>

Ammonia is corrosive in water and contributes to formation of NOₓ.

Green = Capability developed at NPL
Ammonia work within the METROLOGY FOR BIOMETHANE project

**Aim**
To develop stable, metrologically traceable and accurate measurement standards and high-accuracy reference methods for ammonia in biomethane

**Partners:**

- NPL
- National Physical Laboratory
- VSL
- Innovazione e ricerca
- GRUgaz
- RICE
- Research & Innovation Center for Energy
- VTT
Task 2.1: Improved stability of ammonia measurement standards

<table>
<thead>
<tr>
<th>Activity number</th>
<th>Activity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2.1.1</td>
<td>Identify cylinder types</td>
</tr>
</tbody>
</table>

- 6 passivation types were selected

<table>
<thead>
<tr>
<th>Cylinder types</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>BOC spectraseal</td>
<td></td>
</tr>
<tr>
<td>NET</td>
<td></td>
</tr>
<tr>
<td>Effectech Performax</td>
<td></td>
</tr>
<tr>
<td>Scott Aculife IV</td>
<td></td>
</tr>
<tr>
<td>Air products Experis</td>
<td></td>
</tr>
<tr>
<td>SilcoTek Sulfinert</td>
<td></td>
</tr>
</tbody>
</table>

sampling vessel
Task 2.1: Improved stability of ammonia measurement standards

<table>
<thead>
<tr>
<th>Activity number</th>
<th>Activity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2.1.2</td>
<td>Prepare gas reference standards</td>
</tr>
</tbody>
</table>

- 7 reference standards were prepared
How ammonia standards are prepared

- 10 mg/m³ only possible via multi-stage dilution
How ammonia standards are prepared

Lower amount fraction grandparent
(Use more to make parent)

Higher amount fraction grandparent
(Use less to make parent)

Uncertainty vs dilution ratio

![Graph showing uncertainty vs dilution ratio]

- High uncertainty
- Low uncertainty

How ammonia standards are prepared
How ammonia standards are prepared

- Gravimetric preparation

Pure ammonia → Transfer vessel (loop) → High-accuracy weighing → Tare vessel
How ammonia standards are prepared

Example of pure NH₃ being transferred to a small vessel
How ammonia standards are prepared

Transfer to cylinder
How ammonia standards are prepared

Parent mixture transfer to cylinder
How ammonia standards are prepared

Cylinder is weighed accurately against a tare
How ammonia standards are prepared

Balance gas is transferred
How ammonia standards are prepared

Weighing repeated

Tare
How ammonia standards are prepared

- Cylinder is rolled to homogenise
Preliminary results

- Standards initially measured using NDIR spectrometry

<table>
<thead>
<tr>
<th>Cylinder types</th>
<th>Cylinder no.</th>
<th>Certified NH₃ concentration against the reference cylinder 2462</th>
<th>% deviation from gravimetric concentration</th>
<th>Analy. U/C (k=2) rel. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>D679217</td>
<td>10.2</td>
<td>2.3</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>D618312</td>
<td>9.3</td>
<td>-6.3</td>
<td>0.8</td>
</tr>
<tr>
<td>C</td>
<td>2426</td>
<td>10.1</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>D</td>
<td>L53103038</td>
<td>11.6</td>
<td>15.9</td>
<td>1.1</td>
</tr>
<tr>
<td>E</td>
<td>0606</td>
<td>10.0</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>F</td>
<td>APEX1182786</td>
<td>9.8</td>
<td>-2.1</td>
<td>1.6</td>
</tr>
<tr>
<td>G</td>
<td>RK7065</td>
<td>10.0</td>
<td>-0.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Task 2.1: Improved stability of ammonia measurement standards

<table>
<thead>
<tr>
<th>Activity number</th>
<th>Activity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2.1.3</td>
<td>NPL will quantify ammonia interaction with surfaces using a materials testing rig</td>
</tr>
</tbody>
</table>

- Ongoing work
Task 2.1: Improved stability of ammonia measurement standards

<table>
<thead>
<tr>
<th>Activity number</th>
<th>Activity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2.1.4</td>
<td>NPL will generate a <strong>dynamic standard</strong> to compare against static standards</td>
</tr>
</tbody>
</table>

- Ongoing work
### Task 3.1 - Test method for ammonia

<table>
<thead>
<tr>
<th>Activity number</th>
<th>Activity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3.1.4</td>
<td>NPL will develop and validate an applicative method for the analysis of ammonia in biomethane using UV-VIS detection.</td>
</tr>
</tbody>
</table>
Previous measurement of ammonia at NPL

- Simulated FTIR spectra of 10ppm ammonia mixtures
- Matrix comparison: Biogas, methane and nitrogen

- NH3 in N2 (red) and in CH4 (blue),

- NH3 in N2 (red) and in Biogas (blue)
This work was supported by the UK government’s Department for Business, Energy and Industrial Strategy (BEIS)
Measurement technique and test method for measuring total silicone in biogas/biomethane - Method developed at IMBiH

Workshop on conformity assessment of biomethane organised by the project EURAMET EMPIR 16ENG052 “Metrology for Biomethane” and ISO/TC193/SC1/WG25 “Biomethane”

Work done by Katarina Hafner-Vuk and Rialda Kurtić
Presentation prepared by Rialda Kurtić

Workshop on conformity assessment of biomethane
NEN, Vlinderweg 6, Delft, the Netherlands, 22-23 January 2019
Description of instrumental technique
Instrumental method set-up
Sampling of siloxanes from biogas/biomethane
Results
Conclusions
Description of instrumental technique

- Microwave Plasma - Atomic Emission Spectrometer (MP-AES) (Figure 1)
- MP AES technique is based on the emission of photons from atoms or ions that have been excited in microwave nitrogen plasma (Figure 2)
- Simultaneous multi-analyte determination.
- Sample type: Liquid
- Sample introduction: peristaltic pump, nebulizer with nebulizer chamber
Description of instrumental technique

Sample introduction: peristaltic pump, nebulizer with nebulizer chamber

Sample path: nebulizer with nebulizer chamber, N\textsubscript{2} plasma, break down into atoms or ions, get excited and in the end emit the photon

Properties of microwave induced N\textsubscript{2} plasma
- inert
- high temperature of the microwave plasma helps to reduce chemical interferences.

Detector covers near UV and visible part of the spectra.

Figure 2. Explains the principle of MP-AES
## Description of instrumental technique

<table>
<thead>
<tr>
<th>Operating parameters of MP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Instrumentation</strong></td>
</tr>
<tr>
<td><strong>Plasma conditions</strong></td>
</tr>
<tr>
<td>Plasma Gas</td>
</tr>
<tr>
<td>Power of Magnetron Output</td>
</tr>
<tr>
<td><strong>Gas flows</strong></td>
</tr>
<tr>
<td>Plasma Gas Flow-Nitrogen</td>
</tr>
<tr>
<td>Pre-optics Protection (POP) Gas –Air</td>
</tr>
<tr>
<td>Nebulizer gas flow</td>
</tr>
<tr>
<td>Nebulizer</td>
</tr>
<tr>
<td>Spray Chamber</td>
</tr>
<tr>
<td>Solution Uptake</td>
</tr>
<tr>
<td>Pump Tubing</td>
</tr>
<tr>
<td>Plasma Torch</td>
</tr>
<tr>
<td>Plasma Viewing</td>
</tr>
<tr>
<td><strong>Data acquisition parameters</strong></td>
</tr>
<tr>
<td>Sample Uptake Delay</td>
</tr>
<tr>
<td>Stabilization Time</td>
</tr>
<tr>
<td>Read Time</td>
</tr>
<tr>
<td>No. of Replicates</td>
</tr>
<tr>
<td>Background Correction</td>
</tr>
<tr>
<td>Optical System</td>
</tr>
<tr>
<td>Optical Resolution</td>
</tr>
<tr>
<td>Detector</td>
</tr>
<tr>
<td><strong>Analytes (Wavelengths)</strong></td>
</tr>
</tbody>
</table>

### Table 1. Operating parameters of MP AES

The emission intensities for different elements studied depend on gas flow, sample flow rate, and microwave power.

The nebulizer gas flow and other operating parameters were optimized for obtaining higher stability of plasma and maximum emission intensity.
Instrumental method set up

MP Expert Software

**Elements**

**Wavelengths** were set up with respect to possible interferences on Si. 251,611 nm (most sensitive line); 288,158 nm

**Conditions**

Nebulizer pressure and viewing position were set each time prior analysis with one of the calibration standard solution. Conditions described in *Table 1.*

<table>
<thead>
<tr>
<th>Details on optimized MWP AES parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pump speed (rpm)</td>
</tr>
<tr>
<td>Sample introduction</td>
</tr>
<tr>
<td>Replicates</td>
</tr>
<tr>
<td>Uptake time (s)</td>
</tr>
<tr>
<td>Rinse time (s)</td>
</tr>
<tr>
<td>Stabilization time (s)</td>
</tr>
<tr>
<td>QC active</td>
</tr>
<tr>
<td>Element (wavelength, nm)</td>
</tr>
<tr>
<td>Background correction</td>
</tr>
<tr>
<td>Calibration correlation coefficient limit set up</td>
</tr>
</tbody>
</table>

*Table 2. Operating parameters of MP AES*
Instrumental method set up

Calibration

Calibration curve settings (concentration range) set in such a way to cover the expected concentration of Si from the gas sample.

Calibration standards prepared with reference solution of NH₄HSiF₆ (1000 mg/L Si in 2% HNO₃)
Concentration intervals 0.05 - 1 ppm; 1-50 ppm (LOQ at 251,611 nm around 10 ppb).

RSD < 2.5% 

Figure 3 Example of MP Expert Software screen

Figure 5. Examples of calibration curves (emission lines: 251,611 nm; 288,158 nm) obtained in process of method validation
Sampling of siloxanes from biogas/biomethane - method of choice

Sample type for MWP AES: Liquid (an anorganic solvent, for organic solvent additional accessories required)
Sampling in HNO$_3$(conc.) and other acidic media did not show good results with MWP AES technique (TDS>3%, required dilution of concentrated acidic media)

The form of the silicon is highly dependent on the pH of the solution during the derivatization process!

<table>
<thead>
<tr>
<th>Analyte/ Media</th>
<th>NaOH 0,5M + HF 48% (HF in excess, pH&lt;2)</th>
<th>NaOH 0,5M + HF 48% - HF in excess pH=4</th>
<th>NaOH 0,5M + HF 48% - NaOH in excess</th>
<th>NaOH 0,5M + HF 48% + NaF - HF in excess pH=4</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>Soluble + Derivatization + Stable + (2 weeks in PP) Homogenous +</td>
<td>Soluble + Derivatization +/- Stable +/- Homogenous +/-</td>
<td>Soluble + Derivatization - Stable - Homogenous -</td>
<td>Soluble + Derivatization +/- Stable +/- Homogenous +/-</td>
</tr>
<tr>
<td>D4</td>
<td>Soluble + Derivatization + Stable + (2 weeks in PP) Homogenous +</td>
<td>Soluble + Derivatization +/- Stable - (2 weeks in PP) Homogenous -</td>
<td>Soluble + Derivatization - Stable - Homogenous -</td>
<td>Soluble + Derivatization +/- Stable - Homogenous +</td>
</tr>
</tbody>
</table>

Table 3. Overview of L2&D4 behaviour in selected media
Sampling method

Biogas/biomethane sample passed through absorbing liquid (HNO₃ CONC.) heated to around 60°C.

Sampling flow was kept constant at approximately 10 mL/min and the total volume was read from the flow meter after the sampling was finalized.

HNO₃ CONC. from gas impingers was quantitatively transferred to a plastic container and weighed.

Further treatment with concentrated NaOH and HF + dilution with water (Table 3).

The sample was weighted and expected concentration calculated (assuming 100% efficiency of sampling and derivatization process).
Sampling of siloxanes from biogas/biomethane - method of choice

Two gaseous referent mixtures with different concentration of the siloxanes were used for sampling of a siloxane with the purpose of final determination of silicone.

1. One with low Si content containing the following components and concentrations:
   - L2 - 0.24135 ppm (grav.)
   - L3 - 0.03527 ppm (grav.)
   - D4 - 0.87933 ppm (grav.)
   - D5 - 0.05614 ppm (grav.)

2. Second one as D5 parent mixture with nominal concentration of D5 6 μmol/mol
   This mixture corresponds with the overall silicon content of 5 mg/m3.

Flowchart for preparation gaseous sample for MPW AES analysis
### RESULTS

<table>
<thead>
<tr>
<th>Sample/Parameter</th>
<th>Sample 1 (low conc.)</th>
<th>Sample 2 (low conc.)</th>
<th>Sample 3 (low conc.)</th>
<th>Sample 4 (low conc.)</th>
<th>Sample 1 (D5 mixture)</th>
<th>Sample 2 (D5 mixture)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume collected</strong></td>
<td>48,2 dm³</td>
<td>55,10 dm³</td>
<td>48,5 dm³</td>
<td>38,36 dm³</td>
<td>2,70 dm³</td>
<td>2,28 dm³</td>
</tr>
<tr>
<td><strong>Mass of liquid sample</strong></td>
<td>120,46 g</td>
<td>128,92 g</td>
<td>145,53 g</td>
<td>142,3 g</td>
<td>178,9 g</td>
<td>163,0 g</td>
</tr>
<tr>
<td><strong>Dilution factor</strong></td>
<td>100 and 50</td>
<td>100 and 50</td>
<td>100 and 50</td>
<td>100 and 50</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td><strong>Calculated Si conc. assuming 100% efficiency</strong></td>
<td>2,00 ppm</td>
<td>2,14 ppm</td>
<td>1,67 ppm</td>
<td>1,35 ppm</td>
<td>364 ppm</td>
<td>394 ppm</td>
</tr>
<tr>
<td><strong>Read Si concentration</strong></td>
<td>1,72 ppm</td>
<td>1,74 ppm</td>
<td>1,18 ppm</td>
<td>1,19 ppm</td>
<td>294,2 ppm</td>
<td>256,4</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>86%</td>
<td>81%</td>
<td>71%</td>
<td>88%</td>
<td>81%</td>
<td>65%</td>
</tr>
</tbody>
</table>

In order to obtain sufficient volume of absorbed gas at low flow ca. 10 mL/min, the sampling time was split in two to three days in order to collect /absorb around 40/50 L of gas.

The final concentration was calculated using available information on first mixture concentration in the gas mixture and the volume of sampled gas. D5 mixture was sampled with lower volumes of gas considering high concentration.
- Concentrated acidic media used for the collection of silicon present in biogas with derivatization process provides great capacity and robustness towards other components of biogas, enabling relatively smooth operation with raw biogas.

- The method is suitable for the determination of the lower silicon content providing because of the possibility of prolonged sampling pre-concentration for the following derivatization step.

- It is important to note that used instrumentation is not too expensive and that ambient air nitrogen is used as a fuel for the plasma.

- Further work on the stated method is required.
Thank you for your attention!

More about IMBIH at:
www.met.gov.ba
16ENG05 Metrology for Biomethane
Workshop on Conformity Assessment of Biomethane

*Measurement techniques & test methods for measuring total silicon & siloxane content*

Tim Robinson
Tim_Robinson@wavertonanalytics.com
Overview

- Review of main objectives of Task 3.1: Test Method for total silicon and siloxanes:
  - Practical, environmental and commercial considerations for further discussion
- Overview of prototype specification
- Why GC-FTIR?
- Sample collection & thermal desorption tubes (TDTs)
- Reference calibration library
- Data review: Liquid standard
- Some advantages of TDT-GC-FTIR
- Next steps
Main objectives of Task 3.1

A3.1.5:
• To develop and validate a method for the analysis of speciated siloxanes in biomethane using TDT-GC-FTIR spectroscopy

A3.1.6:
• Analysis of data from three different (analytical) methods to select the standardised test method(s) for the contents of total silicon and siloxanes in biomethane

A3.1.7:
• Using input from activities in Task 3.1, write a NWIP for (1) a proposal for a new ISO standard (2) draft text for such an ISO standard for consideration in ISO/TC193/SC1

Parallel considerations:
• In-line monitoring or off-line lab-based analysis of samples
• Control and data acquisition requirements / standards
• ATEX certified equipment
• Price versus uptake by industry
Overview of FTIR prototype

- IR modulator
- Beam optics
- Detector alignment mounting
- DTGS detector
- Gas cell
- GC interface port
Overview of FTIR prototype

- Spectral range: 500-5000 cm\(^{-1}\)
- Resolution: 4 cm\(^{-1}\)
- Gas cell: light-pipe type
  - Low volume gas cell for use with GC
- Detector: DTGS type
  - Effective range 400-5000 cm\(^{-1}\) – covers siloxane quant region down to 600 cm\(^{-1}\)

Ellutia 200-series GC Interfaced to FTIR prototype

FTIR “bread-board” prototype
Why GC-FTIR?

- IR fingerprint region for siloxanes: 600-1400 cm\(^{-1}\)
- CO\(_2\) plus many other oxygen containing compounds (alcohols, ketones, aldehydes & esters) also absorb in this region – many present in biogas
- CO\(_2\) not captured by thermal desorption tubes however many other interfering compounds are…

Quant region of IR spectrum for siloxanes
Why GC-FTIR?

- IR spectrum of raw landfill gas compounds collected on a TDT
- Reference spectrum for octamethylcyclotetrasiloxane (D4) overlaid and scaled to quantified amount present
- Red band primary quant region blue band secondary quant region
- Illustrates analytical challenge associated with interferents

**Raw landfill gas IR spectrum**
Why GC-FTIR?

- Same TDT sample however spectrum associated with point at which octamethylcyclotetrasiloxane (D4) comes off the GC column
- Same, scaled reference spectrum overlaid
- Interferents would present analytical challenge for direct FTIR or NDIR measurements, especially when attempting to achieve target detection limits
Why GC-FTIR?

- GC performance not critical to analytical performance – main purpose is to separate majority of critical interferents with time
- Using Restek MXT-624 (30m X 0.53mm X 3.0µm) column
- Algorithm used for quantification of coeluting compounds

Hexamethyldisiloxane (L2) measured in the presence of two coeluting esters
TDT sample collection apparatus

- Sample collection, TDT desorption & analysis would be automated with in-line system
- Second TDT used for “spiking”
Thermal desorption tubes (TDTs)

- **TDT spiking:**
  - Determines trapping efficiency for each siloxane
  - Spiked quantity ideally similar to that collected on tube during sampling

- **Detection limits:**
  - On tube DL of ~50 ng for each component siloxane
  - Sampling at 100 ml/min for 5 minutes (500 ml of biomethane) → DL of 100 µg/m³ for each siloxane, or 37 µg Si/m³ (assuming ~37% Si content)
  - Target is 0.3 mgSi /m³ (300 µgSi /m³) for grid inject 0.1 mgSi /m³ (100 µgSi /m³) for vehicle fuel
Thermal desorption tubes (TDTs)

- Three-phase media:
  - Texax
  - Carbotrap
  - Carboxen
  - Arranged with increasing sorbent strength
  - Good for general purpose VOC sampling
  - Trapping efficiency for siloxanes >90%
Reference calibration library

- Reference calibration spectra produced for each siloxane by injecting pure compound into gas cell in a flow of N\textsubscript{2} to dilute
  - 5 points of component dilution
  - Broad, linear range: 0 – 85,000 ng
  - Traceable: equipment calibration and materials certificates of analysis linked to reference:
    - MFCs
    - Syringe & syringe pump
    - Ethylene Calibration Transfer Standard & reference calibration records
    - Purity certificate for siloxane
    - Calibration uncertainty calculations

- 240 quantitative library spectra & 5500 compound identification spectra

Decamethyltetrasiloxane (L4) ref. spectrum
Test data – liquid siloxane standard

- Liquid injection of 1,000 ng/µl siloxane standard from Absolute Standards
- Decamethylcyclopentasiloxane (D5) eluting from column
Test data – liquid siloxane standard

- Same liquid standard showing GC separation of all 6 siloxanes

Decamethylcyclopentasiloxane (D5) Quant Region
Quantification of 6 siloxanes at 1000 ng after injecting 1 ul of 1000 ng/ul standard
Some advantages of GC-FTIR

- No vacuum or associated high vacuum pumps required
- Resilient to contamination from components in the sample (ref: ion source contamination with MS-based systems)
- Transportable
- Simple, low cost service requirements (N₂ only, no He or H₂ required)
- Minimal calibration required – uses internal reference spectra
- TDT sampling offers flexibility for inline and offline (lab) analysis
Next steps

A3.1.5:
• To develop and validate a method for the analysis of speciated siloxanes in biomethane using TDT-GC-FTIR spectroscopy:
  – Dec-17 – Jul-19: Prototype development using Absolute Standards ref. mixture
  – Oct-18 – Mar-19: Finish first phase of testing with NPL siloxanes standard
  – Jun-19 – Dec-19: Optimise and produce data sets for comparison in A3.1.6

A3.1.6:
• Analysis of data from three different (analytical) methods to select the standardised test method(s) for the contents of total silicon and siloxanes in biomethane:
  – Jan-20 – Feb-20: Comparison of data collected from three methods

A3.1.7:
• Using input from activities in Task 3.1, write a NWIP for (1) a proposal for a new ISO standard (2) draft text for such an ISO standard for consideration in ISO/TC193/SC1:
  – Mar-20 – Apr-20: ISO standard
Thank you!

Tim Robinson
Tim_Robinson@wavertonanalytics.com