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METROLOGY FOR BIOMETHANE

NWIP - Biogenic carbon fraction fuel gases containing methane

(16ENG05-WP3.7)

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Outline

- Method biogenic carbon fraction
- Biomethane project
- Conclusions and recommendations for NWIP & ISO-standard

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Method requirements

- Suitable for fuel gases containing methane
- Distinguish between carbon from renewable materials and fossil materials
- Including all hydrocarbons in the fuel gas
- Quantify range 0 - 100% biogenic carbon

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Methods available

- Stable Isotope Method: ^{2}H and ^{13}C in CH_4
  - Limited in use
  - Limited in selectivity
  - Limited in quantification ability

→ Not suitable for unknown samples

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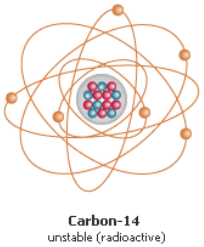
Methods available



- Radiocarbon (^{14}C) method
  - All fuel gases (with carbon)
  - High selectivity
  - Quantification within ±3% biogenic carbon

→ Suitable for NWIP/ISO-standard

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Principle ^{14}C method

Renewable materials: ^{14}C value similar to recent atmospheric $^{14}CO_2$ values

Fossil materials: No ^{14}C anymore due to radioactive decay over millions of years

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^{14}C-based biogenic carbon fraction

$$f_{bioC} = {}^{14}C_{sample} / {}^{14}C_{bioC}$$

Measurement range: 1.5% – 100% biogenic carbon

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^{14}C measurement

Since 1950s

Pretreatment sample material to pure CO_2, C or benzene

Current measurement techniques (natural level):

- Accelerator Mass Spectrometer (AMS) → Counting ^{14}C atoms (C or CO_2)
- Liquid scintillation counter (LSC) → Counting decay events (benzene)

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Existing standards

- ✓ Bio-based products: ASTM D6866 and CEN/TS 16640

- ✓ Waste (SRF): CEN/TS 15440-2
- ✓ Flue gas CO_2: ISO 13833
- ✓ Plastics: ISO 16620-2
- ✓ Rubber: ISO 19984-2

→ No standard is entirely suitable for fuel gases

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Biomethane project

- ^{14}C-based test method for fuel gases containing methane
- Inter-Laboratory Comparison for ^{14}C labs

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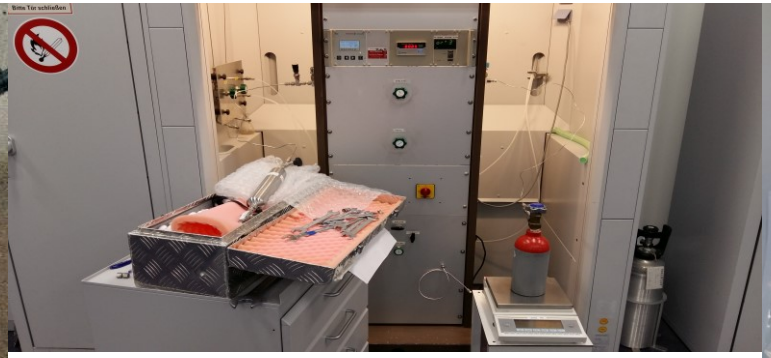
Inter-Laboratory Comparison

- Five European ^{14}C AMS labs
- Set of five samples: 2 biogas and 3 biogas-natural gas blends (45%, 75% and 95% biogenic carbon)



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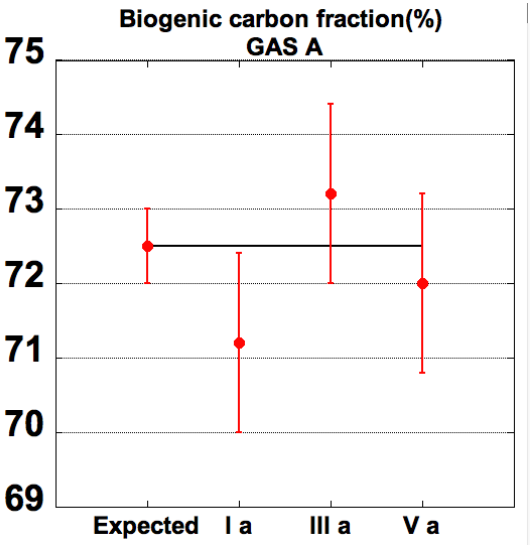
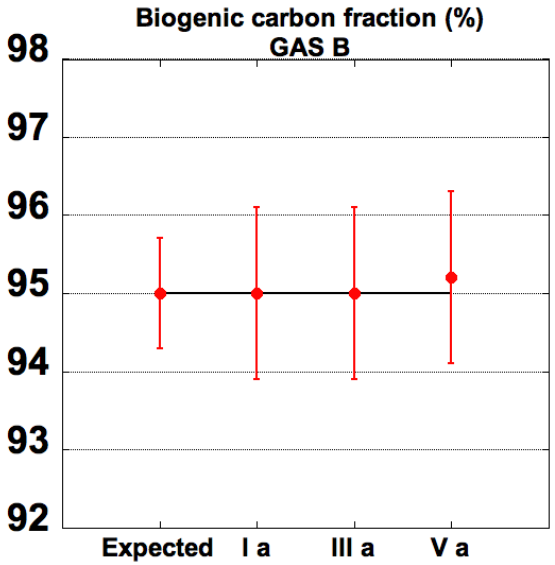
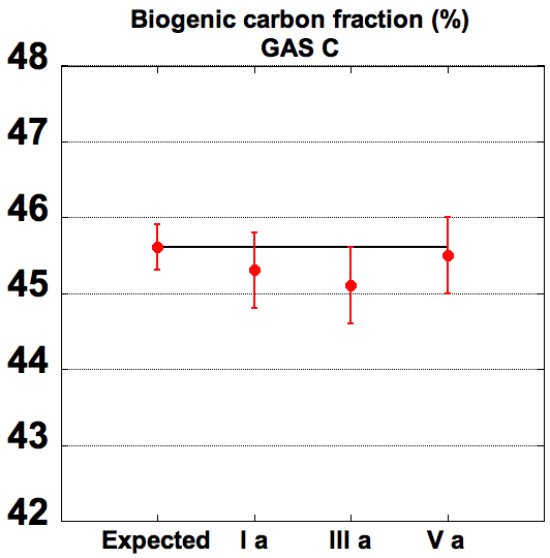
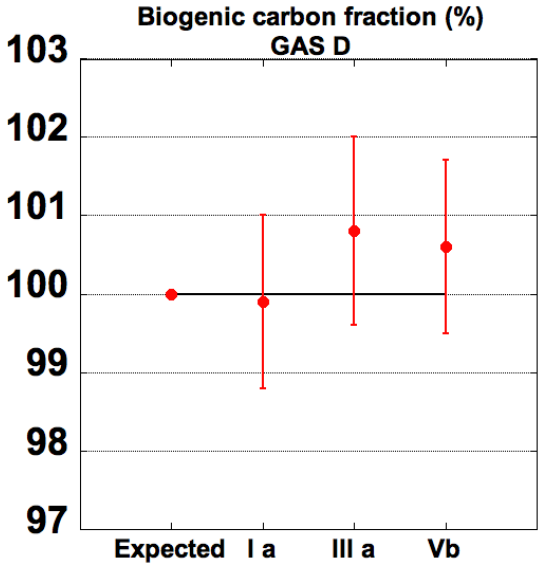
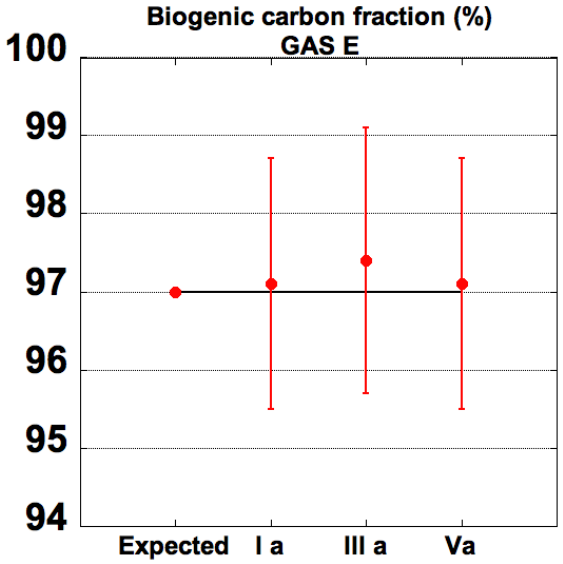
Results (all carbon included)











Results match within 1.5% with expected values

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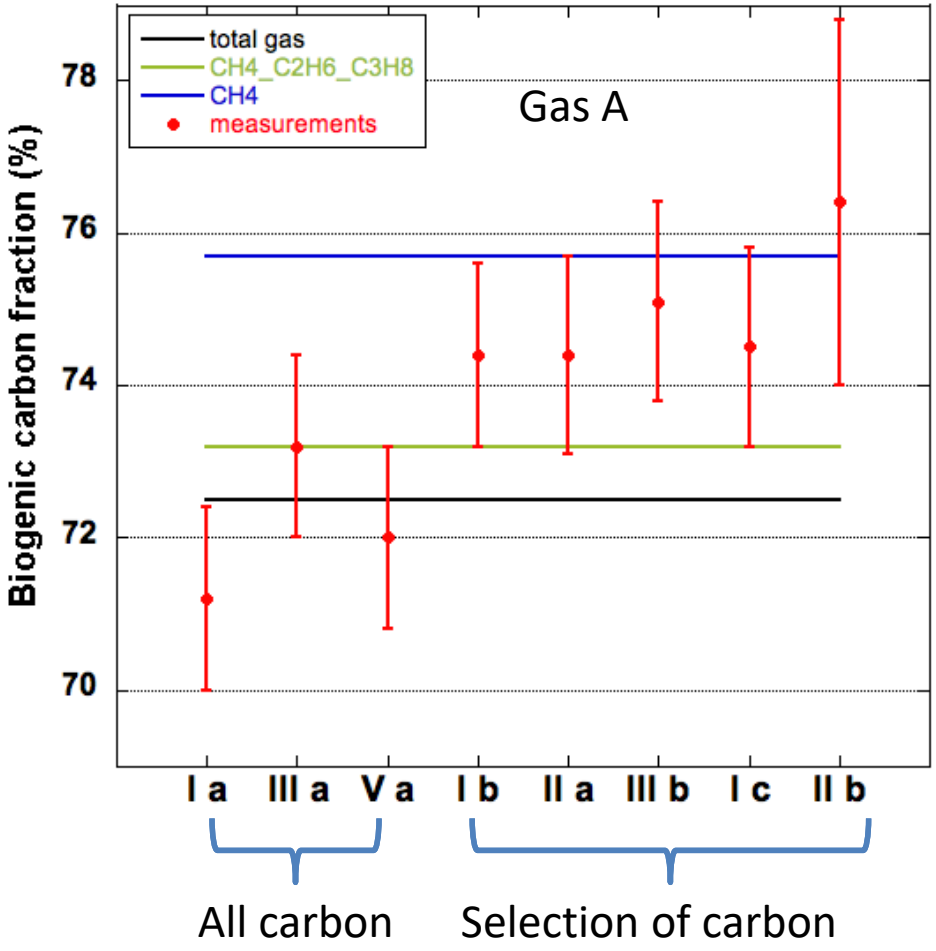
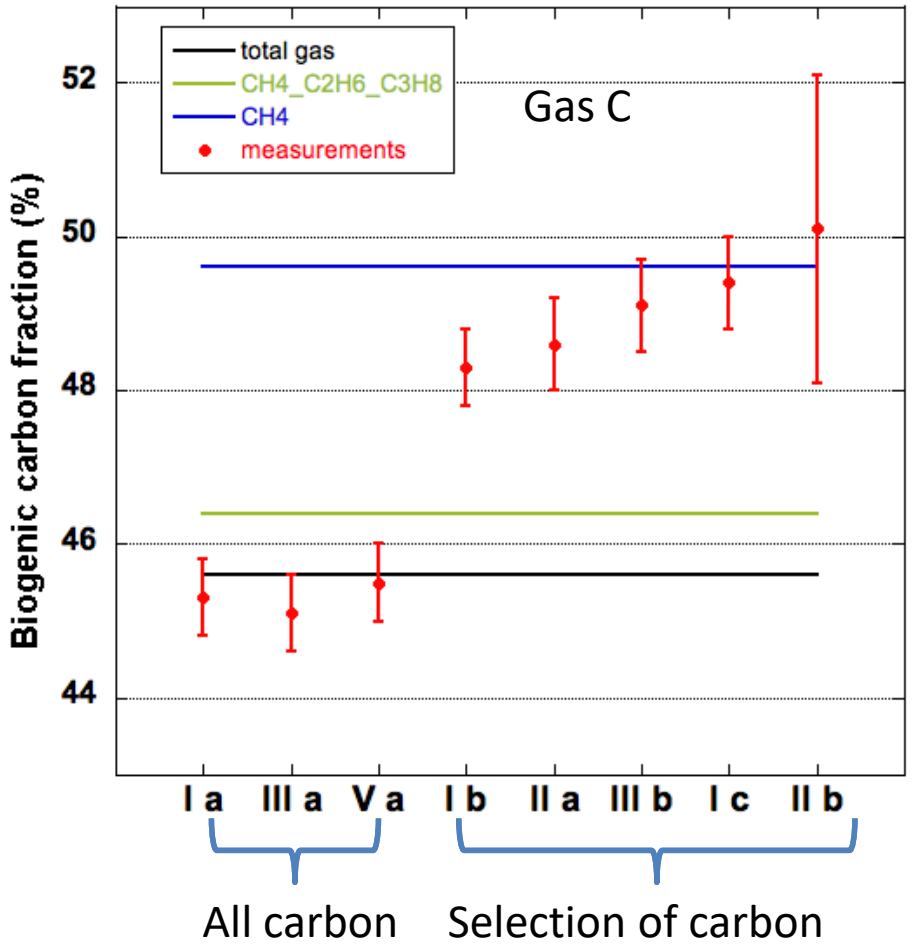
Results (all preparation methods incl. CH_4)





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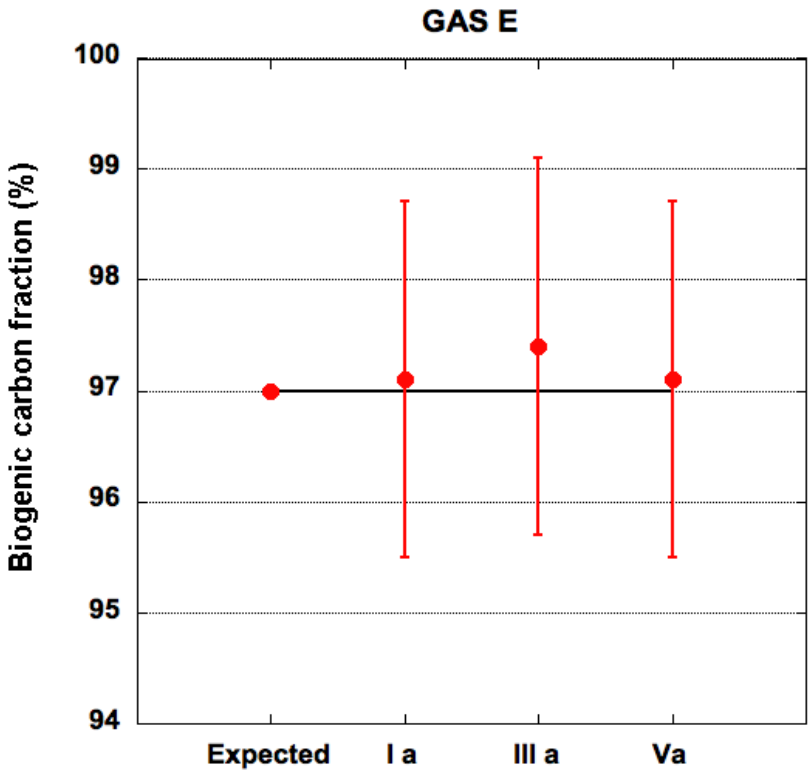
Alternative first check 100% biogas



GAS E = 'biogas' = expected 100% biogenic carbon
Measured: 97%

Gas E contained 2.5% of hydrocarbons (other than CH_4) → natural gas

→ The appearance of other hydrocarbons than CH_4 can <u>in some cases</u> reveal the presence of natural gas in biogas

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Main conclusions

- Very reliable and accurate (max. ±2%) method for fuel gases containing methane or methane and other hydrocarbons
- Sample preparation methods should include all carbon fractions present in sample

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NWIP and ISO standard

Test method for ^{14}C-based verification of biogas, biomethane, mixtures of natural gas with unconventional gases and renewable gases.

Also applicable for other fuel gases containing one hydrocarbon, mixtures of hydrocarbons or hydrocarbons mixed with CO_2 and/or CO.

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Main recommendations

- Labs can use their own sample preparation and ^{14}C measurement techniques as long as:
  - Sample preparation methods select all carbon
  - Lab methods are verified with reference gases

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Project output

- Report of WP 3.7, 16ENG05 Metrology for Biomethane': "Test method (^{14}C-based) for the biogenic carbon fraction in biomethane/biogas and in blends of biomethane/biogas and natural gas"
- NWIP: Analysis of natural gas – Determination of the biogenic carbon fraction – Radiocarbon (^{14}C) method
- Draft ISO-standard. Based on report WP3.7 and its recommendations.
- Peer-reviewed paper (to be submitted)

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Questions?

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