EMPIR JRP 16ENG05
Metrology for Biomethane
Final Workshop

NWIP for total silicon concentration

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Introduction to the topic

EMPIR JRP 16ENG05 has been dedicated to the development and validation of traceable analytical methods for trace pollutants found in biomethane, including silicon containing compounds.

Due to the extensive usage of siloxane compounds, their volatility and great affinity to apolar environments, siloxanes are considered as one of the most important impurities in biogas/biomethane. They are undesired because of their potential for abrasive SiO_2 formation as combustion product that can damage engines and appliances. Furthermore, some of these compounds present a health risk.

This NWIP describes the analytical method for measuring the total silicon concentration in biomethane and similar gaseous matrices.

Scope of the proposed NWIP

The proposed NWIP is applicable to the measurement of the total silicon contained within siloxane compounds in gaseous matrices such as biomethane, biogas and landfill gas. Analytical form of the silicon measured in liquid phase after conducted sampling and derivatisation procedure is soluble hexafluorosilicate anion stable in slightly acidified media. Total silicon is expressed as a mass of silicon in the volume of the analysed gas.

The proposed NWIP is applicable to the mentioned gas matrices with silicon concentrations up to 5 mg/m^3. For the purpose of the EMPIR 16ENG05 the method has been specifically optimized for biomethane containing 0,1 to 0,5 mg/m^3.
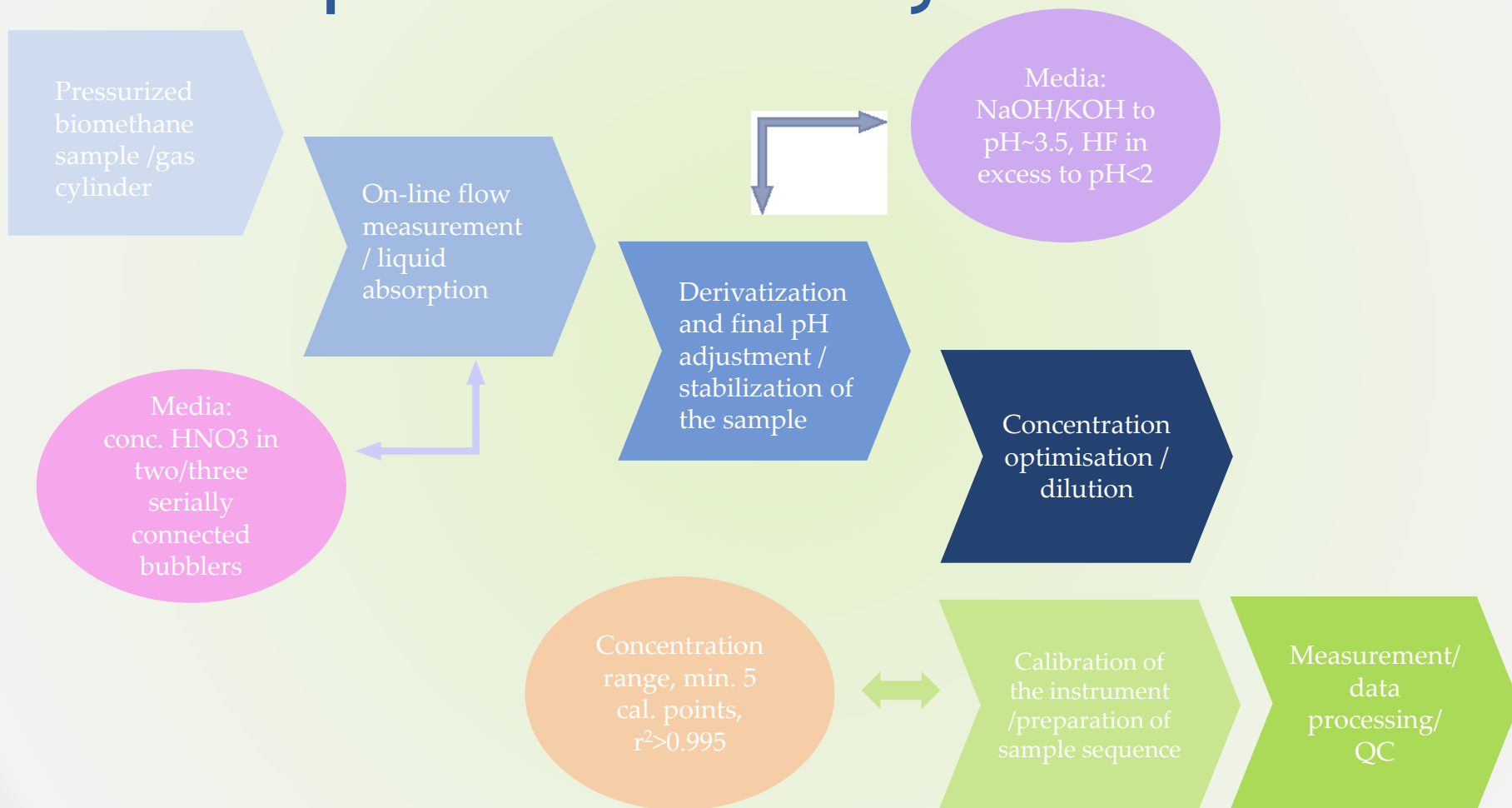
It can be used for higher concentration but then the absorption efficiency needs to be checked before the results can be regarded as valid. The detection limit of the method is estimated as 0,05 mg/m^3 based on a sample volume of 0,020 m^3.

Principle of the analytical method

Methane matrix gas sample containing siloxane compounds is passed through liquid absorbent (nitric acid) in serially connected gas bubblers/impingers to collect the silicon-containing compounds. After sampling of adequate gas volume, content of sampling vessels (gas bubblers) is subjected to derivatisation by adding hydroxide solutions and hydrofluoric acid in order to obtain silicon in analytical from, hexafluorosilicate anion.

Derivatised sample is analysed for silicon content using ICP/MWP atomic emission spectrometer at selected characteristic silicon emission wavelengths by means of weighted linear line calibration generated from standard silicon solutions.

Principle of the analytical method

Pressurized biomethane sample /gas cylinder

On-line flow measurement / liquid absorption

Media: NaOH/KOH to pH~3.5, HF in excess to pH<2

Derivatization and final pH adjustment / stabilization of the sample

Media: conc. HNO3 in two/three serially connected bubblers

Concentration optimisation / dilution

Concentration range, min. 5 cal. points, r²>0.995

Calibration of the instrument /preparation of sample sequence

Measurement/ data processing/ QC

Method flow-chart

Necessary (laboratory) prerequisites

For the conduction of the proposed method the following reagents and labware is required:

- **Absorber media:**

Concentrated nitric acid (HNO_3);

- **Derivatization media:**

a) Sodium or potassium hydroxide pellets;

b) Concentrated hydrofluoric acid (HF);

- **Dilution media:** Reagent water, complying with grade 1 of ISO 3696

Necessary (laboratory) prerequisites

- **Optimization and quality control:**

Pure siloxane compounds:

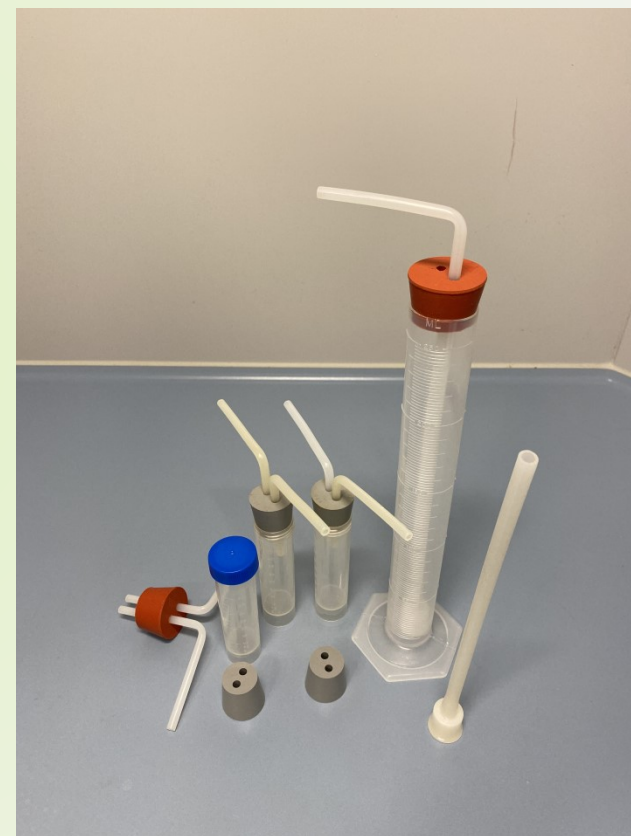a) Linear siloxanes: L2, L3, L4, L5;

b) Cyclic siloxanes: D3, D4, D5, D6.

Pure siloxane compounds used

Necessary (laboratory) prerequisites

- **pH colour-fixed indicator strips**, pH range from 0-14;

- **Volumetric plastic vessels** (50, 100, 200 ml)

- **Plastic gas bubblers/impingers** with tubing, 20-50 ml;

Improvized gas bubblers used

Necessary (laboratory) prerequisites

- **Certified ICP-Si stock standard solution** or pure soluble silicon salt e.g. NH_4SiF_6 for gravimetric preparation

NIST traceable Si standard solutions and solid ammonium hexafluorosilicate

Necessary (laboratory) prerequisites

- **Digital or manual automatic pipettes**, adjustable volume 1-5 mL, and 20 – 200 μl with silicon free tips

- **Plastic vessels** for the derivatisation, 200 ml capacity with stoppers, heat durable

- **Stirring rod**, plastic, silicon free

Examples of plastic vessels used

# Necessary (laboratory) prerequisites

For the conduction of the proposed method the following instrumentation is required:

- **MWP or ICP emission spectrometer** capable of measuring silicon emission lines (250,590 nm; 251,432 nm; 251,611 nm (the most sensitive line); 288,158 nm) with a minimum optical resolution 0,05 nm;

- **Gas flow meter** with temperature sensor, calibrated with methane, range: 0-20 ml/L with the software readout of normalized values for the volume of gas;

- **Gas cylinder**(s) with gas pressure regulator;

- **Analytical balance** accurate to 0,01 mg;

- **Laboratory fume hood** with constant ventilation EX design.

Necessary (laboratory) prerequisites

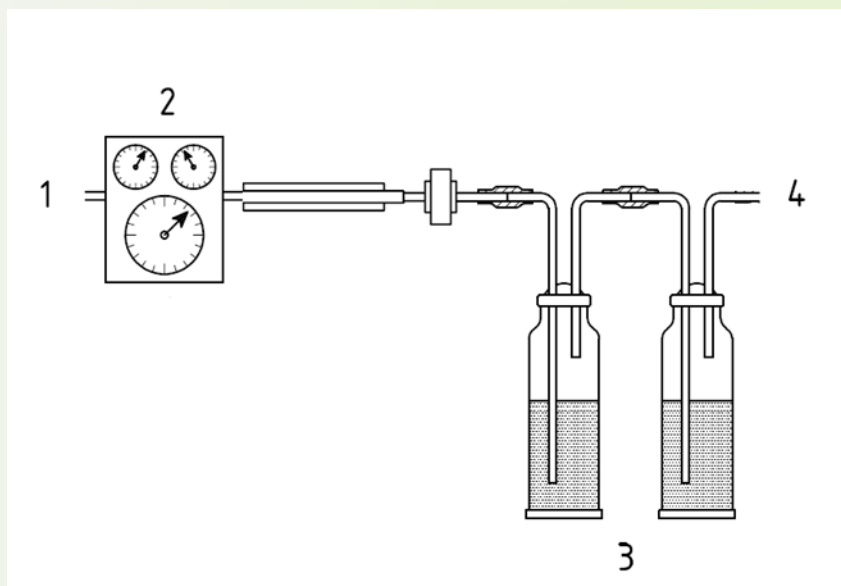MWP emission spectrometer and gas flow meter use in this study:
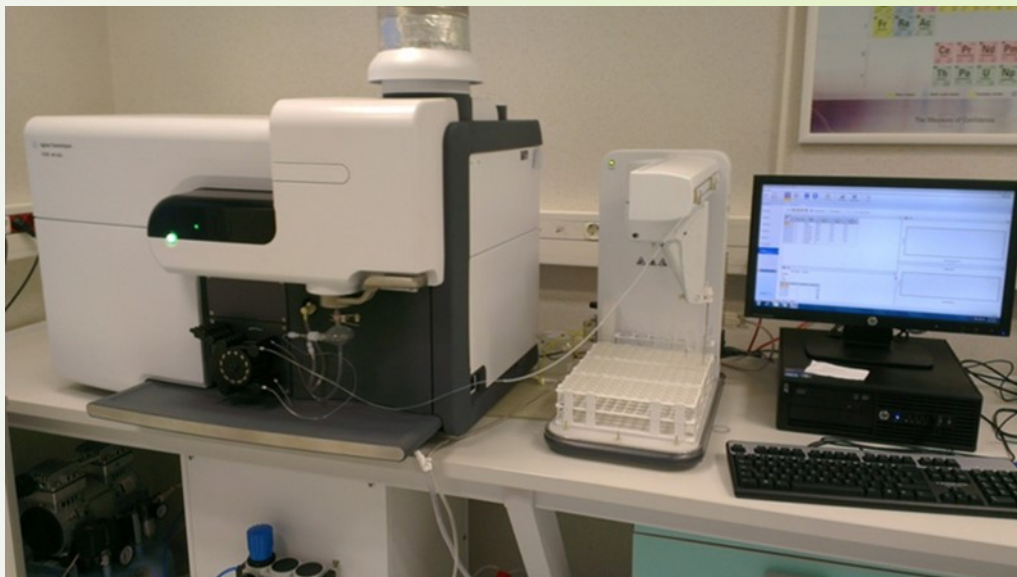
Agilent 4200 MP-AES equipped with peristaltic pump, nebulizOneNeb nebulizer, inert torch and autosampler

Aalborg DFM 26 S-TAL2-AA2

Sampling and sample derivatisation

Legend

1 pressurised gas cylinder with pressure regulator attached
2 gas flow controller with temperature sensor
3 gas bubbler/inpingers containing absorbent
4 exhaust for the excess gas

Sampling is performed from pressurized gas cylinder equipped with gas pressure regulator displaying the pressure inside cylinder as well as the outlet pressure.

Gas regulator is airtight connected to the gas flow meter with plastic silicon free tubing ensuring quantitative measurement of gas flow and volume released.

Gas flow meter is connected with the same type of plastic silicon free tubing with serially connected gas 2 to 3 bubblers containing absorbent media.

Sampling and sample derivatisation

It is necessary to ensure that the opening of the tube through which the gas is being introduced in the bubblers is immersed in the absorbent.

Sampling flow should be kept constant at approximately 10 ml/min and the normalized total volume of gas passed read from the flow meter after the sampling was finalized. Adjust the gas volume sampled in accordance with the expected level of silicon in the sample (total volume should be in the range of 2-20 dm^3 of gas).

Sampling and sample derivatisation

Absorbent media from the bubblers after the sampling is quantitatively transferred to derivatisation vessel. Solution of sodium or potassium hydroxide is added dropwise until slightly basic pH is reached.

After basic pH of the solution is reached, the appropriate volume of concentrated hydrofluoric acid is immediately added dropwise until acidic pH value of around 3,5 is reached. Reagent water is added for dilution. Vessels are weighed prior and after derivatisation for gravimetric calculation of liquid content.

Samples can be subjected to further dilution if needed to obtain concentration within calibration range.

Analytical procedure

The data processing unit of the ICP/MWP spectrometer is used to establish a measuring program in which the intensities of the silicon emission lines 250,590 nm, 251,611 nm and 288,158 nm are measured in the same sample simultaneously or within very short timeframe.

Upon selection of the silicon emission lines, the nebulizer pressure and viewing position are optimized.

This check should be performed prior to every calibration and analysis since it strongly depends on the plasma stability, ionic strength and density of the sample, total dissolved solids and other matrix characteristics.

Analytical procedure

A minimum of five calibration solutions in accordance with expected silicon concentration in the collected sample are prepared using the certified Si solution (exp. range from 10 μg Si/kg to 200 μg Si/kg);
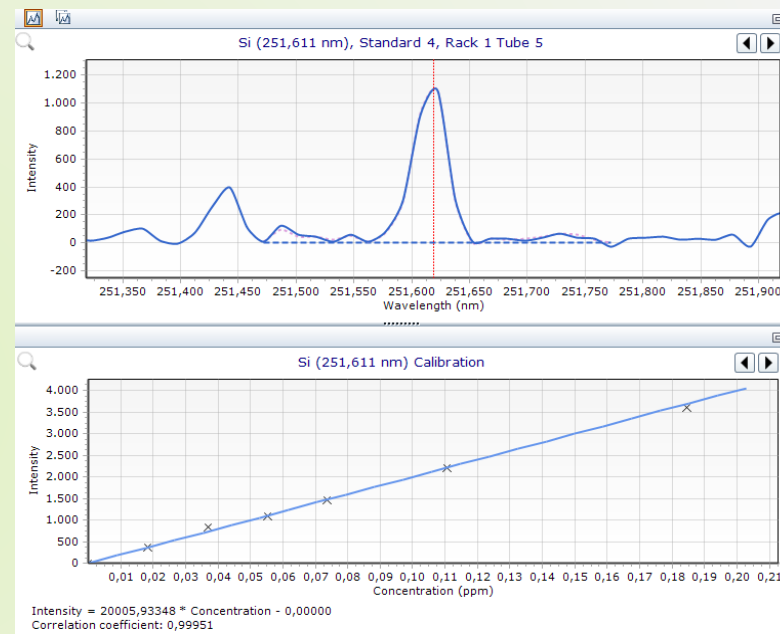
All necessary QC samples including blanks are gravimetrically prepared;

Analytical sequence consisted of standard solutions, QC samples and samples is created and analysis is performed.

Quality control and expression of results

QC samples:

- Blanks:

Three types of blanks are used during the analysis.

a) The **calibration blank** is used in establishing the analytical curve,

b) The **laboratory reagent blank** is used to assess possible contamination from the sample preparation procedure and

c) The **rinse blank** is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

Quality control and expression of results

QC samples:

- **Instrument performance check i.e. wavelength calibration control sample** (mix standard solution usually provided by the producer of the equipment);

- **Calibration Control Sample (CC)** is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The CC must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards.

Quality control and expression of results

QC samples:

- **Derivatization control sample (DC)** is required for initial and periodic verification of the completeness of the derivatization process. For this purpose pure siloxane compounds are used.

- **Reference gas mixture** (methane) with certified silicon content (optional) in the range 0,1 to 0,5 mg/m^3.

Calculations and expression of results

Upon establishment of calibration function by linear regression using the data obtained from the measurement of the calibration solutions, calculation of the mass concentration of silicon ρ(Si) expressed in mg/kg in the liquid derivatised sample including any dilutions prior to readings is done as follows:

$$\rho(Si) = \rho_x(Si) \; x \; D$$

$\rho(Si)$ mass concentration of silicon in liquid sample expressed in mg/kg
$\rho_x(Si)$ mass concentration of silicon in liquid sample expressed in mg/kg read from the calibration curve
D dilution factor (non-dimensional number)

Calculations and expression of results

The mass concentration of silicon $\rho_g(Si)$ in gas sample expressed in mg/m^3 of sample gas is calculated as follows:

$$\rho_g(Si) = \frac{\rho(Si) x\ m_x}{Vx}\ x\ 10^3$$

$\rho_g(Si)$ mass concentration of silicon in gas sample expressed in mg/m^3

m_x mass of the liquid derivatized sample in derivatization vessel expressed in kg

V_x volume of sample gas collected expressed in dm^3 (normalized to STD)

10^3 conversion factor to cubic meters of gas

The values are rounded to the nearest 0,01 mg/m^3.

Conclusions

Developed method for testing total silicon in biomethane and similar gas matrices were presented. The optimization of method parameters was adapted to treated biogas matrices (biomethane), enabling the analysis of low levels (μg/kg range) of total silicon derived from siloxane compounds.

Development of the method compiled all preparation and analytical steps considering different approaches in order to reach optimal conditions with minimal laboratory resources and within a reasonable time.

The application of the described analytical procedure requires laboratory staff well acquainted with the basic principles of analytical chemistry as well as the precautions when handling dangerous chemicals, such as hydrofluoric acid. Analyst must be familiar with spectroscopic analytical principles in order to be able to interpret the results and to prepare the instrumental setting.

Conclusions

The development of the method was entirely performed within the implementation of the 16ENG05 project.

In order to optimize and validate the method with respect to the instrumental part and the efficiency of derivatization, a large number of confirmatory experiments have been carried out on the basis of which it can be concluded that the method is satisfactory in terms of precision and quantitativeness.

At the same time, insufficient number of practical gas sampling experiments were carried out due to the unavailability of suitable gas mixtures due to difficulties in the procedure of import and export of gas cylinders. For this reason, insufficient data were collected to verily confirm absorption efficiency.

Thank You for Your attention!

For additional information please visit: http://empir.npl.co.uk/biomethane/
and/or contact project coordinator and relevant project partners

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