Development of a standardised test method for ammonia in biomethane

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Ammonia in Biomethane: Need for a NWIP

- NH_3 = Common trace impurity in Biomethane
- Product of anaerobic digestion of organic matter (amino acids)
- Corrosive in presence of water – *Equipment damage*
- Fuel quality – *anti-knock processes in combustion*
- Air Quality – *Particulate formation*

  – *Source of NOx (combustion)*

∴ Negative Public Health/Environment Implications

Ammonia in Biomethane: Need for a NWIP

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EN 16723-1
EN 16723-2

EN 16723: 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

NH_3: ≤ 10 mg/m³ (≈14 µmol mol^{-1})

Test Methods Cited: *Neither validated nor harmonised*

Conformity: *Standardised Test Methods Required*

METROLOGY FOR BIOMETHANE

Ammonia within EMPIR 16ENG05 Biomethane

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Aim

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

Traceable gas standards

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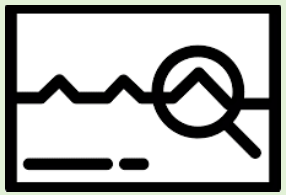

Validated measurement methods

Partners:

NPL National Physical Laboratory

VSL

RICE Research & Innovation Center for Energy

GRTgaz

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Selected Techniques:

- UV/vis
- OFCEAS
- OPO CRDS
- QCL/TDLS

Spectroscopy

- IC
- µGC-TCD

Chromatography

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NWIP Selection Criteria

- Robustness: performance characteristics
- Metrological traceability
- Accessibility: Ease of set up/application
- Commercial Availability
- Measurement time: sampling/analysis
- Gas Consumption

Key Performance Characteristics*

- Repeatability/Reproducibility
- LOD/LOQ
- Stabilisation/Sampling time
- Linearity
- Selectivity
- Accuracy & Analytical Uncertainty

OFCEAS (RICE) and UV/vis (NPL) methods: Selected for NWIP

*Details given in: Ward M., *et al.* **Development of standardised methods for the analysis of ammonia in biomethane,** *(In preparation)*

METROLOGY FOR BIOMETHANE

NWIP – Ammonia content of biomethane

Natural gas – Analysis of biomethane - Determination of ammonia content by *spectroscopic* methods

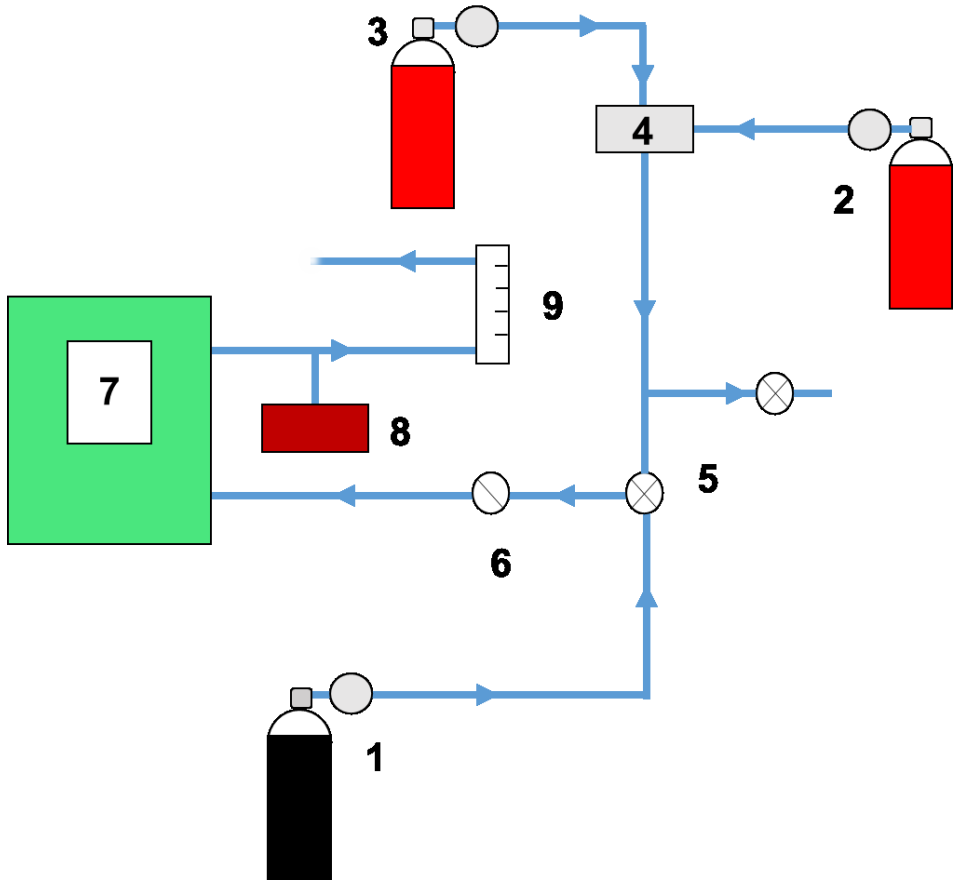
Structure:

- Introduction
- Scope
- Normative References
- Terms and Definitions
- Principle
- Apparatus
- Reagents and Materials
- Sampling
- Calibration
- Interferences
- Procedure
- Analysis
- Expression of Results
- Test Report

***Scope*:**

- NH_3 in biomethane specific test method
- Commercial spectroscopic NH_3 analysers – *black box* (independent of technique, more inclusive *e.g.* TDLS)
- Calibration and measurement of NH_3 @ EN 16723 specification
- Reference to existing ***natural gas*** (sampling), ***air quality*** measurement (analyser characterisation) and ***gas metrology*** (calibration) standards

System Setup: Key Components



Key:

1. *N_2 purge gas cylinder + regulator*
2. *High purity CH_4 cylinder + regulator*
3. *Parent reference gas mixture + regulator*
4. *Dilution system (+ flow controller)*
5. *Open/Close Ball valve*
6. *Needle valve*
7. *NH_3 analyser*
8. *Pressure sensor*
9. *Rotameter/Flow meter*

Sampling: Ammonia in Biomethane

NWIP focus: Cylinder sampling; Safety and Quality Considerations – Refer to ISO 10715

Pressurised Gas: Regulators, system pressure rating

Methane: Flammable mixtures in air – Inert O_2 free purge gas

Ammonia: Toxic – *OEL = 36 mg/m³ (50 ppm) Long term, 14 mg/m³ (20 ppm) Short term (ECHA)*

Adsorptive – *material construction of wetted surfaces important**

Corrosive – *maintain dry system + use corrosive resistant materials*

Flow Control: Purge/passivation of system – *trace NH_3 is slow to stabilise*

Impurities (other than NH_3): Interfering absorbers – *check with analyser manufacturer*

Matrix Gas: *Calibration gas must match sample gas* e.g. *Biogas* vs *Biomethane*

*Vaittinen, O., Metsälä, M., Persijn, S. et al. **Adsorption of ammonia on treated stainless steel and polymer surfaces**. *Appl. Phys. B* 115, 185–196 (2014). https://doi.org/10.1007/s00340-013-5590-3 (Note: NH_3 in N_2)

Calibration

- Perform a multipoint calibration when:
  - the analyser is first installed;
  - the *measurement system* has had maintenance that could affect its response characteristics;
  - the analyser shows drift in excess of performance specifications as determined via comparison with a calibration standard.

Calibration Strategies:

Multiple reference standards:

- Use a series of reference standards over the desired range of interest
- Should be in accordance with ISO 10723

Dynamic dilution system:

- Reference standard + CH_4 diluent
- Should be in accordance with ISO 6145

Materials

- Calibrations gases traceable to a national standard, certified in accordance with ISO 6142, ISO 6143 or ISO 6144.
- Diluent + zero gas (for dynamic calibration only), ≥99.999 % CH_4
- Purge gas (≥99.999 % N_2)

Summary and Concluding Remarks

- Need for standardised test methods for measuring NH_3 in biomethane
- EMPIR 16ENG05 Biomethane – providing measurement infrastructure for industry
- NWIP method selection: **OFCEAS** and **UV/vis**
- Different techniques suitable – standard method open to *spectroscopic* NH_3 analysers
- Existing tools from natural gas, air quality measurement + gas metrology standards

Thank you for your attendance

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