SLOVENSKI STANDARD
oSIST prEN ISO 2613-1:2022

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Analiza zemeljskega plina - Vsebnost silicija v biometanu - 1. del: Določevanje celotnega silicija z atomsko emisijsko spektrometrijo (AES) (ISO/DIS 2613-1:2022)

Analysis of natural gas - Silicon content of biomethane - Part 1: Determination of total silicon content by AES (ISO/DIS 2613-1:2022)

Analyse von Erdgas - Siliziumgehalt von Biomethan - Teil 1: Bestimmung des Gesamtsiliziumgehalts durch AES (ISO/DIS 2613-1:2022)

Analyse du gaz naturel - Teneur en silicium du biométhane - Partie 1: Détermination de la teneur en silicium total par AES (ISO/DIS 2613-1:2022)

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ICS:

75.060	Zemeljski plin	Natural gas

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Analysis of natural gas — Silicon content of biomethane —

Part 1:
Determination of total silicon content by AES

ICS: 75.060

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing documents is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document describes a method for the measurement of the total concentration of silicon in biomethane, biogas and similar gaseous matrices when used in the natural gas grids and when using it as a transport fuel. The method is based on using a liquid impinger to accumulate the silicon from a gas sample, followed by instrumental analysis.

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. 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.

For the purpose of this document, silicon specie measured is quoted as total silicon. Silicon measured is from siloxane compounds that are trapped from the gas phase in liquid media and derivatized into analytical form of hexafluorosilicate (SiF_6^{2-}) ions which remain present in solution when analysed.

Analysis of natural gas — Silicon content of biomethane —

Part 1: Determination of total silicon content by AES

1 Scope

This document is applicable to the measurement of the total silicon content in gaseous matrices such as biomethane and biogas. Silicon is present in a gas phase contained predominantly in siloxane compounds, trimethylsilane and trimethylsilanol. The analytical form of the silicon measured in liquid phase after conducted sampling and derivatization 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.

This document is applicable to stated gaseous matrices with silicon concentrations up to 5 mg/m^3, and it is prevalently intended for the biomethane matrices containing 0,1 mg/m^3 to 0,5 mg/m^3 Si. With adaptation to ensure appropriate absorption efficiency, it can be used for higher concentrations. The detection limit of the method is estimated as 0,05 mg/m^3 based on a gas sample volume of 0,020 m^3. All compounds present in the gas phase are volatile at the absorption and derivatization temperature and gaseous siloxanes are trapped in absorbance media and derivatized into analytical silicon that is measured by this method. The concentration of the silicon is measured in diluted derivatization media using atomic emission spectrometry upon atomisation/ionisation in microwave or inductively coupled plasma.

Unless specified otherwise, all volumes and concentrations refer to normal conditions.

NOTE When using appropriate dilution factors, the method can also be applied for silicon concentrations above 5 mg/m^3.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 14532, *Natural gas — Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

ISO 14912, *Gas analysis — Conversion of gas mixture composition data*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
Siloxanes
functional groups where two silicon atoms are connected via an oxygen atom

Note 1 to entry: Depending on the substrate used to produce biogas and the process used for purification, biomethane can contain siloxanes. During combustion, siloxanes can be oxidized to silicon dioxide, an abrasive compound harmful for mechanical moving parts in e.g. engines and turbines [8].

3.2
atomic emission spectroscopy (AES)
a method of chemical analysis that uses the intensity of light emitted from a flame, plasma, arc, or spark at a particular wavelength to determine the quantity of an element in a sample

4 Principle

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

A methane matrix gas sample (e.g., biomethane, biogas, natural gas and blends thereof) 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 an adequate gas volume, content of sampling vessels (gas bubblers) is subjected to derivatization by adding hydroxide solution and hydrofluoric acid in order to obtain silicon in analytical from, hexafluorosilicate (SiF_6^{2-}) anion.

The derivatized sample is analysed for silicon content using an ICP/MWP atomic emission spectrometer at selected characteristic silicon emission wavelengths using a multipoint calibration using a straight line obtained from analysing a series of standard silicon solutions.

5 Reagents and labware

To carry out the method, the following reagents shall be of a recognized analytical grade and only ISO 3696 grade 1 water. If it is visually determined that the reagents have changed their appearance (colour, consistency, turbidity) they shall be discarded, and fresh ones shall be used.

5.1 Absorber media

5.1.1 Nitric acid (HNO_3), ρ_{20} = 1,41 g/cm^3; 65 % HNO_3 (mass fraction) – for trace elemental analysis.

CAUTION This chemical is especially dangerous if used outside specialized laboratory conditions. Tests have been performed in which other non-oxo mineral acids (HCl) have been used, but they have been shown to be inadequate for the absorption of siloxanes from the gas phase. Special precautions are to be taken when handling this chemical in lab and field conditions.

5.2 Derivatization media

5.2.1 Sodium hydroxide pellets, for the preparation of 8 mol/L – 10 mol/L hydroxide solution.

Accurately weigh an appropriate amount of sodium hydroxide pellets and dissolve these in an appropriate amount of reagent water (5.3). As an example for 100 ml of 10 mol/l sodium hydroxide solutions, weigh 40 g of sodium hydroxide pellets and dissolve in 100 ml water.

Potassium hydroxide can also be used, but sodium hydroxide is preferred due to operation safety.

WARNING — Reaction of dissolving sodium hydroxide in water is highly exothermic! Heat will be released and care should be taken when handling the reaction. Add pellets slowly to the water and cool the dissolution vessel until the dissolution is complete.

5.2.2 Hydrofluoric acid (HF), $\rho_{(20°C)}$ = 1,16 g/cm^3; 48 % HF (mass fraction).

WARNING — Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages: firstly, by hydration that induces tissue necrosis; and secondly, by penetration of fluoride ions deep into the tissue and thereby reacting with calcium. Boric acid and/or other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature for determining the proper protective eyewear, clothing and gloves to use when handling hydrofluoric acid. Always have appropriate treatment materials readily available prior to working with this acid.

CAUTION This chemical is especially dangerous if used outside specialized laboratory conditions. Tests have been performed in which other fluoride donor derivatization reagents (NaF) have been used, but they have been shown to be inadequate for the derivatization of absorbed siloxanes from the gas phase. Special precautions are to be taken when handling this chemical in lab and field conditions

5.3 Water, complying with grade 1 of ISO 3696

5.4 Pure siloxane compounds:

Linear siloxanes Cyclic siloxanes

Hexamethyldisiloxane - L2; $C_6H_{18}OSi_2$ Hexamethylcyclotrisiloxane - D3; $C_6H_{18}O_3Si_3$

Octamethyltrisiloxane - L3; $C_8H_{24}O_2Si_3$ Octamethylcyclotetrasiloxane - D4; $C_8H_{24}O_4Si_4$

Decamethyltetrasiloxane - L4; $C_{10}H_{30}O_3Si_4$ Decamethylcyclopentasiloxane - D5; $C_{10}H_{30}O_5Si_5$

Dodecamethylpentasiloxane - L5; $C_{12}H_{36}O_4Si_5$ Dodecamethylcyclohexasiloxane - D6; $C_{12}H_{36}O_6Si_6$

Use at least one representative of chain and one representative of cyclic siloxane compounds for the purpose of performing initial and regular quality control of the method validity.

5.5 pH colour-fixed indicator strips, pH range from 0 - 14, or, alternatively, a pH meter with HF resistant electrode

5.6 Calibration solutions

5.6.1 General

The following procedure for the preparation of standard and calibration solutions of silicon is adjusted to the lower range of silicon concentration in gas sample. If higher concentrations of silicon shall be measured, adjust the concentrations of the working standard and calibration solutions accordingly.

When determining silicon in aqueous samples, only plastic, PTFE or quartz labware shall be used from time of sample collection to completion of analysis.

5.6.2 Certified ICP-Si stock standard solution

Example of certified Si standard solution is (water, traces HF) 10 000 µg/ml ± 0,5 % or better. It is used for the purpose of demonstration of the calibration solutions preparation.

Certified Si standard solutions of other concentrations can also be used. Adjust the procedure for preparing standard solution accordingly.

If Si stock standard solution is prepared in-house gravimetrically from salt-containing silicon, apply required statistical procedure for obtaining accurate concentration accompanied with uncertainty value.

NOTE References[1][2] provide guidance.