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Determination of total silicon content in biomethane: Development of a validation approach for ISO 2613-1, as a practical application of the ISO guide under preparation: Biomethane – Performance evaluation for analytical systems

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ABSTRACT
This study presents a validation protocol for the atomic emission spectroscopy (AES) method for determining total silicon in biomethane, developed in alignment with ISO 2613-1:2023. The work serves as a practical demonstration, contributing to the forthcoming ISO validation guide for analytical methods assessing impurities in biomethane, prepared within ISO/TC 193 WG 25: Biomethane. The protocol describes the complete analytical process: absorption of volatile siloxane compounds in mineral acid, chemical derivatization into a suitable form for spectroscopy, and measurement of the resulting liquid sample using an optical plasma emission instrument. Method development included optimisation of sampling, derivatization, sample preparation, and quality control procedures. Validation was carried out through rigorous evaluation of linearity, stability, robustness, selectivity, sensitivity, precision, bias, and measurement uncertainty. Results confirmed the method's reliability for detecting very low mass fractions of silicon (µg/kg range) originating from siloxane species, such as L2, L3, D4, and D5, in biomethane. By demonstrating both methodological robustness and practical applicability, this study provides a model example for ISO's upcoming guidance on validation of analytical methods, supporting the harmonisation of impurity testing in renewable gases.

Section: RESEARCH PAPER

Keywords: total silicon; biomethane; atomic emission spectroscopy; validation; measurement uncertainty

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1. INTRODUCTION

Biomethane, a renewable gaseous fuel derived from organic materials through anaerobic digestion or gasification, has emerged as a key player in the global transition toward low-carbon energy systems. It offers a carbon-neutral alternative to fossil natural gas, supports circular economy principles by valorising organic waste, and enhances energy security through decentralized production. Biomethane contributes significantly to the EU's climate targets, aiming for a 55 % reduction in greenhouse gas emissions by 2030 and net-zero emissions by 2050 [1]. Biomethane is typically produced by upgrading raw biogas, which originates from the anaerobic digestion of a wide variety of organic feedstocks. Due to the diverse nature of these feedstocks and the variability of production parameters (e.g. temperature, retention time), the composition of the resulting biogas can vary significantly. Not only do the concentrations of major components like methane and carbon dioxide fluctuate, but the levels of impurities such as hydrogen sulphide, ammonia, hydrogen chloride, organic silicon compounds, oxygen, and nitrogen are also inconsistent. In particular, the substrate type strongly influences the profile of volatile organic compounds (VOCs) in biogas—including siloxanes, which are a major concern for gas quality and combustion systems. Siloxanes, originating from a wide range of sources including personal care products, detergents, and industrial lubricants, persist through wastewater treatment and enter the biogas stream [2]. Silicon, primarily from siloxanes in biogas, can form silica deposits upon combustion, leading to equipment damage and reduced efficiency. These abrasive deposits lead to mechanical wear, reduced efficiency, unplanned downtime, and increased maintenance costs.

Ensuring that biomethane content complies with regulatory standards, particularly through the measurement of silicon content, is essential. Accurate silicon measurement is crucial for meeting industry standards, protecting machinery, and optimising biogas purification processes [3]. Given the operational and environmental risks posed by excessive silicon levels, precise quantification has become a priority in both industrial and regulatory monitoring frameworks.

To ensure reliable and reproducible results for regulatory compliance and quality control, traceability in measurements is essential. This requires standardised methods, certified reference materials, and rigorous quality assurance protocols, aligning with international best practices. In this context, this study provides an analytical approach and demonstrates validation of all relevant parameters for the successful application of ISO 2613-1: 2023 Analysis of natural gas — Silicon content of biomethane — Part 1: Determination of total silicon by atomic emission spectroscopy (AES) [4].

Furthermore, the approach aligns with the principles of ISO/IEC 17025:2017 [5], ensuring that testing laboratories implementing the ISO 2613-1 method maintain technical competence, measurement reliability, and full compliance with accreditation requirements. This reinforces the integrity of silicon measurement in biomethane and supports the broader goals of sustainable energy production and regulatory conformity.

2. MATERIALS AND METHODS

2.1. Reagents and labware

For the purpose of sample preparation, the following chemicals were used: concentrated Nitric acid (ultrapure grade, 69.0–70.0 %, Fisher Scientific®, Waltham, Massachusetts, USA), Hydrogen peroxide (ultrapure, 30 %, Roth®, Karlsruhe, Germany), Potassium hydroxide pellets (Fisher Scientific®, Waltham, Massachusetts, USA), concentrated fluoric acid (ultrapure, 48 %, Merck®, Darmstadt, Germany), pure siloxane compounds such as Octamethylcyclotetrasiloxane (D4) (100 %, Merck®, Darmstadt, Germany) and Hexamethyldisiloxane (L2) (99,6 %+/Acros Organics®, Geel, Belgium), Si standard solution (1000 mg/L) (Supelco®, Bellefonte, Pennsylvania, USA), Certified Reference Standard traceable to NIST® SRM 3150, Water, complying with grade 1 of ISO 3696. Prior to the analysis step, the instrument was calibrated using Wavelength Calibration Concentrate for ICP-OES & MP-AES, 50 mg/L, 500 mg/L, No. 6610030000 (Agilent Technologies®, Santa Clara, California, USA) containing Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Zn at nominal concentrations of 50 mg/L and K at nominal concentration of 500 mg/L. The use of high-purity chemicals is essential for the accurate and reliable analysis of silicon in biomethane. These chemicals ensure minimal contamination, precise calibration, and consistent results, supporting robust analytical procedures and quality control in biomethane production and utilisation. The purity of the used chemicals was further tested by means of different quality control samples and blanks.

Plastic (Polypropylene - PP) gas bubblers with tubing, 20–50 mL capacity with stoppers, silicon free, plastic (Polypropylene-PP) vessels for the derivatization, 200 mL capacity with stoppers, heat durable, plastic (Fluorinated Ethylene Propylene – FEP) hoses of different profile were used as gas carriers for sampling procedure and flow measuring, inert and silicon free.

2.2. Instrumentation

Gas flow meter. Accurate measurement of biomethane volume in a gas bubbler system is essential for precise silicon quantification. A gas flow meter with an integrated temperature sensor ensures accurate readings by compensating for temperature variations. This system provides real-time flow monitoring, allowing immediate adjustments and maintaining optimal sampling conditions. High-resolution sensors enhance accuracy, while temperature compensation ensures reliable data in fluctuating environments. Consistent flow and temperature measurements are crucial for reproducible silicon analysis, with regular calibration maintaining long-term reliability. For the purpose of this study the Aalborg® DFM 26 S-TAL2-AA2 gas flow meter calibrated for methane and with integrated temperature sensor was used [6].

Gas bubbler system. A gas bubbler system captures gaseous samples by passing them through a liquid medium, typically concentrated nitric acid (HNO_3), for silicon analysis in biomethane. This setup efficiently absorbs siloxanes, converting them into soluble silicates or silicon dioxide for analysis. HNO_3, a strong oxidizer, ensures complete silicon capture while preventing re-volatilization. Simple to operate, the system is suitable for routine sampling, with regular maintenance ensuring reliability. The bubbler system used in this study was laboratory-constructed, following ISO 2613-1 standard [4] recommendations. It consisted of three serially connected bubbler-vessels, connected with gas cylinder, where gas supply was maintained and controlled by gas flow meter.

MP-AES. Atomic emission spectrometry (AES) is a powerful analytical technique used to determine the concentration of elements in a sample by measuring the intensity of light emitted from excited atoms or ions. This technique leverages the unique emission spectra of elements, allowing for precise identification and quantification. In particular, microwave plasma atomic emission spectrometry (MP-AES) has gained prominence due to its advantages in terms of cost-effectiveness, efficiency, and environmental impact. MP-AES method development was performed using microwave plasma—atomic emission spectrometer—4200 MP-AES (Agilent Technologies®, Santa Clara, California, USA) [7].

Auxiliary equipment. Auxiliary equipment included digital micropipettes (Thermo Scientific®, Waltham, Massachusetts, USA) covering the range 0.01 mL–10 mL and an analytical balance, MSE225S-0CE-DU (Sartorius®, Göttingen, Germany).

2.3. Method development

Sampling and sample preparation procedure. The gas flow meter with an integrated temperature sensor is installed between the biomethane source and the gas bubbler system, ensuring secure connections and proper sensor positioning. Calibration is performed according to the manufacturer's instructions, with periodic checks to maintain accuracy. During sampling, biomethane flows through the system at an adjusted rate, while real-time monitoring ensures stable conditions. Flow and temperature data are continuously or periodically recorded to calculate the sampled gas volume accurately. After sampling, the recorded data is used to determine the total biomethane volume, which, combined with silicon concentration measurements, allows for precise silicon content analysis.

Procedure for gas collection. To collect biomethane samples using a gas bubbler system with concentrated nitric acid, the bubbler is filled to a specified level, while ensuring proper safety measures, including personal protective equipment (PPE) and fume hoods. The inlet is securely connected to the biomethane source, with the outlet directed to an exhaust system or additional bubblers, if needed. A gas flow controller regulated the flow rate at 10 mL/min to optimize bubbling and maximize contact time with the nitric acid media. Biomethane is bubbled through the acid for a set period, allowing efficient capture of silicon compounds while maintaining stable flow. After sampling, the nitric acid solution containing the captured silicon is quantitatively transferred to a suitable container for analysis, with the bubbler rinsed to ensure complete silicon recovery.

MP-AES method. MP-AES, a specialized atomic emission spectroscopy technique, uses microwave energy to generate a nitrogen plasma, providing a stable environment for element excitation [7]. This method is ideal for analysing metals and non-metals, including silicon in biomethane. Method development involved selecting silicon emission lines (251.611 nm as the most sensitive line), while minimizing spectral interferences, optimising plasma conditions, and refining sample introduction. Plasma pressure, gas flow, and microwave power were fine-tuned for stability and accuracy, as well as rinse, stabilization, and sample uptake time. Samples were introduced via a nebuliser, ensuring efficient aerosol formation. The instrument was calibrated using NIST-traceable Si standards (1000 mg/L), with a weighted linear fit ($r^2 > 0.995$) covering 0.05–1 mg/kg. Calibration included seven calibration levels—seven standards excluding blank, gravimetrically prepared in ~2 % HNO_3. Quality control checks with certified standard solutions and various blanks ensured reliable performance. The flow chart of the optimized and validated method is shown in Figure 1.

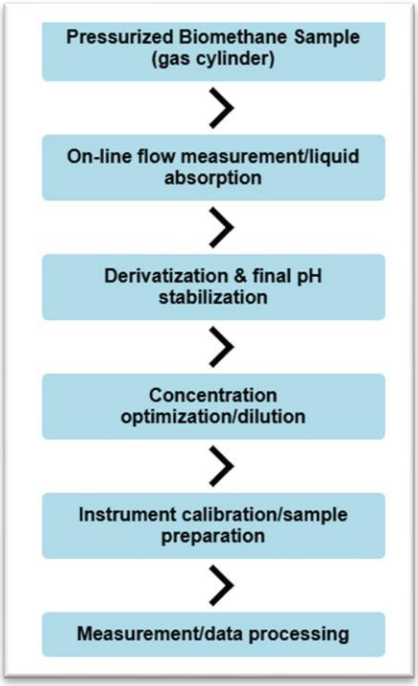

Figure 1. Flow chart of the optimized and validated method.

3. RESULTS – METHOD VALIDATION PARAMETERS

3.1. Stability and selectivity

The stability and selectivity of the atomic emission spectrometry (AES) method for silicon analysis in a matrix containing HNO_3, KOH, and HF has been demonstrated by matrix considerations, instrument calibration, and interference management.

Matrix considerations. The presence of HNO_3, KOH, and HF in the sample preparation process can influence the stability and accuracy of AES measurements, because these reagents may introduce matrix effects, i.e., changes in signal intensity that are not caused by the analyte itself. To ensure that such effects did not impact the determination of silicon, the matrix effect was thoroughly evaluated. This evaluation included monitoring various quality control samples, such as calibration blanks, sample blanks, and derivatization controls. Their responses were compared across the full analytical sequence. Importantly, no spectral interferences or abnormal deviations in intensity were observed in any of these controls. This confirmed that the sample matrix and reagents did not introduce measurable spectral overlap, background enhancement, or suppression of the analyte signal. As a result, the method was considered free from significant matrix effects under the tested conditions.

Instrument calibration. Instrument calibration is done for each batch of samples (20–30 consecutive samples), using traceable standards that closely match the sample matrix.

Interference management. A very important quality criterion of an analytical method is its capability to deliver signals that are free from interferences and give "true results" [8]. Background correction is utilised to address any spectral interferences caused by the matrix components. Bearing in mind the nature and source of the sample, the absence of other, possibly interfering elements is expected and confirmed by analysis. Stated elements are not present in the sample, providing selectivity of the instrumental setting. Blank measurements—reagents and water—proved no contamination with silicon from outside sources. Matrix-matched calibration standards, to mitigate matrix effects, are used. Table 1 shows the possible spectral interferences at the used analytical line. Given the composition of biomethane, it can be concluded that this gaseous matrix is free of interfering elements. This was confirmed in practice, as no emission peaks were observed other than the analytical signal from silicon.

Table 1. Possible spectral interferences for silicon at selected analytical line.

Selected element Si ● **Recommended** ○ **All**

Add

Wavelength (nm)	Ion	Intensity	Order
251.611	I	43664.5	1
288.158	I	18890.1	2
250.690	I	13929.5	3
252.851	I	13768.4	4
251.432	I	12783.8	5
252.411	I	10501.1	6
251.920	I	9185.8	7
221.667	I	3364.5	8
212.412	I	2524.1	9
243.515	I	2429.9	10
390.552	I	1563.7	11
187.518	I	1348.3	12
221.089	I	1302.7	13
187.247	I	996.8	14

Possible interferences on Si (251.611 nm)

Symbol	Wavelength(nm)	Ion	Intensity
Os	251.325	I	706.8
Ru	251.332	II	225.7
Ho	251.366	II	237.7
Er	251.394	II	196.7
Si	251.432	I	12783.8
Os	251.504	I	192.2
Hf	251.548	II	301.6
Si	251.611	I	43664.5
Hf	251.688	II	8183.3
Os	251.792	I	178.2
Fe	251.810	I	1763.6
Os	251.844	I	264.9
Ho	251.873	II	155.6

3.2. Repeatability and reproducibility

All individual analyses are conducted in at least seven replicates with %RSD < 3 to prove repeatability. Reproducibility was conducted as replicate measurements of the same sample from several calibration curves, and calculated by means of pooled standard deviation, also used for assessing method precision.

Quality control measures, such as analysing standard reference materials and control samples, are regularly implemented. The instrument's analytical parts, the sample introduction system and the plasma torch, have been regularly maintained and cleaned to prevent contamination and ensure consistent performance. The cleaning of the plasma torch with a mixture of trace element nitric and chloric acids, prepared as 50 % aqua regia, was done on a weekly basis. The stability of the emission signal is maintained by optimizing the analytical parameters, such as rinsing time, sample uptake time, plasma stabilization time, and reading time, as part of a validation process. These parameters can differ depending on the instrumental setting used, such as the autosampler, the sample introduction system, and the connecting tubing.

3.3. Linearity

Linearity is assessed by plotting calibration curves and evaluating correlation coefficients, ensuring that the method accurately measures analyte concentrations across its intended linear range, without significant deviation from linearity [9]. Figure 2a) and Figure 2b) also show the linear equation and the correlation coefficient related to each calibration curve. The correlation coefficient is close to 1 (R^2 > 0.9999), thus, it indicates a strong linear correlation between the measured response and the analyte concentration. Linearity was assessed using residual plots and the root mean square error (RMSE) to measure average residual magnitude. Normalized RMSE (N.RMSE) was also calculated to adjust for data scale, enabling easier comparison across datasets or models. A lower RMSE value indicates a better fit of the calibration curve to the data, and N.RMSE values close to 1 % demonstrate very good accuracy of the calibration fit [10]. Figure 3 shows an example of calculated residuals given in chart and calculated RMSE value and RMSE value normalized for the linear range.

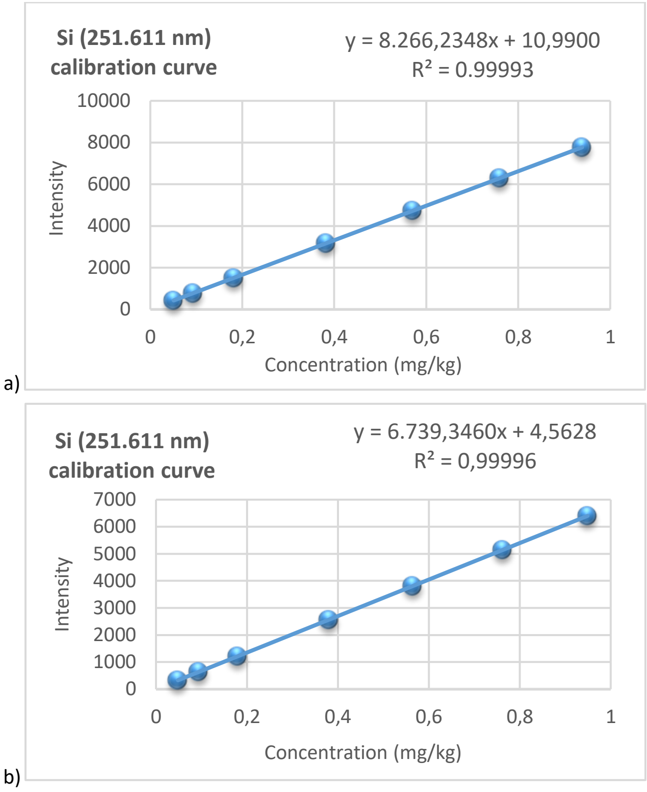

Figure 2. Examples of used calibration curves for silicon at selected analytical line (generated by MP-AES software).

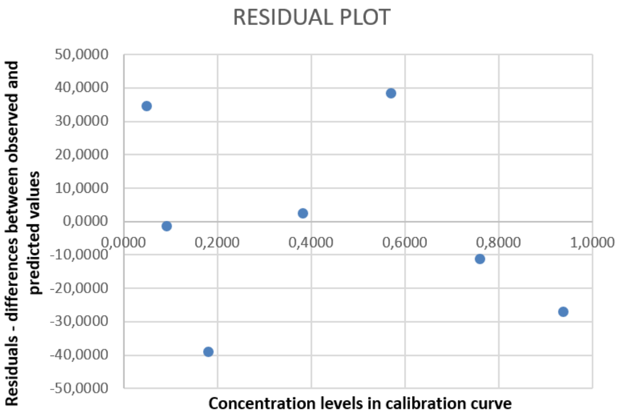

Figure 3. Residual plot for one of the calibration curves used given in Figure 2 a).

The root mean square error $\boldsymbol{RMSE}$ and the normalized root mean square error $\boldsymbol{N.RMSE}$ were calculated using the following equations:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(y_i - y_i')^2}{n}}\,, \tag{1}$$

where n is the number of measurements, y_i is the actual value for the i^{th} measurement, and y_i' is the predicted value for the i^{th} measurement; and

$$N.RMSE = \frac{RMSE}{MAX_{y_i} - MIN_{y_i}} \cdot 100\,, \tag{2}$$

where MAX_{y_i} is the maximum value of the actual data set and MIN_{y_i} is the minimum value of the actual data set.

3.4. Sensitivity

Analytical sensitivity is the change in instrument response, which corresponds to a change in the measured quantity (for example an analyte concentration), i.e. the gradient of the response curve [9]. Sensitivity depends on factors such as the sample matrix, the concentration range, the detection system performance, and the analytical line selected. Optimising these parameters improves overall method performance. Sensitivity was evaluated through the determination of the limits of detection (LOD) and quantification (LOQ). LOD is the lowest concentration of the analyte that can be detected by the method at a specified level of confidence [9]. For validation purposes, LOD was assessed by measuring the sample at a concentration halfway between the blank measurement and the first calibration point in 10 replicates, while LOD was calculated by multiplying the pooled standard deviation of two sets of 10 replicates by a factor of 3. LOQ is the lowest level of analyte that can be determined with acceptable performance in terms of precision and trueness [9]. LOQ is crucial for ensuring that analyte concentrations can be accurately determined, rather than just detected. For validation purposes, LOQ was calculated by multiplying the pooled standard deviation of two sets of 10 measurements by a factor of 10. LOD value is 0.0038 mg Si/kg of analytical solution, and LOQ value is 0.0116 mg of Si/kg of analytical solution. Replicate readings for the calculation of LOD and LOQ, spiked blank (0.02 mg/kg and 0.015 mg/kg, respectively), are given in Table 2.

Table 2. Raw experimental data serving as the basis for LOD and LOQ.

No.	Set 1. Readings	Set 2. Readings
	(spiked blank at 0,020 mg/kg)	(spiked blank at 0,015 mg/kg)
1	0.0186	0.0133
2	0.0173	0.0137
3	0.0198	0.0137
4	0.0185	0.0124
5	0.0168	0.0131
6	0.0178	0.0149
7	0.0179	0.0124
8	0.0196	0.0115
9	0.0171	0.0111
10	0.0187	0.0109
Std deviation	0.00101 mg/kg	0.00128 mg/kg
Pooled std deviation	0.00116 mg/kg	
LOD	3*pooled std deviation	0.0038 mg/kg
LOQ	10*pooled std deviation	0.0116 mg/kg

3.5. Precision

Precision is a measure of how close the results of replicate measurements are to one another [9]. It is assessed using statistical parameters such as standard deviation or relative standard deviation. High precision indicates minimal variation, ensuring reliable quantitative analysis. For validation, intra-laboratory reproducibility for the sample at a concentration close to the middle of the linear range was measured in seven replicates and evaluated using the Grubbs outlier test and the F test, confirming data reliability. No outliers were detected, and the F test (α = 0.1) was passed. Pooled standard deviation was used to measure method precision. Precision given as the pooled standard deviation of four data sets in seven replicates is 0.0081 mg of Si/kg of analytical solution.

3.6. Derivatization efficacy

The derivatization efficacy assessment for total silicone measurement involved evaluating the recovery data of total silicone measurement from siloxane compounds subjected to derivatization. Selected siloxane compounds (L2 and D4) were derivatised, according to a specified procedure, to form a more stable or detectable derivative of silicon, namely SiF_6^{2-} anion that is stable in acidic media (2 % nitric acid). The derivatized samples were analysed by means of the described AES method. Recovery [9] is calculated by comparing the measured concentration of total silicone from derivatized siloxanes to the predicted calculated concentration, assuming a 100 % derivatization efficacy. Recovery data for two selected siloxanes, D4 and L2, ranged from 99.53 % to 101.90 %, respectively, proving that the derivatization process is optimised and quantitative.

3.7. Bias

Gas-phase sampling was carried out using the reference gas mixture NPL ID A623. This mixture includes the target components at their respective concentrations in a methane matrix, as shown in Table 3.

This reference mixture was analysed as an unknown sample for the purpose of estimating the bias of the optimized method, including sampling, derivatization, dilution, and analysis steps. The bias was estimated by means of the recovery value. Table 4 presents the results for the three reference gas samples—each analysed in seven replicates—including the collected gas volume, the dilution factor, the calculated and measured silicon mass fractions, the measured silicon concentration, recovery (efficiency), linearity (R^2), and the standard deviation of measurements. The values of relative bias demonstrated quantitative analysis with values close to 100 % recovery rate [11]. The uncertainty for bias [12] was calculated using the following equation:

Table 3. Composition of reference gas mixture.

Component	Amount fraction (mg/m³)	Amount fraction (µmol/mol)
L2	0.125	0.054
L3	0.125	0.036
D4	0.125	0.027
D5	0.125	0.021
This mixture corresponds with the overall silicon content of 0.500 mg/m³ ± 0.08 mg/m³.		

Table 4. Measurement results for the reference gas mixture (NPL A623) used to evaluate recovery and bias.

Parameter	Sample 1	Sample 2	Sample 3
	(NPL A623) Silicon content 0.5 mg/m³ ±0.08 mg/m³		
Volume collected at ambient pressure in dm³	4.360	5.368	4.010
Dilution factor	2	2	2
Calculated Si mass fraction assuming 100 % efficiency in mg/kg	0.0201	0.0139	0.0124
Measured Si mass fraction from calibration curve in mg/kg	0.0211	0.0134	0.0125
Measured Si concentration in mg/m³	0.53	0.48	0.51
Efficiency – recovery in % as a measure of bias	105	96	101
Linearity as squared correlation coefficient r²	0.9964	0.9987	0.9974
Standard deviation of measurements (7 replicates) in mg/kg	0.0007	0.0005	0.0005

$$u_{\mathrm{bias}} = \sqrt{u^{2}{}_{\bar{x}} + u_{\mathrm{ref}}^{2}}\,, \tag{3}$$

where u_{bias} is the uncertainty from bias, u_{ref} is the standard measurement uncertainty of silicon concentration in reference gas mixture, and $u_{\bar{x}}$ is the mean standard deviation of measurement results for three reference samples, each analysed in seven replicates.

The calculated Si mass fraction, assuming 100 % efficiency and expressed in mg/kg of the analytical solution, was determined through a series of steps. First, the mass of Si in the collected reference gas volume was calculated based on the certified value. Next, it was assumed that the same mass of Si was fully transferred into the liquid absorbent and derivatization reagents, considering a theoretical absorption and derivatization efficiency of 100 %. Finally, this value was adjusted to mg/kg of the analytical sample and compared to the measured results to determine the recovery rates.

3.8. Measurement uncertainty

The combined measurement uncertainty was determined using an empirical approach [12], [13]. After identifying all relevant uncertainty sources, the combined uncertainty was calculated as the square root of the sum of the squared individual contributions, using equation (4), expressed in concentration units for silicon determination (see Table 5).

$$u_{\mathrm{c}} = \sqrt{u_{\mathrm{prec}}^{2} + u_{\mathrm{bias}}^{2} + u_{\mathrm{cal\ curve}}^{2} + u_{\mathrm{Si\ standard}}^{2}}\,, \tag{4}$$

where u_{prec} is the pooled standard deviation of silicon measurements under reproducibility conditions, u_{bias} is the uncertainty of the bias from silicon measurement using a reference gas mixture, $u_{\mathrm{cal\ curve}}$ is the uncertainty of the calibration curve (linear fit), and $u_{\mathrm{Si\ standard}}$ is the uncertainty of the certified Si solution used for calibration standards (NIST® SRM 3150).

Expanded measurement uncertainty is calculated by multiplying the combined measurement uncertainty with the coverage factor $k = 2$ (which indicates approximately 95 % confidence).

Table 5. Measurement uncertainty budget.

Measurement uncertainty sources and budget		
Individual uncertainties	***u***	**unit**
u_{prec}	0.0081	mg/kg of Si
u_{bias}	0.0040	mg/kg of Si
$u_{\mathrm{cal\ curve}}$	0.0024	mg/kg of Si
$u_{\mathrm{Si\ standard}}$	0.0015	mg/kg of Si
Combined measurement uncertainty	0.0095	mg/kg of Si
Expanded measurement uncertainty (*k*=2)	0.0190	mg/kg of Si
Relative expanded measurement uncertainty	1.9	%

4. DISCUSSION AND CONCLUSIONS

This study has demonstrated the reliability of the AES for silicon determination in biomethane, ensuring compliance with ISO 2613-1 and alignment with ISO/IEC 17025 requirements for testing laboratories. The method showed excellent stability and selectivity in complex matrices, strong repeatability with %RSD below 3 %, and high reproducibility confirmed through pooled standard deviation. The linearity of the method was verified with correlation coefficients exceeding 0.9999, while sensitivity assessments established LOD at 0.0038 mg Si/kg and LOQ at 0.0116 mg Si/kg, ensuring the capability to detect low silicon concentrations accurately. Precision validation showed no outliers, and measurement uncertainty evaluation yielded a combined uncertainty of 0.0095 mg Si/kg, with a relative expanded uncertainty of 1.9 %. Derivatization efficacy assessments confirmed quantitative conversion, with recovery rates between 99.53 % and 101.90 %. These findings confirm that the AES method is fit-for-purpose in silicon quantification within biomethane, supporting industry compliance and regulatory requirements.

Compliance with ISO 2613-1 was demonstrated, establishing this method as a suitable guideline for testing laboratories performing silicon analysis in biomethane. The validation approach [14], [15] provides a framework for laboratories utilizing AES or similar methodologies, ensuring accurate, precise, and reliable silicon measurement, in line with international quality and metrology standards. Furthermore, it aligns with the broader framework of EN 16723 [16], which establishes quality specifications for biomethane injection into the natural gas grid and its use as a transport fuel. A key aspect of EN 16723 is ensuring that biomethane meets strict impurity limits, including silicon, to prevent damage to combustion engines and gas infrastructure. The findings of this study fit within the scope of the report *Requirements for the Performance Assessment Protocol for Measurement Systems Used in Biomethane Conformity Assessment*, generated during the realization of the 21NRM04 BiometCAP project. Both this study and the report emphasize the importance of precision, selectivity, sensitivity, and measurement uncertainty in biomethane analysis. Our research confirms that the biomethane matrix is free from interfering elements, ensuring accurate silicon quantification, in line with the need for selective and interference-free methods highlighted in the report. Additionally, the limits of detection and quantification determined in this study, as well as relatively low estimated overall uncertainty of measurement results, provide a robust basis for traceable silicon measurement, addressing the critical requirement for accurate impurity assessment in biomethane quality control. The assessment of biomethane quality must be conducted using metrological principles to ensure reliable, comparable, and traceable results across different laboratories and measurement systems. The presence of silicon, primarily from siloxanes in biogas, poses a significant risk to engines, turbines, and natural gas grid infrastructure due to the formation of abrasive silica deposits upon combustion. By applying a rigorously validated method for silicon determination, this research contributes to the broader goal of maintaining biomethane as a high-quality, sustainable fuel that meets regulatory standards and protects energy infrastructure. The demonstrated compliance with ISO 2613-1 ensures that this method can serve as a guideline for testing laboratories conducting silicon analysis in biomethane or similar gaseous matrices, reinforcing the role of metrology in safeguarding fuel quality and optimizing the biomethane supply chain.

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