VSL

Dutch Metrology Institute

Welcome to session 2: siloxanes content

Joint Workshop of the consortium of “Metrology for biomethane” and ISO/TC193/SC1/WG25 Biomethane

Tuesday 08 September 2020

Topics

1. NWIP for total silicon concentration (IMBiH)
2. NWIP for siloxanes (NPL)
3. NWIP for halogenated VOCs (VSL + INERIS + RISE)
4. NWIP for HCl + HF (wet chemistry) (INERIS + ISSI)
5. NWIP for ammonia (NPL + VSL + RICE)
6. NWIP for terpenes (RICE + RISE + NPL)
7. NWIP for compressor oil concentration (RISE + INERIS)
8. NWIP for amines concentration (RICE + VSL)
9. NWIP for biogenic methane fraction (RUG)

Workshop objectives

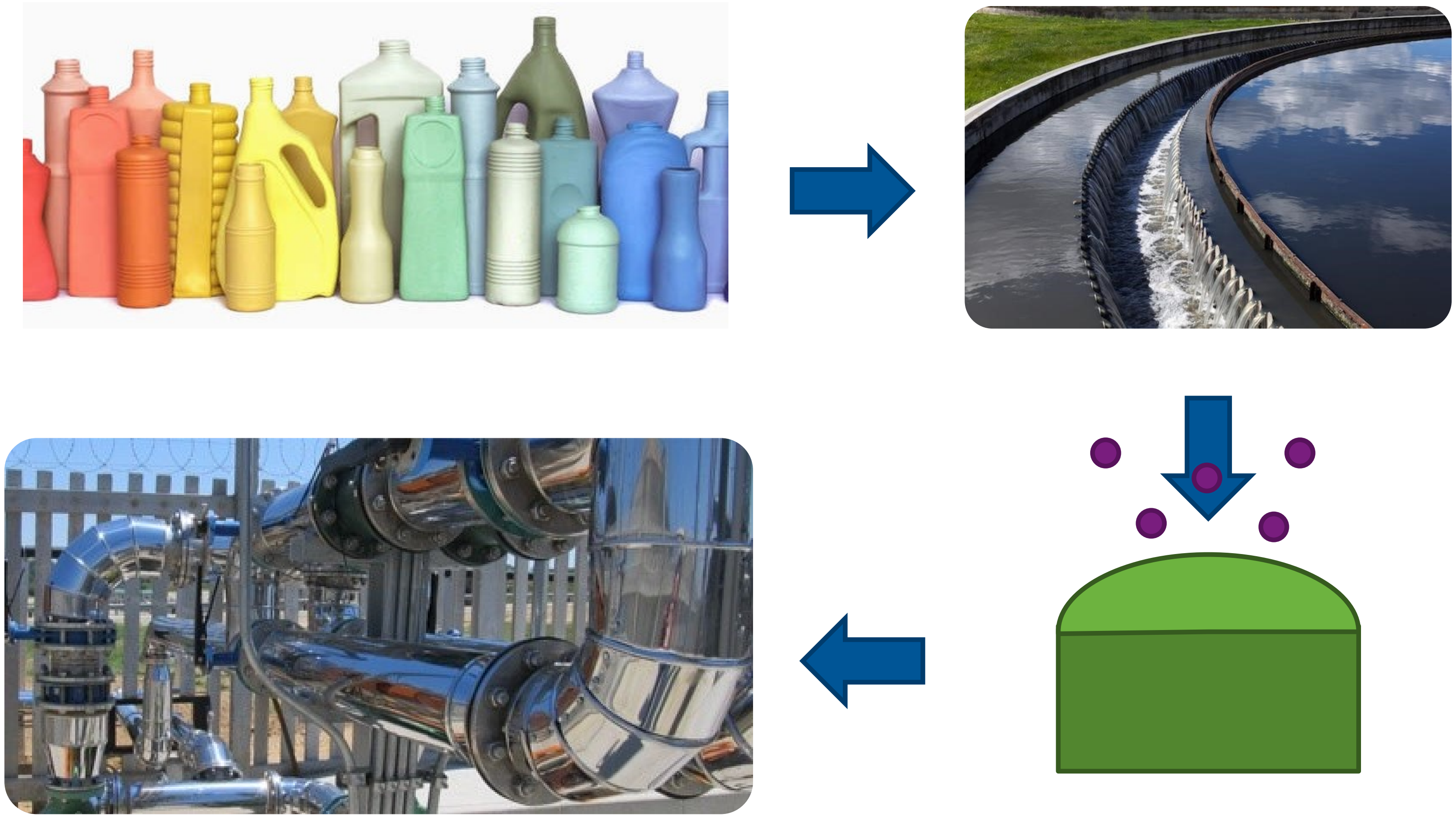
- Presentation of the methods developed in “Metrology for Biomethane” (EMPIR, 16ENG05) in support of the biomethane specification EN 16723
- Presentation of the validation performed on the methods
- Q&A on the project outcomes
  - Ask questions using the “chat” function in MS Teams
  - You can post your questions any time during the presentation
  - After the presentation, the questions will be addressed
- Sessions are recorded for developing records from the meeting; they will not be made public
- Presentations will be made available on the workshop website

Development of a standardised test method for siloxanes in biomethane

Lucy Culleton
Senior Research Scientist, NPL

16ENG05 Final Workshop, 8th September 2020, virtual meeting

Need for a NWIP



Need for a NWIP

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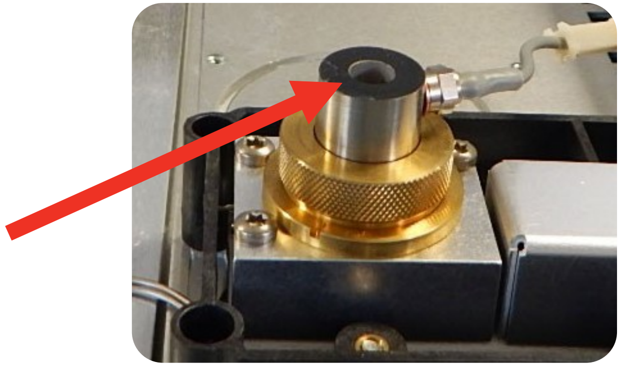

METROLOGY FOR BIOMETHANE

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EN 16723-1
EN 16723-2

Parameter	EN 16723-1	EN 16723-2
Silicon concentration	≤ 0.3 to 1 mg/m^3	≤ 0.5 mg/m^3
Hydrogen fraction	See EN 16726	≤ 2 %
Hydrocarbon dew point	See EN 16726	≤ -2 °C
Oxygen fraction	See EN 16726	≤ 1 %
Sulphur concentration	≤ 20 mg/m^3	≤ 5 mg/m^3
Methane number	See EN 16726	≥ 65 (80 for high grade)
Compressor oil content	“de deminis”	“de deminis”
Dust impurities	“de deminis”	≤ 10 mg/L
Amines content	≤ 10 mg/m^3	≤ 10 mg/m^3
Water dew point	See EN 16726	≤ -10 °C
Chloride concentration	“de deminis”	
Fluoride concentration	“de deminis”	
Carbon monoxide fraction	≤ 0.1 %	
Ammonia concentration	≤ 10 mg/m^3	

METROLOGY FOR BIOMETHANE

Siloxanes work within METROLOGY FOR BIOMETHANE project

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Aim

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

Traceable gas standards + Validated measurement methods

Partners:

NPL National Physical Laboratory

VSL

INNOVHUB STAZIONI SPERIMENTALI PER L'INDUSTRIA – Innovazione e ricerca

IMBIH

WAVERTON Analytics

METROLOGY FOR BIOMETHANE

NWIP – siloxanes

Analysis of natural gas — Biomethane — Determination of siloxane content by Gas Chromatography Ion Mobility Spectrometry

- GC-IMS technique
- Suitable for measurement at EN 16723-1 & EN 16723-2 levels
- Applicable to laboratory and field analysis

Scope

Application range:

Component	Abbreviation	Formula	Lower limit (mg m^{-3})	Upper limit (mg m^{-3})
hexamethyldisiloxane	L2	$C_6H_{18}Si_2O$	0.1	10.0
octamethyltrisiloxane	L3	$C_8H_{24}Si_3O_2$	0.1	10.0
decamethyltetrasiloxane	L4	$C_{10}H_{30}Si_4O_3$	0.1	10.0
dodecamethylpentasiloxane	L5	$C_{12}H_{36}Si_5O_4$	0.1	10.0
hexamethylcyclotrisiloxane	D3	$C_{12}H_{18}O_3Si_3$	0.1	10.0
octamethylcyclotetrasiloxane	D4	$C_8H_{24}O_4Si_4$	0.1	10.0
octamethylcyclotetrasiloxane	D5	$C_{10}H_{30}O_5Si_5$	0.1	10.0
dodecamethylcyclohexasiloxane	D6	$C_{12}H_{36}O_6Si_6$	0.3	10.0

(EN 16723 lower limit specifications are between 0.3 – 1 mg/m^{-3})

Example instrument for application

A GC-IMS instrument tested within the project

- Linearity
- Trueness
- Repeatability
- Within-lab reproducibility
- Limit of detection
- Selectivity and interferences

Siloxanes tested: L2, L3, D4 and D5

Note on L3 measurement

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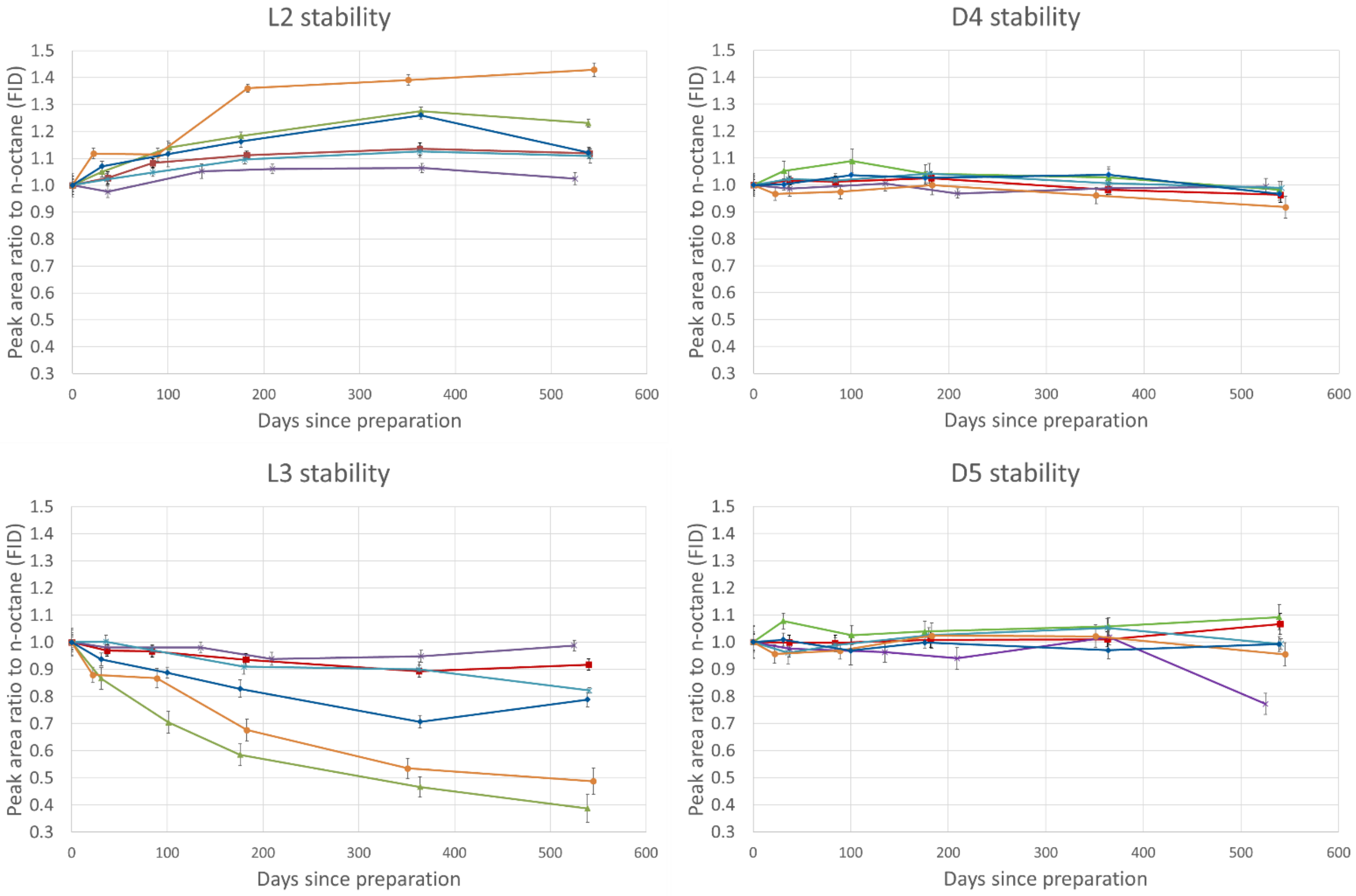
- L3 instability noted in certain vessel types

Stability of siloxanes in different vessel types



Agreement between static & dynamic standards

	ppm-level		ppb-level	
Component	**Relative difference in response factor (NPL 3882 vs 40.4 x dilution of NPL 3894)**	**Expended uncertainty of measurement (*k* = 2)**	**Relative difference in response factor (NPL 3875 vs 161.8 x dilution of NPL 3894)**	**Expended uncertainty of measurement (*k* = 2)**
L2	0.33 %	1.45 %	5.58 %	1.87 %
L3	0.37 %	1.49 %	-40.58 %	2.11 %
D4	0.10 %	1.66 %	0.96 %	2.14 %
D5	-1.07 %	6.09 %	-3.86 %	4.39 %

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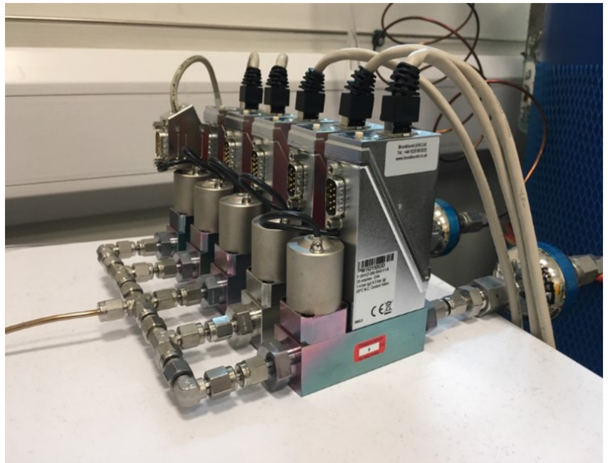
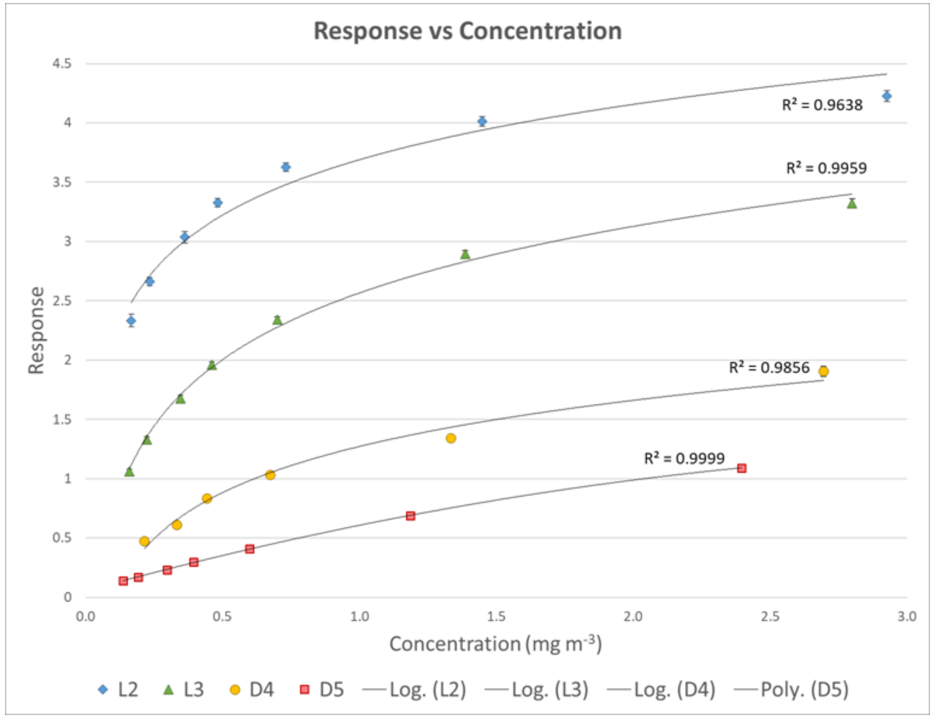
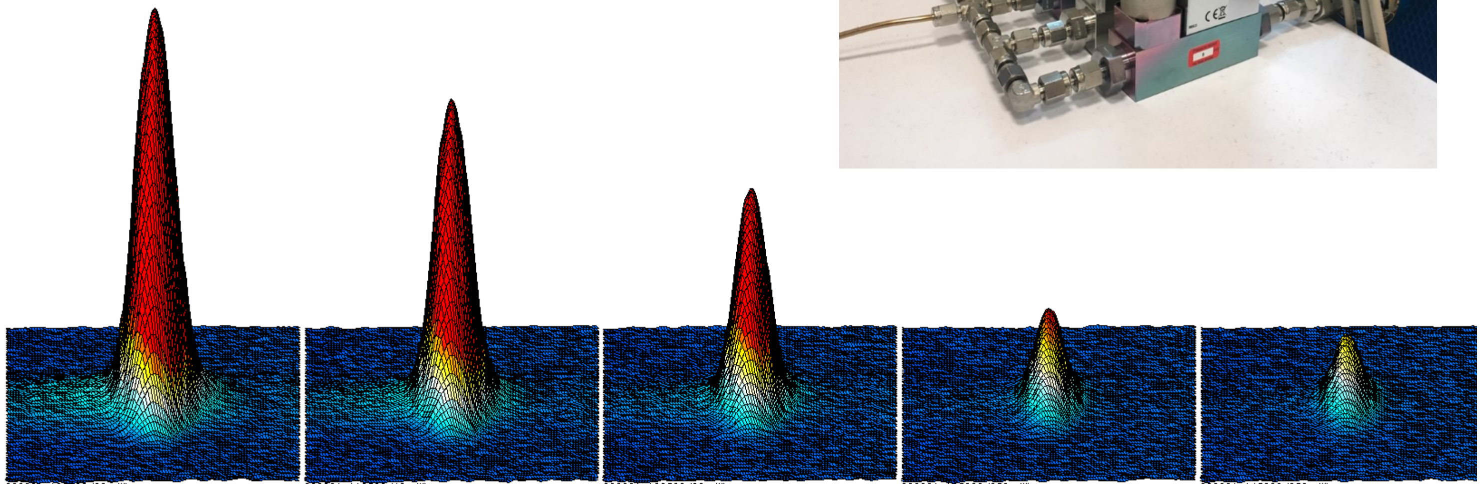
Linearity

- Dynamic system used to generate multiple calibration points
- Important to calibrate over whole range of interest if response is non-linear







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Trueness

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$$\Delta_m = |c_m - c_{ref}|$$

where:

Δ_m absolute difference between the mean measured value and the reference value from NPL

c_m the mean measured value

c_{ref} the gravimetric standard reference value

- L2, L3 and D4 agreed within 14% of the gravimetric values, which was within the uncertainty of the measurements.
- D5 over-reporting observed. Thought to be due to adsorption effects.
- Dynamic measurement standards may be required for quantifying low level (ppb) L3, due to stability effects in certain cylinder types

Repeatability & Reproducibility

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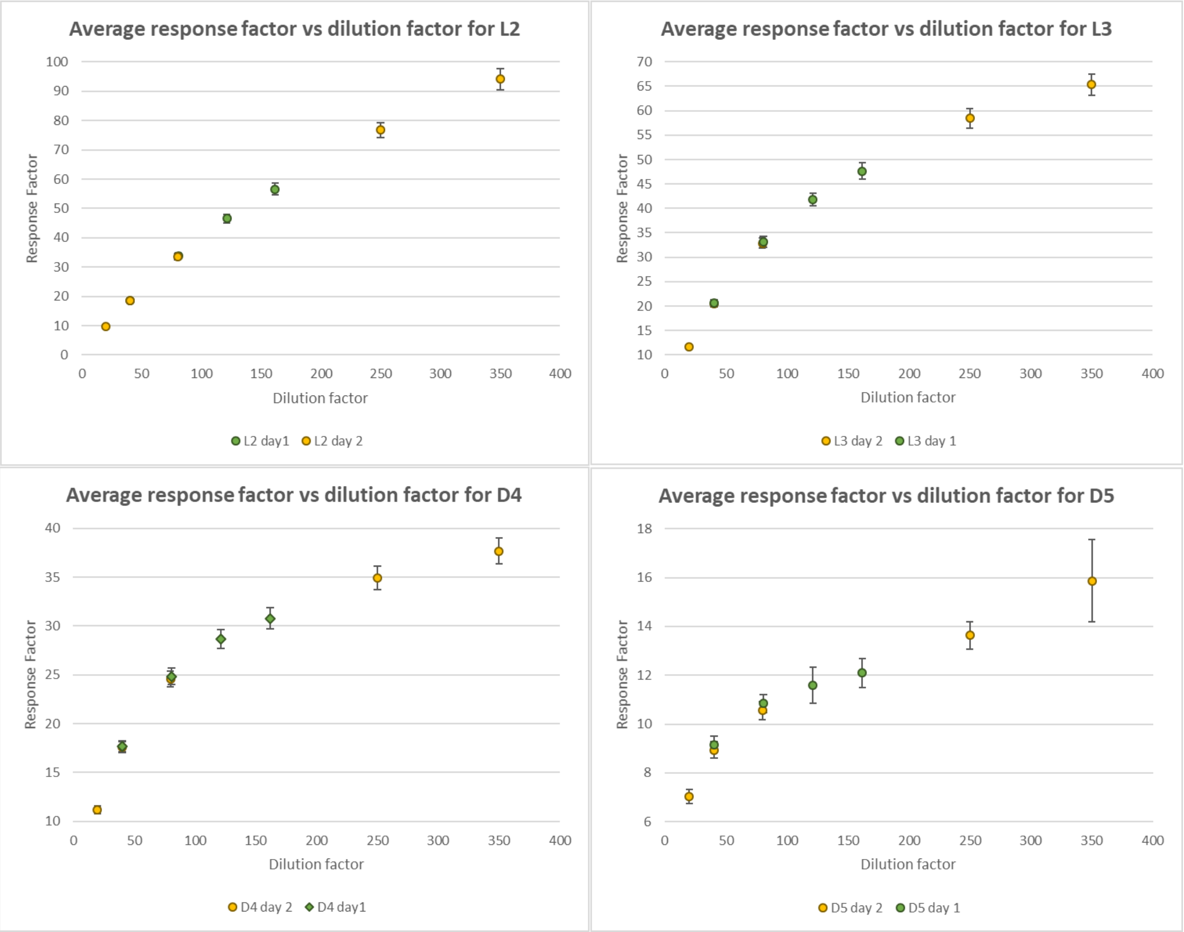
- Repeatability <3% for all.
- D5 higher value due to adsorption effects

Component:	L2	L3	D4	D5
NPL 3882 s(r) (%)	0.11	0.12	0.20	2.54
NPL 3875 s(r) (%)	0.11	0.38	0.24	0.66

- Method found to be reproduceable <7% for all siloxanes tested

Component:	L2	L3	D4	D5
NPL 3875 RF difference (%)	0.42	-6.46	-1.22	-0.78
NPL 3882 RF difference (%)	0.47	0.10	-0.43	-0.64



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Limit of detection

- Dynamic system used for total Si for measurement.
- Blanks ran using N6.0 methane.
- Limit of detection found to be below the specified EN 16723 levels (0.3 – 1 mg/m^3).

350 x dilution of NPL 3894	L2	L3	D4	D5	Total silicon (based on D5 value)
LOD (nmol mol^{-1})	12.58	8.33	4.35	1.71	0.63
U_Δ (nmol mol^{-1})	3.22	1.69	1.87	0.74	0.27

Total Si LOD is equivalent to 0.28 mg/m^3).

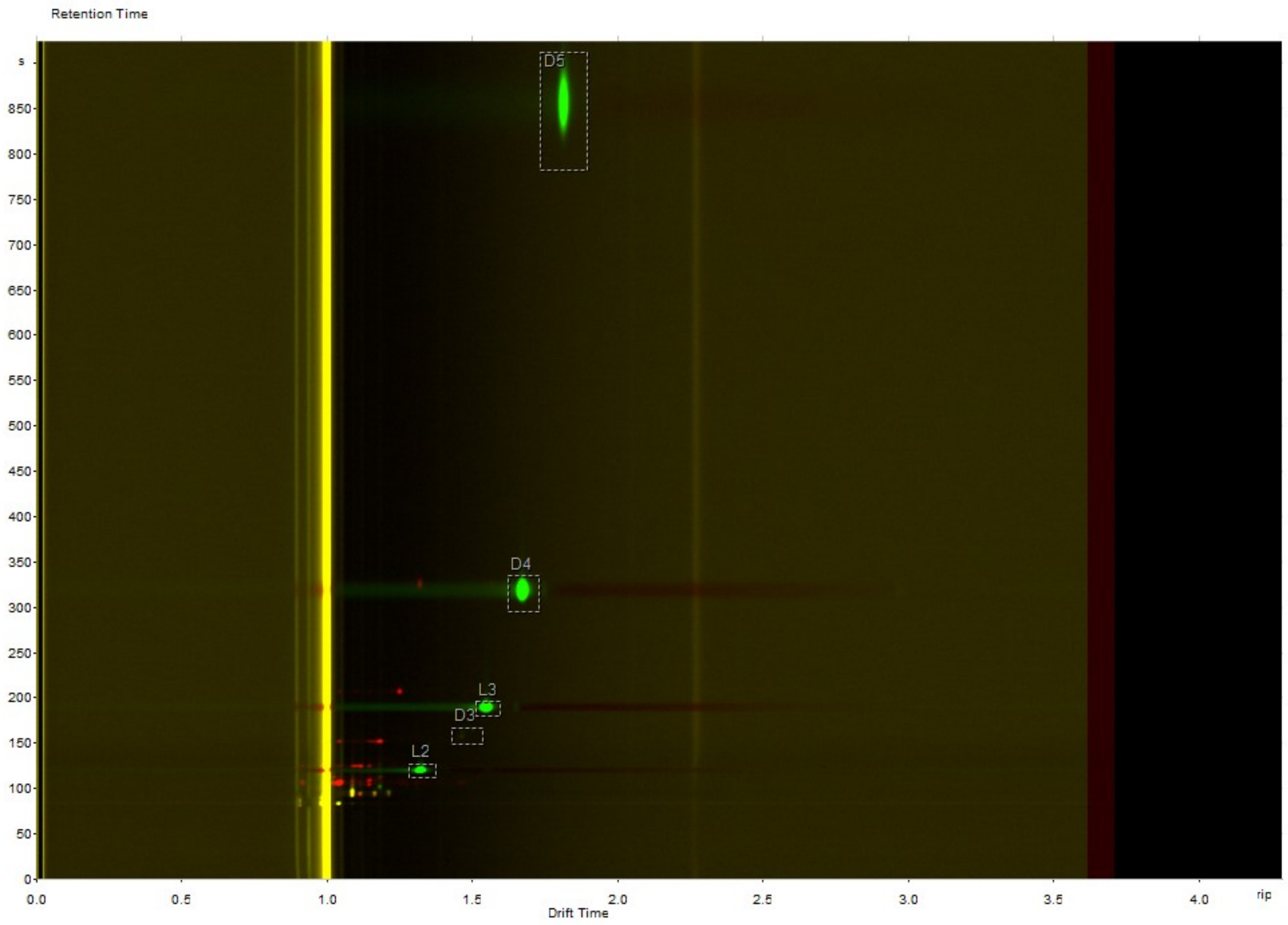
METROLOGY FOR BIOMETHANE

Interferences

- Two mixture types tested

Component	Amount fraction (µmol mol^{-1})	
	Mixture 4: NPL A431	Mixture 5: NPL 2059
n-hexane	983.6	-
n-heptane	100.7	-
n-octane	37.8	-
n-nonane	10.5	-
n-decane	5.8	-
Hydrogen sulphide	-	151.4
Ethyl methyl sulphide	-	103.3
Ethyl methyl sulphide	-	102.1
Dimethyl sulphide	-	102.0
Methanethiol	-	100.4
Ethanethiol	-	98.4
Carbonyl sulphide	-	98.2
2-propanethiol	-	98.1
Diethyl sulphide	-	96.1
Balance	Methane	Methane

GC-IMS chromatogram of a C6-C10 hydrocarbon mixture, NPL A431 (red) overlaid with a siloxane mixture NPL3894: 20 x dilution (green).

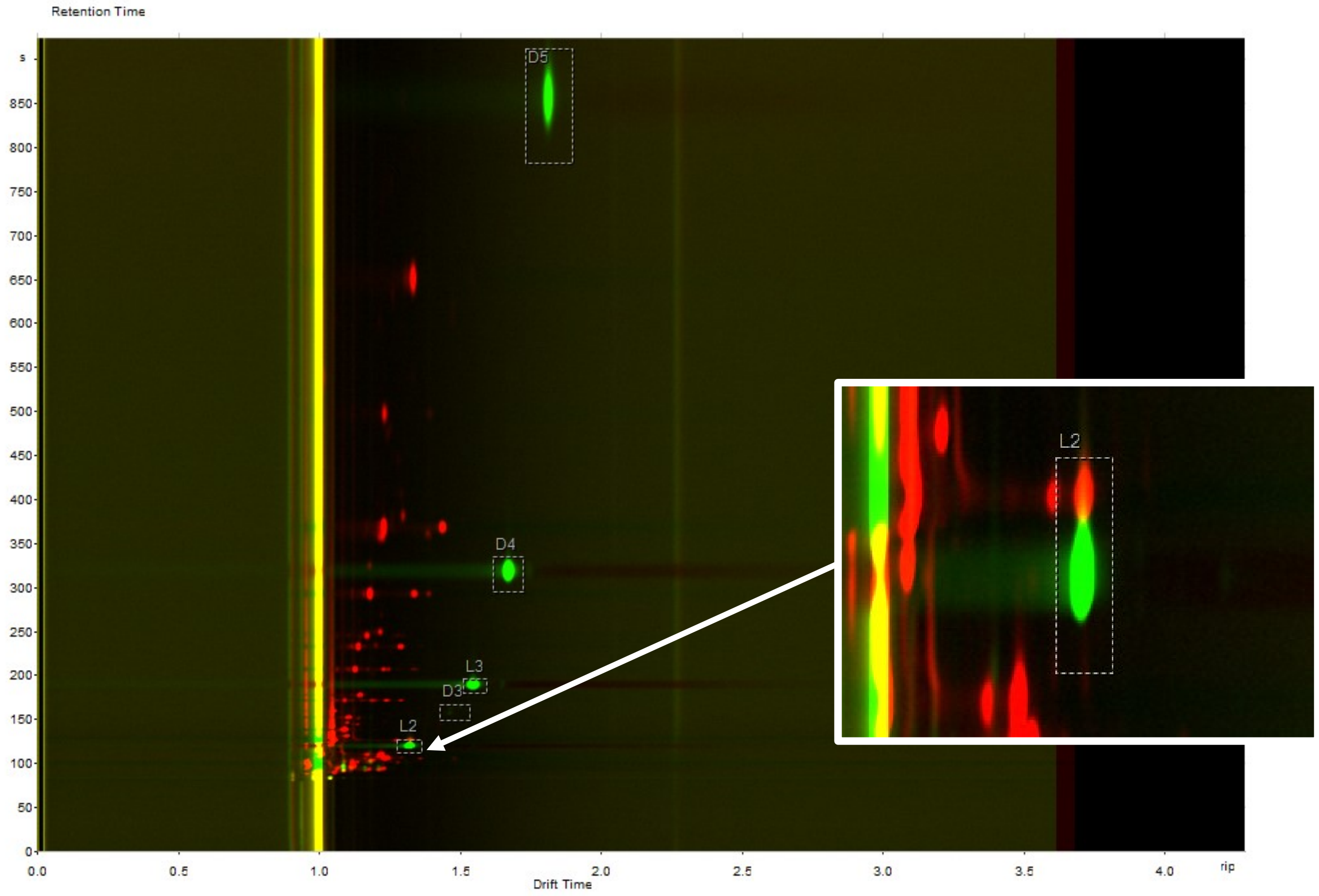


Interferences

- Interference noted with sulphur compound

Component	Amount fraction (µmol mol^{-1})	
	Mixture 4: NPL A431	Mixture 5: NPL 2059
n-hexane	983.6	-
n-heptane	100.7	-
n-octane	37.8	-
n-nonane	10.5	-
n-decane	5.8	-
Hydrogen sulphide	-	151.4
Ethyl methyl sulphide	-	103.3
Ethyl methyl sulphide	-	102.1
Dimethyl sulphide	-	102.0
Methanethiol	-	100.4
Ethanethiol	-	98.4
Carbonyl sulphide	-	98.2
2-propanethiol	-	98.1
Diethyl sulphide	-	96.1
Balance	Methane	Methane

GC-IMS chromatogram of an odorant mixture, NPL 2059 (red) overlaid with a siloxane mixture NPL3894: 20 x dilution (green).

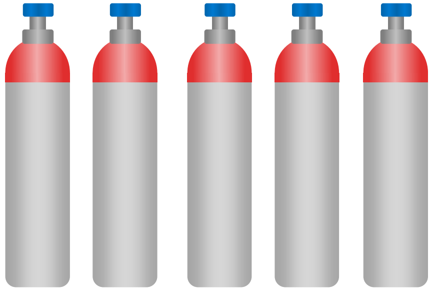


ISO standard - overview

The following slides give an overview of items within the proposed ISO standard

Materials

- Calibrations gases traceable to a national standard, certified in accordance with ISO 6142, ISO 6143 or ISO 6144.



- Diluent gas (for dynamic calibration only), ≥99.999 % CH_4

- Carrier & drift gas (≥99.999 % N_2)

Apparatus

- GC-IMS analyser
- Pressure regulator
- Auxilary valves, tubing & accessories

Sampling (refer also to ISO 10715)

- Siloxanes are highly adsorptive
- Sampling considerations should be of high importance

- Temperature should be controlled to prevent condensation of samples and calibration gases

- Appropriate sampling materials should be used

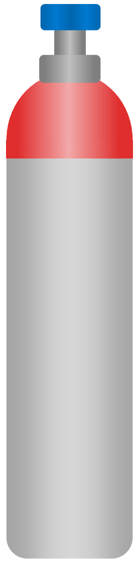
- Connections should be kept clean (free of debris and contaminants)

Sampling into vessels

- Appropriate for use when biomethane is at or above atmospheric pressure
- Source temperature can be greater or less than sample container.
- Use of evacuated vessel (e.g. gas cylinder or sample cannister)
- Wetted surfaces should be of appropriate material or passivation to prevent adsorption

Installing the calibration gas cylinder

- Minimise flow path surface area by installing close to the analyser
- Minimise number of connections



Pressure control

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- May require sample pump is sample pressure is close to atmospheric
- Ensure pressure regulators are of appropriate material & passivation
- Do not use a calibration mixture below the stated certificate pressure
- Use the same injection pressure for both sample and standard

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Purging of wetted flow path

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- Important to ensure accurate results are achieved for siloxane analysis
- Minimum number of “Fill & empty” cycles or continuous flow required
- Additional purging required if switching from high to low siloxane content

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Flow & diffusion control

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- Flow rate recommended to be between 20 ml min^{-1} and 50 ml min^{-1} (Based on 1/8 in or 1/4 in tubing)
- Sample pump can be used to achieve this
- Non-permeable membranes in pressure regulators
- Be aware of diffusion of humidity through certain polymer materials

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Calibration

- Perform a multipoint calibration when:
  - the analyser is first installed;
  - the analyser 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

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

Procedure

- Follow safety precautions as recommended by manufacturer
- Perform quantitative analysis in accordance with ISO 6143

Conclusion

- GC-IMS is a suitable technique for performing quantitative analysis of siloxane content within biomethane.
- It is capable of achieving measurement within the EN 16723 total Si values.

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Department for
Business, Energy
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