An international comparison of measurement capability for total silicon and siloxanes content in biomethane

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Abstract

The measurement of siloxanes and total silicon in biomethane is required for conformity assessment and process control applications. Recommended threshold concentrations for total silicon in biomethane are specified in European standards EN 16723-1 [1] and EN 16723-2 [2] as 0.5 mg m^{-3} – 1.0 mg m^{-3}. This paper describes a traceable international comparison of measurements using ten different measurement methods, across nine laboratories according to ISO 17043 – General Requirements for Proficiency Testing [3]. The analytical techniques compared are Gas Chromatography Mass Spectroscopy (GC-MS), Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS) Gas Chromatography coupled with a Flame Ionization Detector (GC-FID), Gas Chromatography Ion Mobility Spectrometry (GC-IMS), Automated Thermal Desorption Gas Chromatography Flame Ionisation Detection (ATD-GC-FID), Gas Chromatography Inductively Coupled Plasma Mass Spectrometry (GC-ICP-MS) and Gas Chromatography Atomic Emission Detection (GC-AED).

Of the four measurands studied (L2 (hexamethyldisiloxane), D4 (Octamethylcyclotetrasiloxane), D5 (Octamethylcyclotetrasiloxane) and total silicon), the agreement between labs was found to be the most consistent for D4 siloxane (100% of labs receiving satisfactory z-scores), and the least consistent for L2 siloxane (70% of labs receiving satisfactory z-scores). The reported uncertainties ranged between 0.2% – 57% relative. The paper presents the results and addresses metrological traceability and uncertainty.

Key words

Biomethane, measurement, sampling, siloxanes, silicon, metrology

1. Introduction

Due to the need to diversify the European natural gas supply to accommodate renewable and low carbon energy gases, biomethane has been introduced within Europe as a solution. Due to the presence of impurities within biomethane, it is necessary to ensure conformance assessment is appropriate. In response to mandate M/475, CEN/PC 408 developed specifications for biomethane (i.e. EN 16723-1 for injection into natural gas grids and EN 16723-2 for transport fuel). In line with the development of these standards, the EMRP project ENG54 Metrology for biogas (2014 - 2017) developed traceable methods and reference materials for selected groups of parameters (impurities) specified in EN 16723. These parameters include total silicon content at a specified threshold of 0.5 mg m^{-3} – 1.0 mg m^{-3}.

Inaccurate measurement of these parameters can cause extensive damage to gas infrastructure. Sampling and measurement of trace impurities are challenging, specifically for total silicon and siloxanes due to their highly adsorptive nature. These impurity measurements are currently being performed throughout Europe. However, there is a lack of traceability meaning that robust validation (using traceable gas standards) through a coordinated comparison of measurement capability was required.

The aim of this work was to provide industry with a metrologically traceable validation of their measurement methods through use of traceable gas mixtures developed in the EMRP ENG54 project. The results of the comparison are presented, along with an assessment of their implication and recommendations.

2. Proficiency test method and reference values

2.1. Measurands

The mixtures used within this comparison contained siloxane components L2 (hexamethyldisiloxane), D4 (Octamethylcyclotetrasiloxane) and D5 (Octamethylcyclotetrasiloxane) in a matrix of synthetic biomethane (methane). The total silicon content of each mixture was chosen to be slightly above the EN 16723 limit value at 1.5 mg m^{-3}.

2.2. Measurement protocol

The measurement protocol requested the participants to perform at least 3 measurements, with an independent calibration for each. The protocol informed the participants of the nominal amount fraction ranges. The laboratories were requested to submit a description of their calibration method, along with their results and uncertainty calculation. The comparison was conducted between November 2020 and August 2021.

2.3. Preparation and distribution of gas standards

Nine NPL Primary Reference Materials (PRMs) were prepared gravimetrically in accordance with ISO 6142-1 [4]. Grade N6.0 methane (CH$_4$) was used as the balance gas for all standards. Pure siloxanes L2 (CAS 107-46-0), D4 (CAS 556-67-2) and D5 (CAS 541-02-6) were purchased from Sigma Aldrich and Alfa Aesar and purity analysed using Gas Chromatography with Flame Ionisation Detection and Mass spectrometry (GC-FID/MS) in accordance with ISO 19229 [5].

The mixtures were prepared in Air Liquide 10 litre high-pressure cylinders treated internally with a proprietary "Megalife" passivation. The cylinders were all fitted with non-treated stainless-steel diaphragm valves (Hale Hamilton, UK). The mixture compositions were designed to contain 1.5 mg m^{-3} total silicon per mixture and with nominally identical compositions within the batch of cylinders produced (**Table 1**).

Table 1: Compositions of traceable reference materials provided to participants

	Laboratory Code	NPL	L01	L02	L03	L04	L05	L06	L07	L08, L09
	Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957
L2 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.221	0.221	0.221	0.221	0.221	0.222	0.221	0.222	0.222
	Expanded uncertainty, k=2 (µmol mol^{-1})	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018
D4 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113
	Expanded uncertainty, k=2 (µmol mol^{-1})	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
D5 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083
	Expanded uncertainty, k=2 (µmol mol^{-1})	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007
	Balance	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4	CH_4
	Nominal total silicon content (mg m^{-3})	1.55	1.55	1.55	1.55	1.55	1.56	1.55	1.56	1.56
	Mixture Pressure (bar)	106	106	107	108	108	108	106	107	108
	Date of Preparation	17/12/20	14/10/20	02/12/20	06/11/20	14/10/20	14/10/20	14/10/20	14/10/20	19/11/20

Relative uncertainties of components are 8% for L2, D4 and D5 and 8% for total silicon. The main contribution to the PRM uncertainty was the repeatability of the validation measurements.

2.4. Calibration method and value assignment

A reference method based on gas chromatography with flame ionisation detection and mass spectrometry (GC-FID/MS) was used at NPL to validate the compositions of the mixtures. Measurements were performed using existing validated NPL PRMs. Method parameters are provided in Table 4 in Appendix 1.

The PRMs were connected to the GC-MS (via an automated switching valve) using purpose-built NPL minimised dead volume connectors and Silcosteel® passivated stainless-steel tubing of 1/16" internal diameter. The flow rates of the gas mixtures were controlled to approximately 25 ml min^{-1} using NPL-designed specialist low volume flow restrictors to minimise the effect of adsorption, reduce the stabilisation time for the measurements and to allow a stable sample flow to be maintained throughout the analysis.

The lines were thoroughly purged, and flow rates stabilised before commencing analysis. The reference method was set up to alternate between the PRMs every 9 minutes and the GC oven took approximately 40 seconds to stabilise between sequential runs. For verification of PRMs the method was run in an A/B/A/B switching sequence. All measurements included a minimum of 6 injections of each mixture (up to a maximum of 20 depending on stabilisation time required due to siloxane adsorption) to obtain a comprehensive dataset. The GC-FID was calibrated using a single point calibration in accordance with ISO 12963 [6].

The dispatched PRMs were assigned values and uncertainties in accordance with ISO 6143 [7] using a direct comparison method. Details are provided in annex A2.

2.5. Reference values, homogeneity, and stability evaluation

The reference values were established according to the following parameters:

a) Preparation data, including purity analysis
b) Homogeneity study data
c) Stability study data

Based on results of stability and homogeneity testing, the reference values and associated uncertainties are as provided in Table 1. Measurement data is provided in Annex A2. The uncertainty in the reference value was calculated by combining the gravimetric uncertainty of the primary reference gas standard and the uncertainty in the validation. As the amount fraction deviation range for validation standards was within the linear response ranges of the detectors, the uncertainty contribution from analyser linearity was considered to be negligible. The calculated relative expanded uncertainties (k = 2) for component i in reference mixture x were defined as:

$$\frac{U(x_i)}{x_i} = 2 \times \sqrt{\left(\frac{u(g_{i,ref})}{g_{i,ref}}\right)^2 + \left(\frac{u(g_{i,val})}{g_{i,val}}\right)^2 + \left(\frac{u(r_{i,ref})}{\bar{r}_{i,ref}}\right)^2 + \left(\frac{u(r_{i,val})}{\bar{r}_{i,val}}\right)^2} \qquad \text{Equation 1}$$

Where:

- U denotes the expanded uncertainty (k = 2) of the variable between parenthesis,
- u is the standard uncertainty (k = 1);
- $g_{i,\text{ref}}$ is the gravimetric amount fraction of component i in the reference mixture;
- $g_{i,\text{val}}$ is the gravimetric amount fraction of component i in the validation mixture;
- $r_{i,\text{ref}}$ is the GC peak area of component i in the reference mixture;
- $r_{i,\text{val}}$ is the GC peak area of component i in the validation mixture,.

The results of the stability measurements indicated that all cylinders measured did not experience any change in composition outside of the assigned 8% relative uncertainty. Historic data for mixture compositions within this cylinder type has demonstrated that such mixtures should remain stable for a minimum of 18 months with correct usage under the uncertainties given.

2.6. Evaluation criteria

z-scores and E_n number are methods frequently used to evaluate the results of an intercomparison or proficiency testing scheme. The calculation methods from ISO 13528 [8] were used within this comparison.

The z-score for component i, z_i, is defined as:

$$z_i = \frac{\left(x_i - X_{ref}\right)}{\hat{\sigma}} \qquad \text{Equation 2}$$

Where:

- 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)

The interpretation of the *z*-score is as follows:

$|z| \leq 2$ Satisfactory result
$2 < |z| < 3$ Questionable result
$|z| > 3$ Unsatisfactory result

In addition, an E_n-score was calculated for those laboratories which reported expanded uncertainties. The E_n-score is defined as:

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

Equation 3

Where:

- $E_{n,i}$ 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

The interpretation of the E_n-score is as follows:

$|E_\mathrm{n}| \leq 1$ Satisfactory result
$|E_\mathrm{n}| > 1$ Unsatisfactory result

2.7. Participant methods

Each participant used a unique method to determine the composition of the dispatched PRMs. There was some overlap between the measurement techniques and the methods of calibration. These are summarised in Table 2.

Table 2: Summary of analytical measurement techniques and calibration methods

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.

3. Results and discussion

The results for L01 and L04 were reported as a mass fraction and converted into amount fraction based on the standard conditions stated in EN-16723, based on a temperature of 288.15 K and a pressure of 101325 Pa. Notes on results provided are given in Appendix A3.

The following graphs and table depict the results of the comparison. Yellow error bars indicate the expanded uncertainty in the reference values. Black error bars represent the expanded uncertainty reported by participants. Orange dashed line approximately indicates the $z = 2$ boundary. Red dashed line approximately indicates the $z = 3$ boundary. Blanks indicate no results reported.
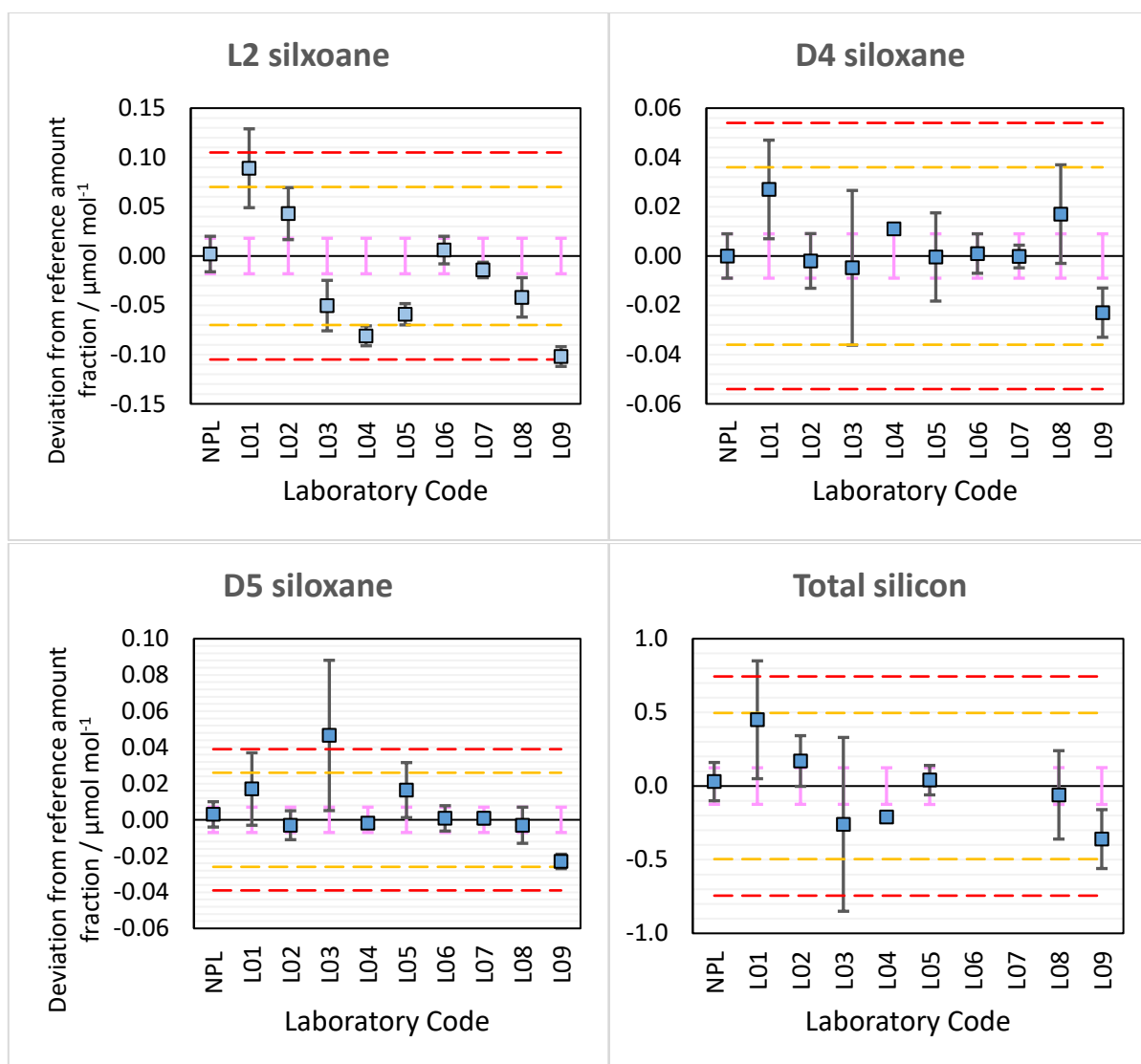
Figure 1: Evaluation of reported results for siloxanes L2, D4, D5 and total silicon.

Table 3: Summary of *z*-scores and E_n numbers for L2, D4, D5 and total silicon. Dashes indicate no result was reported. For evaluation criteria, green indicates "satisfactory", orange indicates "questionable", red indicates "unsatisfactory".

Participant code	Analytical Technique	L2		D4		D5		Total silicon	
		z-score	E_n number	*z*-score	E_n number	*z*-score	E_n number	*z*-score	E_n number
NPL	GC-MS	0.06	0.12	0.00	-0.01	0.20	0.39	0.10	0.14
L01	TD-GC-MS	2.29	1.68	1.49	1.14	0.90	0.54	1.61	0.97
L02	GC-MS	1.22	1.35	-0.11	-0.14	-0.23	-0.29	0.69	0.80
L03	GC-MS	-1.42	-1.62	-0.27	-0.15	3.51	1.11	-1.05	-0.43
L04	GC-IMS	-2.29	-3.98	0.61	1.19	-0.14	-0.27	-0.85	-
L05	GC-FID	-1.67	-2.84	-0.02	-0.02	1.23	0.99	0.16	0.25
L06	ATD-GC-FID	0.17	0.27	0.06	0.08	0.06	0.08	-	-
L07	GC-ICP-MS	-0.40	-0.73	-0.01	-0.02	0.06	0.11	-	-
L08	GC-AED	-1.19	-1.57	0.94	0.77	-0.23	-0.25	-0.24	-0.18
L09	GC-MS	-2.88	-5.00	-1.27	-1.71	-1.73	-2.97	-1.44	-1.53

The largest deviations were seen in the **L2 siloxane** results, where 7 out of 10 laboratories achieved satisfactory z-scores and 3 out of 10 achieved satisfactory E_n numbers. The cause of one of the questionable z-scores was identified to be due to systematic error in the measurement procedure, whereas the reasons for the other two require further investigation following stability trial results indicating stability was not a root cause. The more volatile nature of L2 renders it prone to issues with sampling via sorption tubes, which was proposed as a potential cause for some of the questionable results following discussions with participants. For the labs that achieved satisfactory scores for both criteria, the associated L2 results were all within 23% of the reference values. This figure increases to 46% when considering all L2 results.

The results for **D4 siloxane** were the most consistent, with all participant laboratories achieving satisfactory z-scores and 7 out of 10 achieving satisfactory E_n numbers. For the labs that achieved satisfactory scores for both criteria, the associated D4 results were all within 15% of the reference values. This figure increases to 24% when considering all D4 results.

For **D5 siloxane**, 9 out of 10 laboratories achieved satisfactory z-scores and 8 out of 10 achieved satisfactory E_n numbers. For the labs that achieved satisfactory scores for both criteria, the associated D5 results were all within 20% of the reference values. This figure increases to 57% when considering all D5 results.

For **total silicon**, 8 out of 8 laboratories achieved satisfactory z-scores and 7 out of 8 achieved satisfactory E_n numbers. For the labs that achieved satisfactory scores for both criteria, the associated total silicon results were all within 29% of the reference values. This figure remains at 29% when considering all total silicon results.

4. Conclusion

This comparison provided an insight into the performance of ten laboratories for the measurement of total silicon and siloxanes in biomethane at amount fractions of between 83 - 222 nmol mol^{-1}, (approximately 1.55 mg m^{-3} total silicon per mixture). Ten different analytical methods were used, including GC-MS, TD-GC-MS, GC-IMS, GC-FID, ATD-GC-FID, GC-ICP-MS and GC-AED. The reported uncertainties ranged between 0.2% – 57% relative.

The results demonstrate that the measurement of siloxanes and total silicon was achieved successfully by the majority of participants, with some challenges identified, particularly for L2 siloxane. As siloxanes have a tendency to adsorb onto surfaces, this may be a cause of some of the issues seen if materials were not appropriately passivated during calibration, sampling and analysis. Typically the effect of adsorption is more prevalent for heavier siloxanes such as D4 and D5 rather than L2.

A further study would be recommended to ascertain whether the differences observed are due to calibration, sampling or the measurement method, as this would give an insight into how to inform best practice. An example of how this could be investigated would be as follows:

1. Use of the same sampling and analysis method, testing different calibration techniques
2. Use of the same calibration and analysis method, testing different sampling techniques.
3. Use of the same calibration and sampling techniques, testing different analysis methods.

Future goals for the measurement of siloxanes and total silicon in biomethane would be to expand on the list of siloxanes tested and also investigate the influence of interferences expected within real biogas and biomethane samples (i.e. by having participants measure a sample containing other impurities that may cause interferences, such as e.g. terpenes and water). Such a test would be more

representative of the challenges encountered within real-world measurements, and provide further insight into best practice for siloxanes and total silicon measurement.

5. Acknowledgements

6. References

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6. International Organization for Standardization, "ISO 12963 Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration", **2017**
7. International Organization for Standardization, "ISO 6143 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures", **2001**
8. ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons **2005**

Appendix A1: Method for verification of PRMs

Table 4: GC-FID/MS method parameters used for validation of PRMs

Parameter	Setting	
Instrument:	Agilent 7890A GC with FID and Agilent 5975C MS	
Column:	J&W, DB-624, 75 m x 530 µm x 3 µm	
Sample volume:	1mL	
GC oven program:	Initial T: 120 °C (held 4.2 minutes). Ramp: 100 °C / min to 200 °C (held at final value for 4 minutes)	
Valve box temp:	195 °C	
Injection mode:	Split	
Detector ->	FID	MS
Temp:	300 °C	230 °C (Source), 150 °C (Quad)
Hydrogen flow:	30 mL/min	-
Air flow:	350 mL/min	-
Helium makeup flow:	2 mL/min	-
L2 (m/z):	-	147
n-octane (m/z):	-	41, 43
L3 (m/z):	-	221.10
D4 (m/z):	-	281.05
D5 (m/z):	-	355.10

Appendix A2: Stability and verification data of PRMs

	Laboratory Code	NPL	L01	L02	L03	L04	L05	L06	L07	L08, L09
	Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957
L2 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.221	0.221	0.221	0.221	0.221	0.222	0.221	0.222	0.222
	Uncertainty from preparation, k=1 (µmol mol^{-1})	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
	Uncertainty from verification, k=1 (µmol mol^{-1})	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
	Uncertainty from stability, k=1 (µmol mol^{-1})	0.0040	0.0040	0.0040	0.0040	0.0040	0.0040	0.0040	0.0040	0.0040
	Combined expanded uncertainty, k=2 (µmol mol^{-1})	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018
D4 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113
	Uncertainty from preparation, k=1 (µmol mol^{-1})	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004	0.0004
	Uncertainty from verification, k=1 (µmol mol^{-1})	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021
	Uncertainty from stability, k=1 (µmol mol^{-1})	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017
	Combined expanded uncertainty, k=2 (µmol mol^{-1})	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
D5 Siloxane	Gravimetric Amount fraction (µmol mol^{-1})	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083
	Uncertainty from preparation, k=1 (µmol mol^{-1})	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
	Uncertainty from verification, k=1 (µmol mol^{-1})	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	Uncertainty from stability, k=1 (µmol mol^{-1})	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016
	Combined expanded uncertainty, k=2 (µmol mol^{-1})	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007

Appendix A3: Measurement results and notes

Table 5: Reported and reference amount fractions for L2 siloxane.

Laboratory code	NPL	L01	L02	L03	L04	L05	L06	L07	L08	L09
Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957	2957
Reported amount fraction [µmol/mol]	0.223	0.302	0.264	0.1707	0.140	0.1629	0.227	0.2078	0.180	0.120
Reported uncertainty k=2 [µmol/mol]	0.002	0.045	0.0264	0.0256	0.010097	0.0108	0.014	0.0079	0.020	0.010
Reference amount fraction [µmol/mol]	0.221	0.221	0.221	0.221	0.221	0.222	0.221	0.222	0.222	0.222
Reference uncertainty k=2 [µmol/mol]	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018

Table 6: Reported and reference amount fractions for D4 siloxane.

Laboratory code	NPL	L01	L02	L03	L04	L05	L06	L07	L08	L09
Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957	2957
Reported amount fraction [µmol/mol]	0.113	0.140	0.111	0.1082	0.124	0.1126	0.114	0.1128	0.130	0.090
Reported uncertainty k=2 [µmol/mol]	0.001	0.022	0.0111	0.0314	0.001992	0.0179	0.008	0.0046	0.020	0.010
Reference amount fraction [µmol/mol]	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113	0.113
Reference uncertainty k=2 [µmol/mol]	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009

Table 7: Reported and reference amount fractions for D5 siloxane.

Laboratory code	NPL	L01	L02	L03	L04	L05	L06	L07	L08	L09
Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957	2957
Reported amount fraction [µmol/mol]	0.086	0.095	0.080	0.1296	0.0812	0.0994	0.084	0.0838	0.080	0.060
Reported uncertainty k=2 [µmol/mol]	0.001	0.021	0.0080	0.0415	0.000127	0.0152	0.007	0.0031	0.010	0.004
Reference amount fraction [µmol/mol]	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083	0.083
Reference uncertainty k=2 [µmol/mol]	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.007

Table 8: Reported and reference amount fractions for total silicon.

Laboratory code	NPL	L01	L02	L03	L04	L05	L06	L07	L08	L09
Cylinder ID	2953	2951	2944A	2956	2955	2945	2949	2958	2957	2957
Reported amount fraction [mg/m³]	1.58	1.95	1.72	1.29	1.34	1.6	-	-	1.5	1.2
Reported uncertainty k=2 [mg/m³]	0.13	0.392	0.172	0.59	-	0.1	-	-	0.3	0.2
Reference amount fraction [mg/m³]	1.55	1.55	1.55	1.55	1.55	1.56	1.55	1.56	1.56	1.56
Reference uncertainty k=2 [mg/m³]	0.124	0.124	0.124	0.124	0.124	0.125	0.124	0.125	0.125	0.125

Notes on results provided:

Note 1: lab 08 noted that they encountered an excessive amount of carbon background interference in their measurement method in late November 2020, shortly before the cylinder was shipped to them. The issue was not resolved until early June 2021 (after the cylinder was returned to the coordinator). It was determined to be caused by contamination within the O2 reagent gas used by the AED plasma. It is believed to have caused bias within some of the reported results for lab 08.

Note 2: lab 09 noted that due to human error the estimated concentration calculations for the tube loading were off by a factor of 10; a volume of 1 to 3 litres was sampled rather than the appropriate volume of 10 to 30 litres which would have been required to reach the desired concentration range). Therefore lab 09 determined that the procedure used was not in line with ASTM D8230 and is believed to have caused some bias within the reported results of lab 09.

Note 3: Not all labs reported results for total silicon. This is represented by blanks in the graph and tables in the total silicon results section. Lab 04 reported a total silicon value without an uncertainty, which has been included.