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18SIP03: Improvement of the European quality infrastructure for the measurement of total silicon and sulphur content of biogas

Project workshop 24/11/2021

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National Physical Laboratory

Project overview

To improve the quality infrastructure for the measurement of total silicon and sulphur content of biogas

Round robin comparisons → Total silicon, Total sulphur

Knowledge transfer and trainings → Webinars and Workshop, Publications

Impact on Standardisation → ISO/TC193/SC1/WG25, EN 16723

- Standardisations
- Gas producers
- Gas grid operators
- Testing laboratories
- Instrument manufacturers
- Other end-users

Project objectives

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- To evaluate the measurement capability of industrial laboratories performing measurement of total silicon and total sulphur concentration in biomethane with traceable primary gas standards, and to publish the results in an industry publication or an open-access peer-reviewed journal.
- To disseminate knowledge outputs of EMRP project ENG54 Metrology for biogas in best practice sampling and analysis of total silicon and total sulphur concentration of biomethane to industrial analysis laboratories.
- To increase the awareness of standards EN 16723-1 and EN 16723-2 within the wider biogas and biomethane industry to support their wider uptake, and to provide input to ISO working group ISO/TC193/SC1/WG25 Biomethane.

Si and S content of BIOGAS

Compositions

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Siloxanes comparison

Table 1: Nominal ranges of amount-of-substance fractions

Component	Chemical formula	Mixture nominal amount fractions *x (mol/mol)*
Hexamethyldisiloxane (L2)	$C_6H_{18}OSi_2$	Between $(50 – 300) \cdot 10^{-9}$
Octamethylcyclotetrasiloxane (D4)	$C_8H_{24}O_4Si_4$	Between $(50 – 300) \cdot 10^{-9}$
Decamethylcyclopentasiloxane (D5)	$C_{10}H_{30}O_5Si_5$	Between $(50 – 300) \cdot 10^{-9}$
Methane	CH_4	Balance

Sulphur comparison

Component	Chemical formula	Mixture nominal amount fractions *x (mol/mol)*
Hydrogen sulphide	H_2S	Between $(1.0 – 10.0) \cdot 10^{-6}$
Carbonyl sulphide	COS	Between $(1.0 – 10.0) \cdot 10^{-6}$
Methyl mercaptan	CH_3SH	Between $(1.0 – 10.0) \cdot 10^{-6}$
Ethyl mercaptan	C_2H_5SH	Between $(1.0 – 10.0) \cdot 10^{-6}$
Tetrahydrothiophene (THT)	C_4H_8S	Between $(1.0 – 10.0) \cdot 10^{-6}$
Dimethyl sulphide (DMS)	CH_3SCH_3	Between $(1.0 – 10.0) \cdot 10^{-6}$
Diethyl sulphide (DES)	$(C_2H_5)_2S$	Between $(1.0 – 10.0) \cdot 10^{-6}$
Dimethyl disulphide (DMDS)	CH_3SSCH_3	Between $(1.0 – 10.0) \cdot 10^{-6}$
Methane	CH_4	Balance

Siloxanes in Biomethane

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European Commission

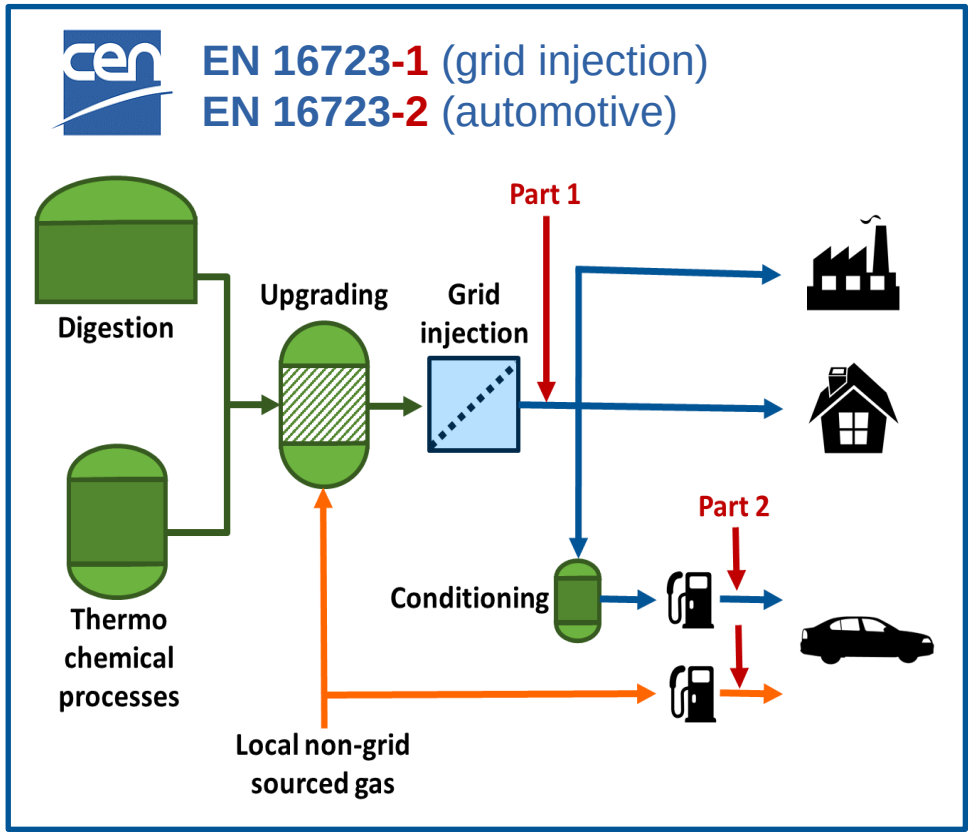
EC Mandate M/475

- 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



Si and S content of BIOGAS

Support for Impact Project

Total Silicon Round Robin

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

Si and S content of BIOGAS

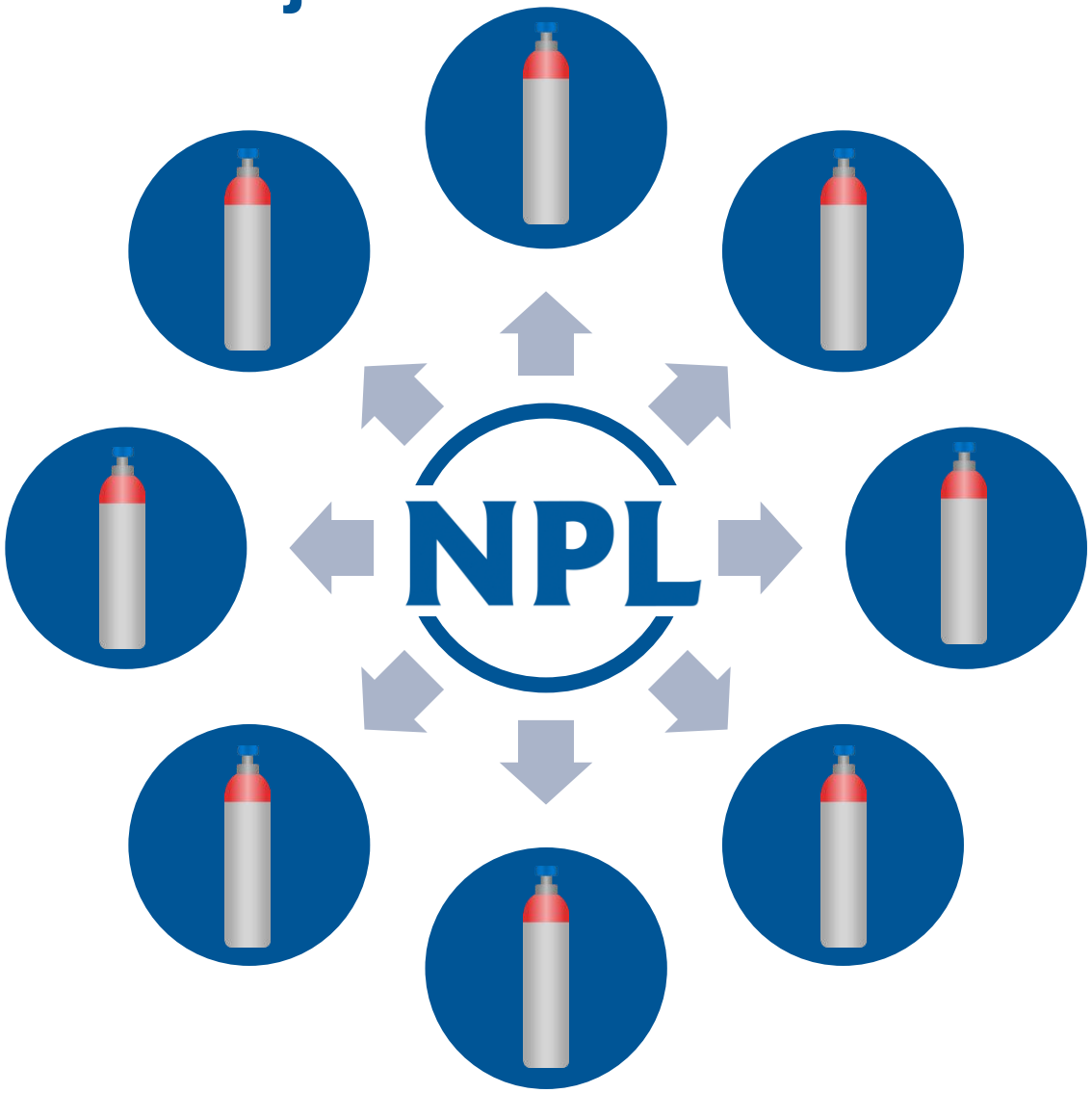
Support for Impact Project

NPL National Physical Laboratory

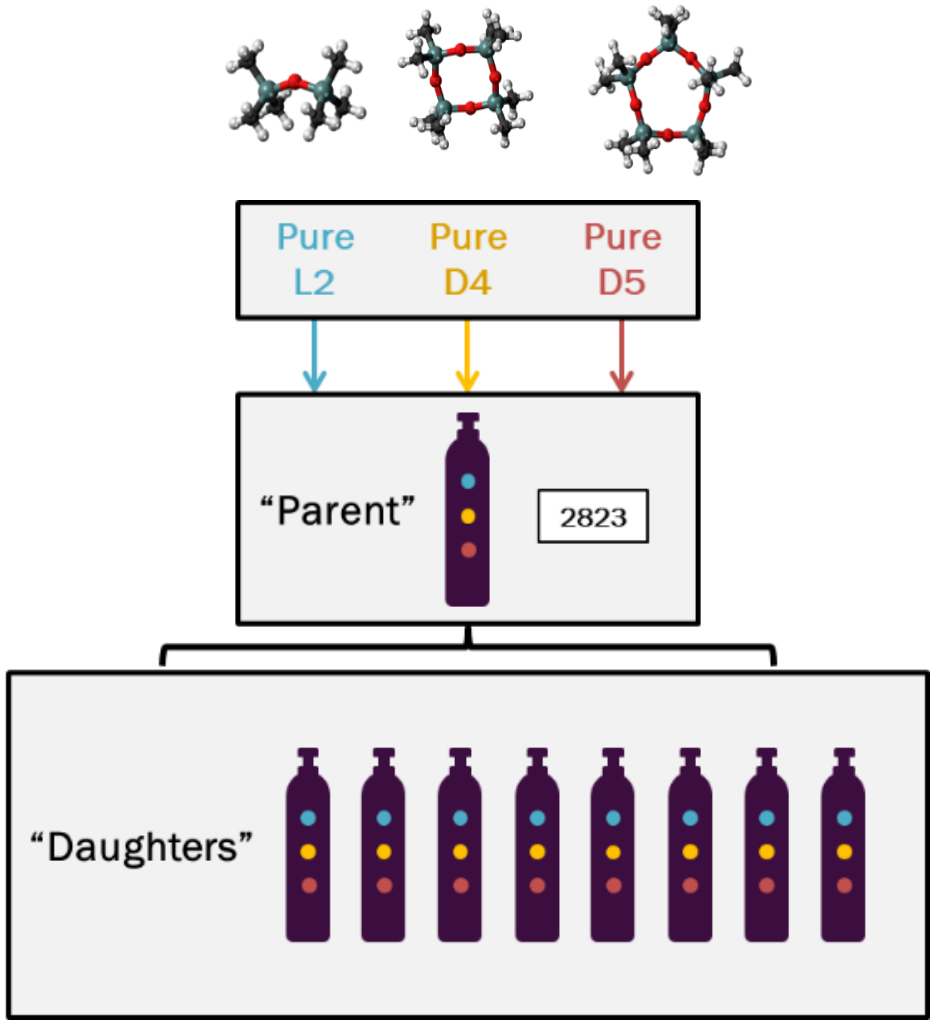
- The National Physical Laboratory has successfully established novel methods for **high accuracy** preparation and analysis of **traceable reference gas mixtures** containing siloxanes (L2, D4 and D5) in methane.

Support for Impact Project

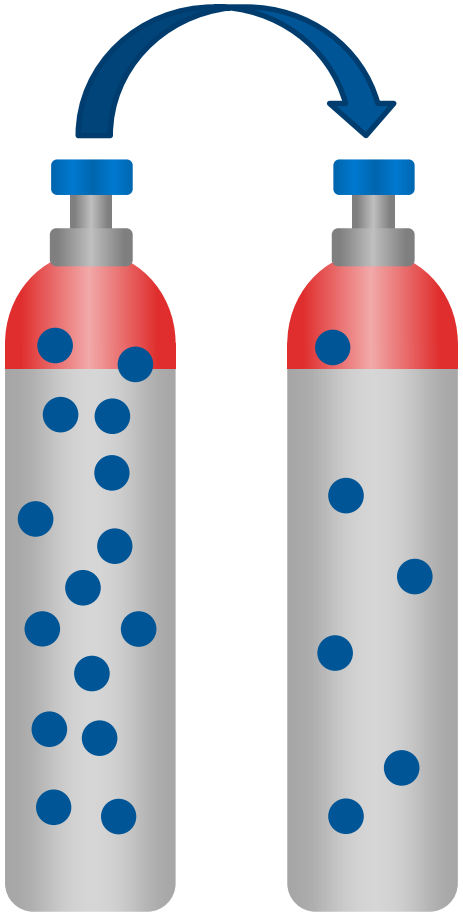
- 9 participating laboratories (including NPL)



Standard Preparation

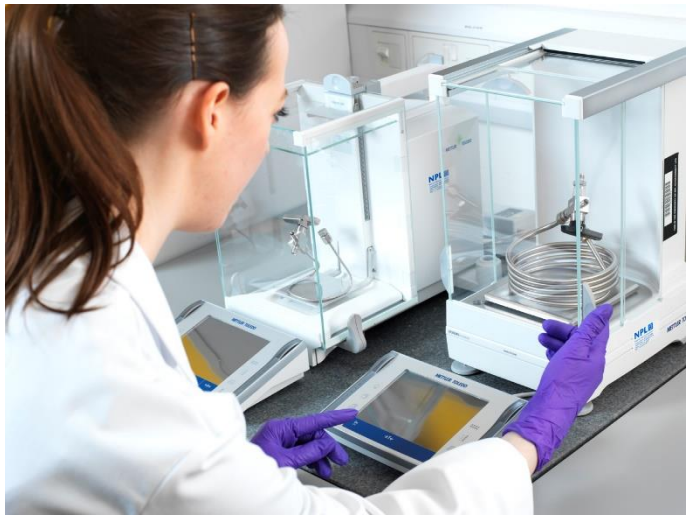


Gas standards prepared to a total silicon mass fraction of **1.5 mg/m³** via multi-stage dilution



Standard Preparation

- The gas mixtures were prepared by NPL in accordance with ISO 6142-1[3] (gravimetric method) in **high-pressure passivated cylinders**.

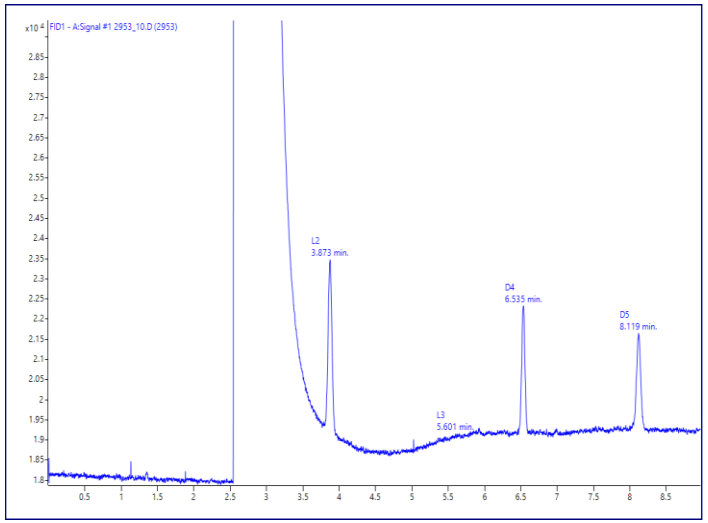


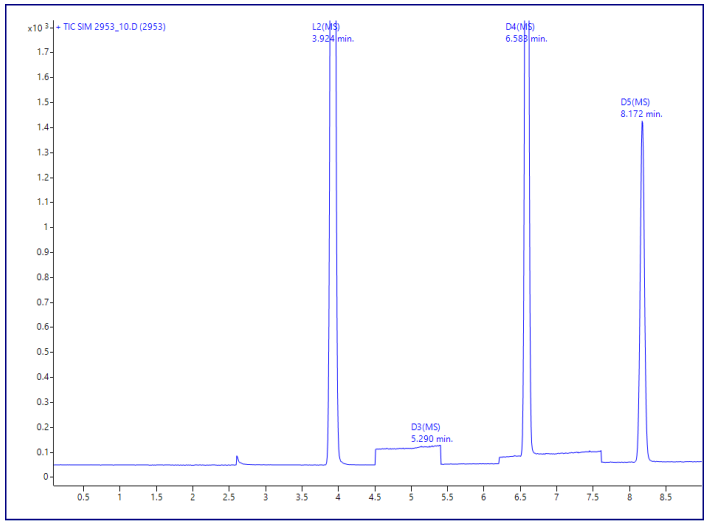
- Bespoke custom made '**micro-loops**' used to prepare a '**parent**' mixture from pure liquid siloxanes, which is diluted to the amount-of-substance fractions.

3 - International Organization for Standardization, "ISO 6142-1 Gas analysis - Gas analysis - Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures, ISO Geneva, 2015

Standard Validation

- The comparison mixtures were assigned a value in accordance with ISO 6143[4] using a **direct comparison method**.





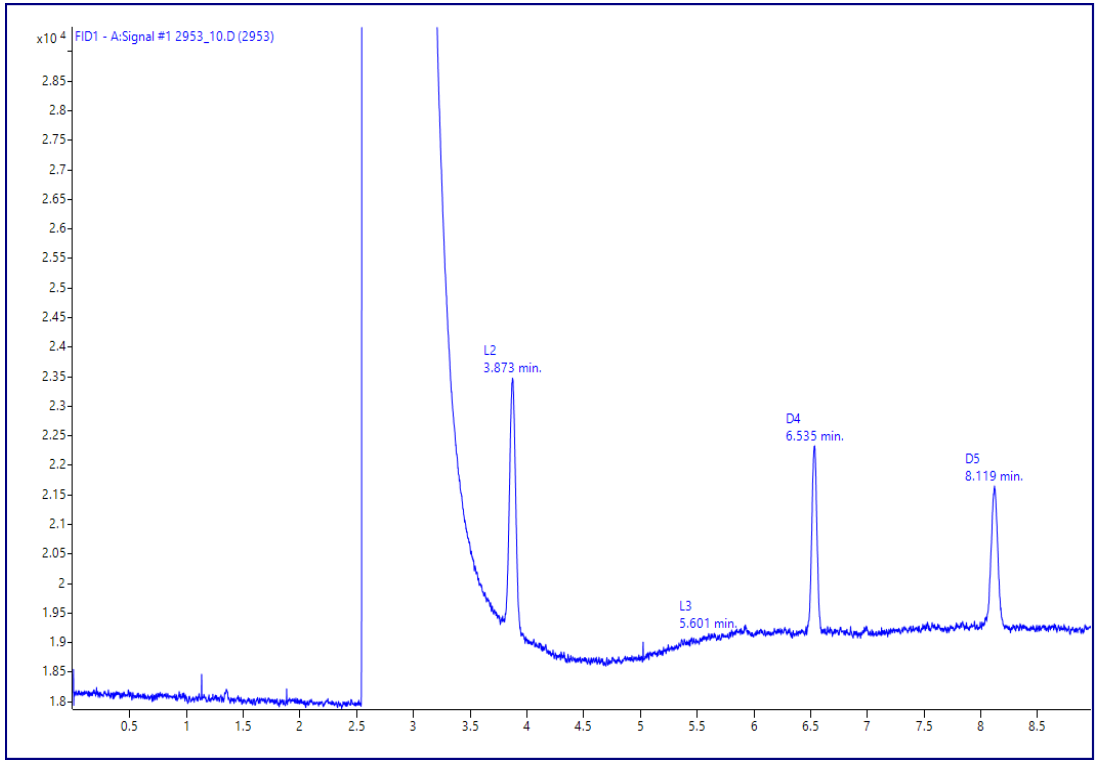
- A Gas Chromatograph system fitted with a **Flame Ionisation Detector** and a **Mass Selective Detector** was used at NPL to determine amount fractions.

4 - International Organization for Standardization, “ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”

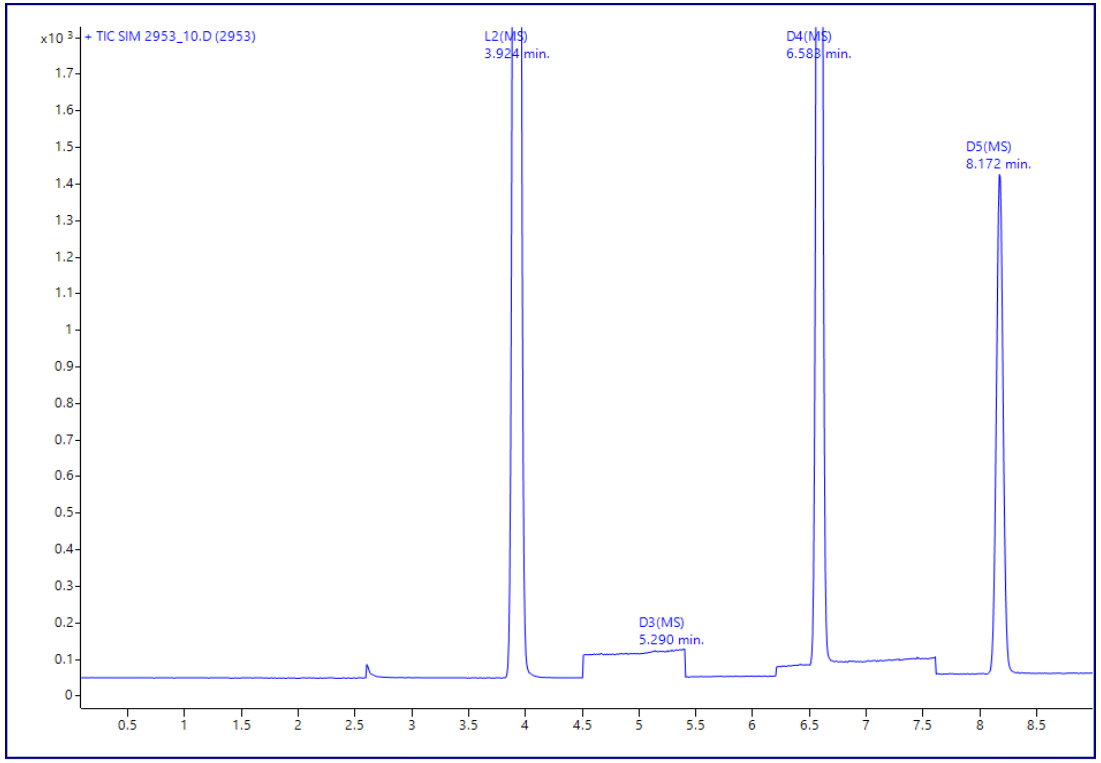
Standard Validation

NPL National Physical Laboratory

FID

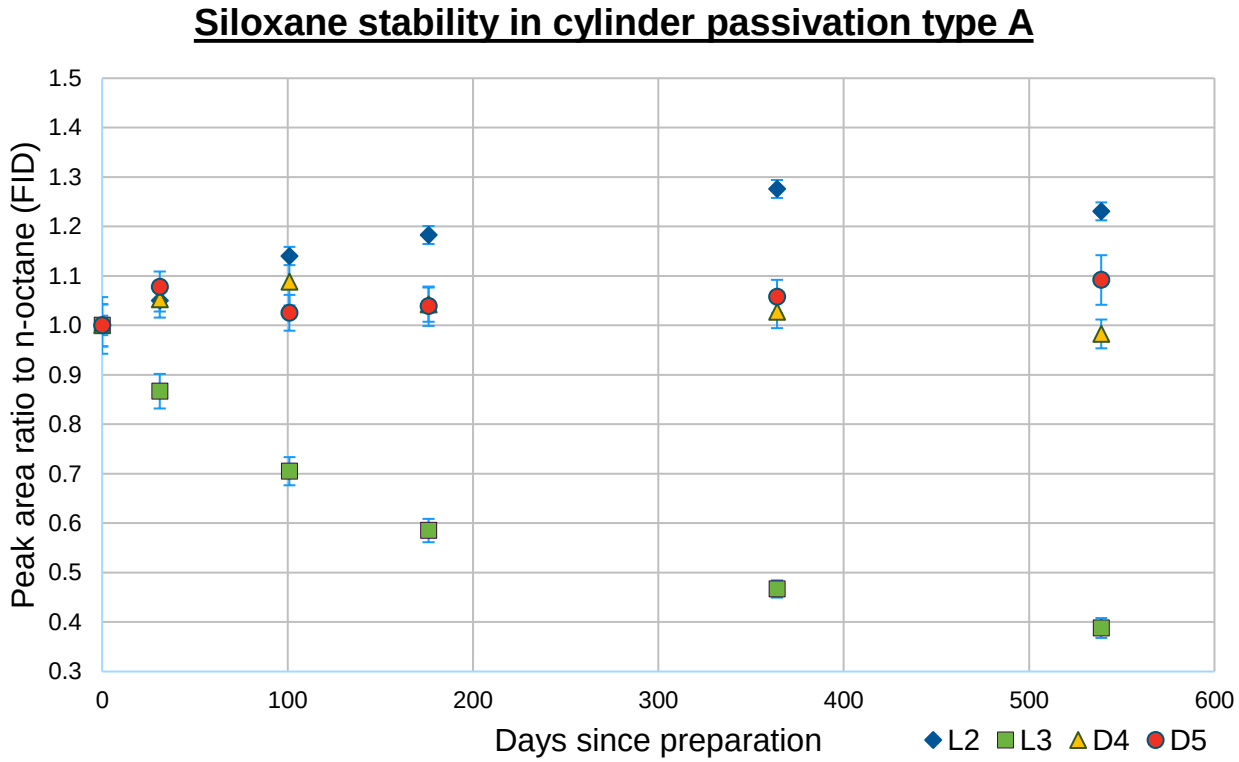


MS



Standard re-verification

- Some siloxanes have been known to exhibit stability challenges with certain cylinder passivation **in previous projects (e.g. L3/L2 siloxane)**.[5]



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

5 - EMPIR 16ENG05 Metrology for Biomethane, Deliverable D1, NPL and VSL

Measurement technique summary

Participant code	Analytical Technique	Calibration
NPL	**GC-MS** *(Gas Chromatography Mass Spectrometry)*	Gas standard prepared. Sampling by direct gas injection. Single-point calibration according to ISO 12963.
L01	**TD-GC-MS** *(Thermal Desorption Gas Chromatography Mass Spectrometry)*	Liquid standard prepared in methanol. Sampling in thermal desorption tubes following ISO 16017-1.
L02	**GC-MS** *(Gas Chromatography Mass Spectrometry)*	Reference solution prepared. Sampling in nitrogen filled Tedlar bags. Single-point calibration.
L03	**GC-MS** *(Gas Chromatography Mass Spectrometry)*	Liquid standard prepared in toluene. Sampling in methane filled Tedlar bags. Three-point calibration.
L04	**GC-IMS** *(Gas Chromatography Ion Mobility Spectrometry)*	Gas standard prepared by automatic gas-dilution. Sampling in Certified permeation tubes.
L05	**GC-FID** *(Gas Chromatography Flame Ionisation Detection)*	Liquid standard prepared. Sampling in nitrogen filled Tedlar bags.
L06	**ATD-GC-FID** *(Automated Thermal Desorption Gas Chromatography Flame Ionisation Detection)*	Gas standard prepared according to ISO 6142-1. Sampling in thermal desorption tubes following ISO 16017-1.
L07	**GC-ICP-MS** *(Gas Chromatography Inductively Coupled Plasma Mass Spectrometry)*	Liquid standard prepared in isopropanol. Sampling by "liquid quench system".
L08	**GC-AED** *(Gas Chromatography Atomic Emission Detection)*	Gas standard. Sampling by direct gas injection following ASTM D8230.
L09	**GC-MS** *(Gas Chromatography Mass Spectrometry)*	Liquid standard prepared. Sampling in sorbent tube following ASTM D8230.

Comparison criteria

$$z_i = \frac{(x_i - X_{ref})}{\hat{\sigma}}$$

- Z_i denotes the *z* score of laboratory *i*
- x_i denotes the reported result of laboratory *i*
- X_{ref} denotes the reference value of the mixture assigned to lab *i*
- $\hat{\sigma}$ denotes the standard deviation for proficiency assessment, defined for this comparison as double the uncertainty in the reference values, equating to 16% of X_{ref} (0.035 for L2, 0.018 for D4, 0.013 for D5 and 0.248 for total silicon for labs NPL, L01, L02, L03, L04 and L06 and 0.250 for labs L05, L07, L08 and L09)

Interpretation:

$\|z\| \leq 2$	Satisfactory result (shown in green within tables)
$2 < \|z\| < 3$	Questionable result (shown in orange within tables)
$\|z\| > 3$	Unsatisfactory result (shown in red within tables)

Comparison criteria

$$E_{n,i} = \frac{x_i - X_{ref}}{\sqrt{(U_i)^2 + \left(U_{ref}\right)^2}}$$

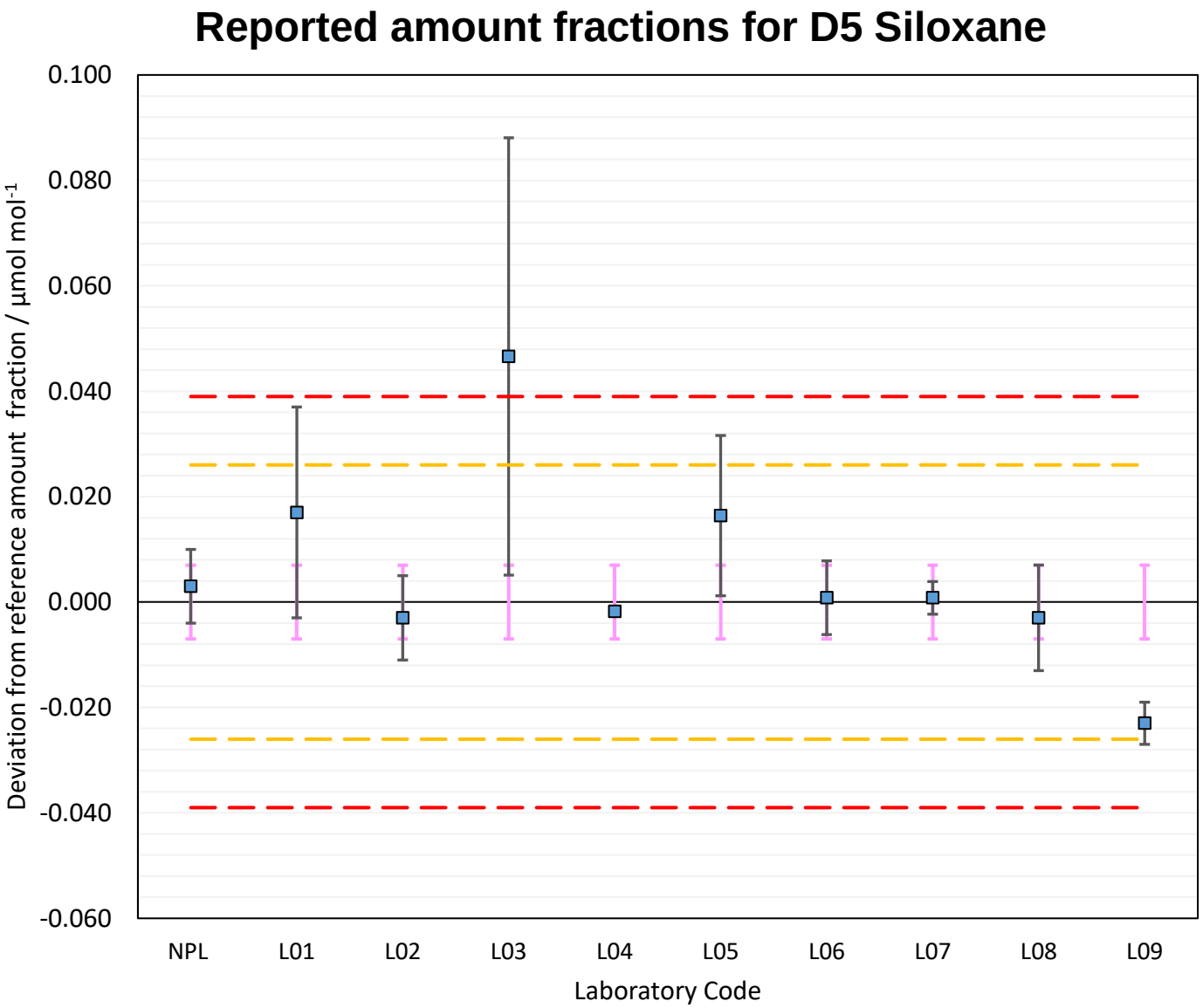
- $E_{n,i}$ denotes the E_n-score of laboratory *i*
- x_i denotes the reported result of laboratory *i*
- X_{ref} denotes the reference value
- U_i denotes the expanded uncertainty (with coverage factor k=2) given by laboratory *i*
- U_{ref} denotes the expanded uncertainty (with coverage factor k=2) of the reference value

Interpretation:

$|E_n| \leq 1$ Satisfactory result (shown in green within tables)

$|E_n| > 1$ Unsatisfactory result (shown in red within tables)

D5 results

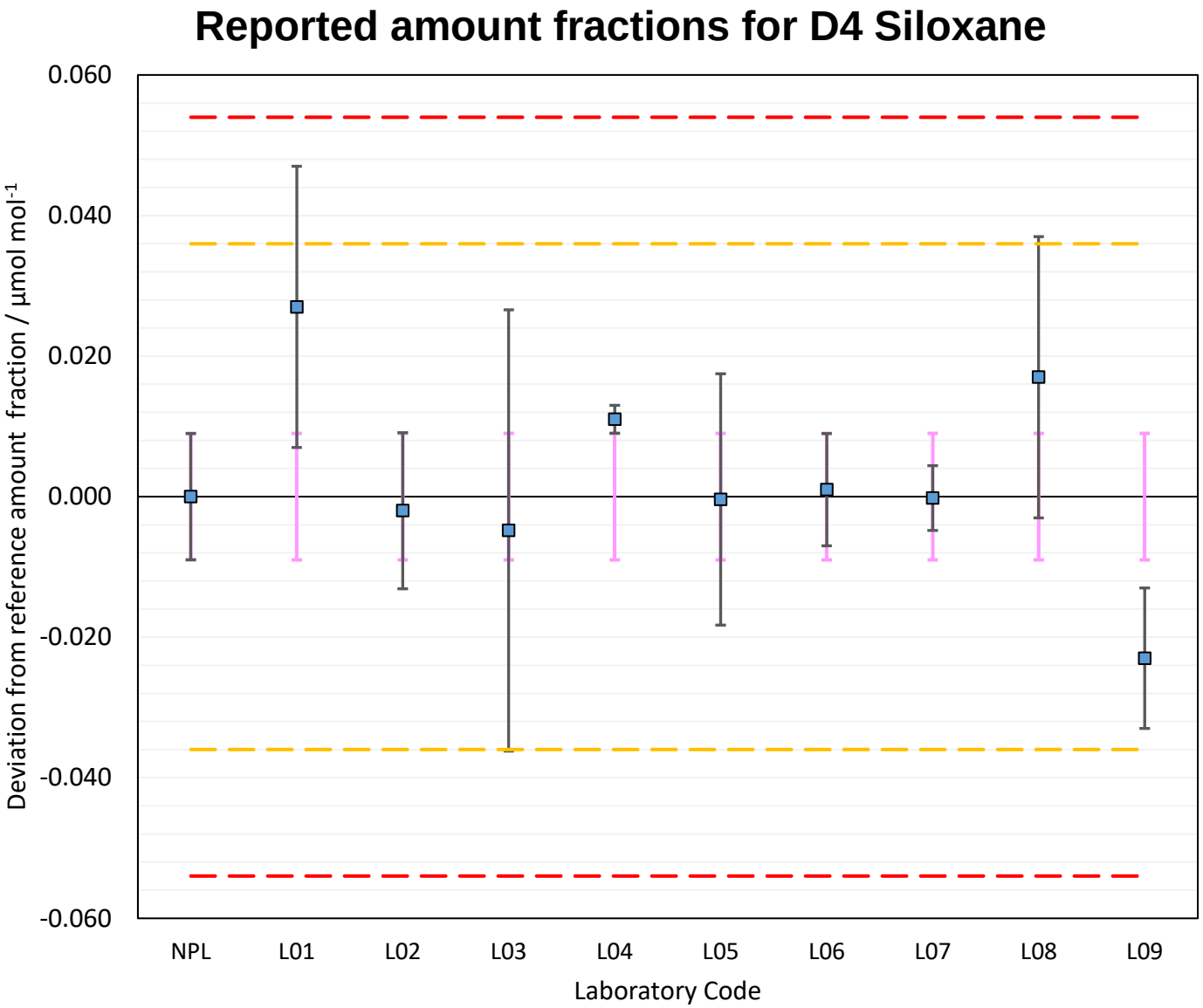


Participant code	Analytical Technique	Z-score	Quality of result	E_n number	Quality of result
NPL	GC-MS	0.20	Satisfactory	0.39	Satisfactory
L01	TD-GC-MSD	0.90	Satisfactory	0.54	Satisfactory
L02	GC-MS	-0.23	Satisfactory	-0.29	Satisfactory
L03	GC-MS	3.51	Unsatisfactory	1.11	Unsatisfactory
L04	GC-IMS	-0.14	Satisfactory	-0.27	Satisfactory
L05	GC-FID	1.23	Satisfactory	0.99	Satisfactory
L06	ATD-GC-FID	0.06	Satisfactory	0.08	Satisfactory
L07	GC-ICP-MS	0.06	Satisfactory	0.11	Satisfactory
L08	GC-AED	-0.23	Satisfactory	-0.25	Satisfactory
L09	GC-MS	-1.73	Satisfactory	-2.97	Unsatisfactory

Key points:

- L09 noted issues (incorrect sampling volume used for sorbent tubes resulting in low recovery)

D4 results

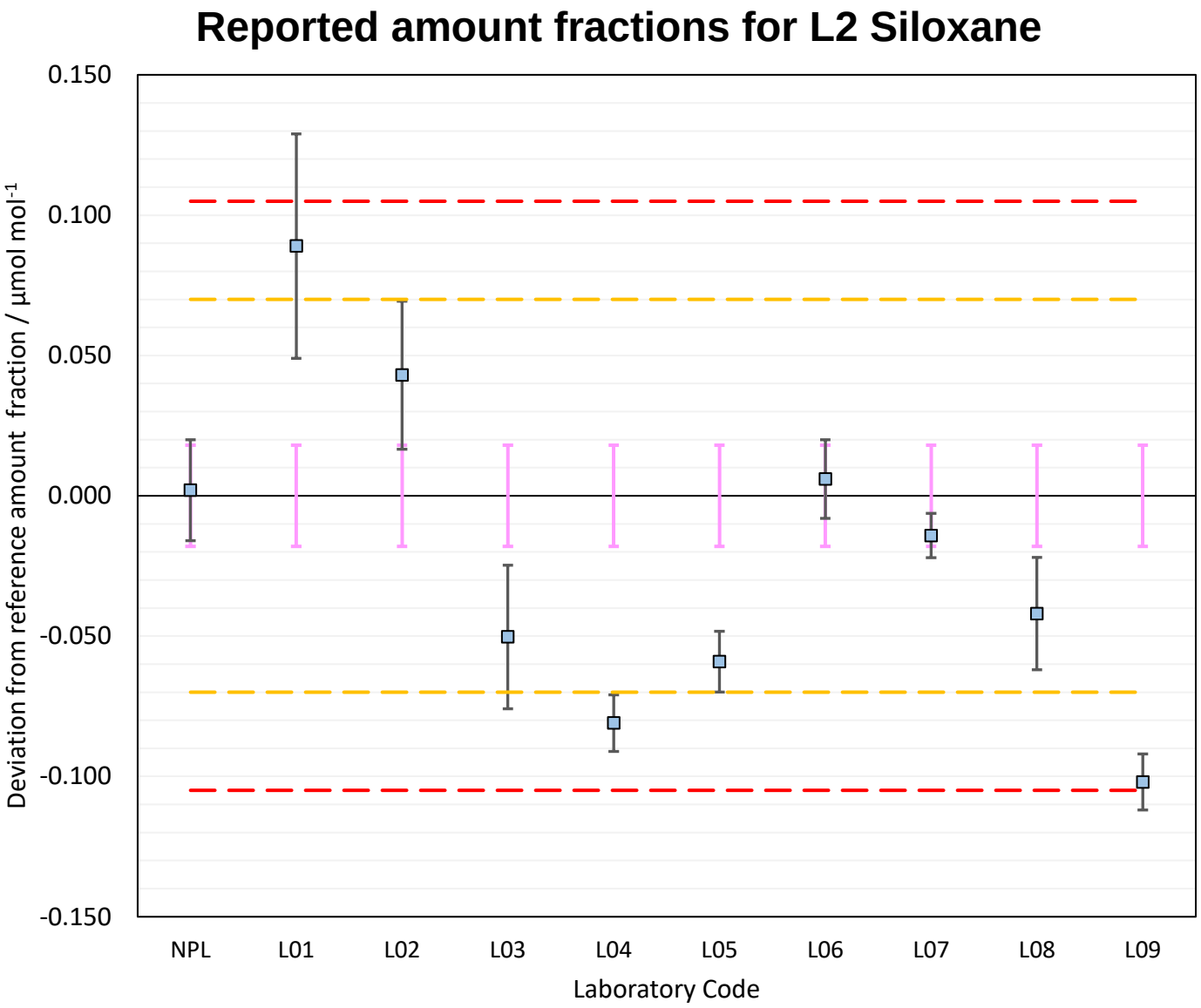


Participant code	Analytical Technique	Z-score	Quality of result	E_n number	Quality of result
NPL	GC-MS	0.00	Satisfactory	-0.01	Satisfactory
L01	TD-GC-MSD	1.49	Satisfactory	1.14	Unsatisfactory
L02	GC-MS	-0.11	Satisfactory	-0.14	Satisfactory
L03	GC-MS	-0.27	Satisfactory	-0.15	Satisfactory
L04	GC-IMS	0.61	Satisfactory	1.19	Unsatisfactory
L05	GC-FID	-0.02	Satisfactory	-0.02	Satisfactory
L06	ATD-GC-FID	0.06	Satisfactory	0.08	Satisfactory
L07	GC-ICP-MS	-0.01	Satisfactory	-0.02	Satisfactory
L08	GC-AED	0.94	Satisfactory	0.77	Satisfactory
L09	GC-MS	-1.27	Satisfactory	-1.71	Unsatisfactory

Key points:

- Best agreement
- L09 noted issues (incorrect sampling volume used for sorbent tubes resulting in low recovery)

L2 results

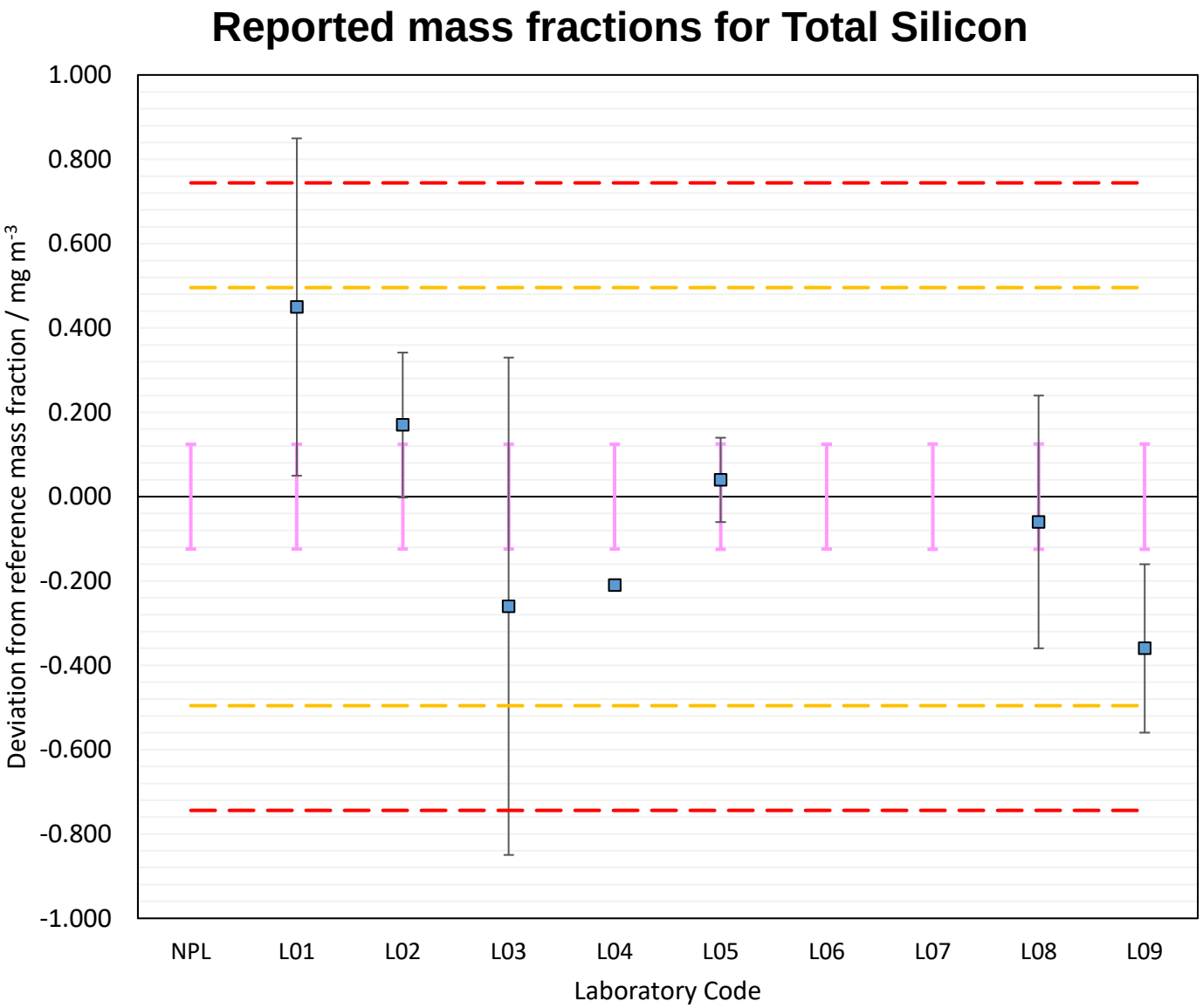


Participant code	Analytical Technique	Z-score	Quality of result	E_n number	Quality of result
NPL	GC-MS	0.06	Satisfactory	0.12	Satisfactory
L01	TD-GC-MSD	2.29	Questionable	1.68	Unsatisfactory
L02	GC-MS	1.22	Satisfactory	1.35	Unsatisfactory
L03	GC-MS	-1.42	Satisfactory	-1.62	Unsatisfactory
L04	GC-IMS	-2.29	Questionable	-3.98	Unsatisfactory
L05	GC-FID	-1.67	Satisfactory	-2.84	Unsatisfactory
L06	ATD-GC-FID	0.17	Satisfactory	0.27	Satisfactory
L07	GC-ICP-MS	-0.40	Satisfactory	-0.73	Satisfactory
L08	GC-AED	-1.19	Satisfactory	-1.57	Unsatisfactory
L09	GC-MS	-2.88	Questionable	-5.00	Unsatisfactory

Key points:

- Poorest agreement of all siloxanes
- L04 noted the permeation tube used had passed it's expiry date
- L08 notes issues with GC-AED (solved after comparison-carbon in reagent O2)
- L09 noted issues (incorrect sampling volume used for sorbent tubes resulting in low recovery)

Total silicon results



Participant code	Analytical Technique	Z-score	Quality of result	E_n number	Quality of result
NPL	GC-MS	-	-	-	-
L01	TD-GC-MSD	1.61	Satisfactory	0.97	Satisfactory
L02	GC-MS	0.69	Satisfactory	0.80	Satisfactory
L03	GC-MS	-1.05	Satisfactory	-0.43	Satisfactory
L04	GC-IMS	-0.85	Satisfactory	-	-
L05	GC-FID	0.16	Satisfactory	0.25	Satisfactory
L06	ATD-GC-FID	-	-	-	-
L07	GC-ICP-MS	-	-	-	-
L08	GC-AED	-0.24	Satisfactory	-0.18	Satisfactory
L09	GC-MS	-1.44	Satisfactory	-1.53	Unsatisfactory

Key points:

- Total silicon not reported by all labs
- Generally good agreement

Summary

- Final report to be distributed this week

- Generally good agreement for siloxanes and total silicon, with notable issues for L2 siloxane

- Further study recommended to ascertain whether differences are due to calibration, sampling or the measurement method

e.g.

  - Use of the same sampling and analysis method, testing different calibration techniques
  - Use of the same calibration and analysis method, testing different sampling techniques.
  - Use of the same calibration and sampling techniques, testing different analysis methods.

- Expand on number of siloxanes and investigate influences of likely interferants