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Analysis of natural gas — Silicon content of biomethane —

Part 1: Determination of total silicon by atomic emission spectroscopy (AES)

Analyse du gaz naturel — Teneur en silicium du biométhane —

Partie 1: Détermination de la teneur totale en silicium par spectrométrie d'émission atomique (SEA)

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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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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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 408, *Biomethane for use in transport and injection in natural gas pipelines,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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 species measured is quoted as total silicon. Silicon measured is from organosilicon species 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 by atomic emission spectroscopy (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 with Si mass concentration of 0,1 mg/m^3 to 0,5 mg/m^3.

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 organosilicon species 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 standard reference conditions (temperature, 273 K, and pressure, 101,325 kPa).

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, *Water for analytical laboratory use — Specification and test methods*

ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*

ISO 14532, *Natural gas — Vocabulary*

ISO 10715, *Natural gas — Gas sampling*

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
siloxane
functional group 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.

3.2
atomic emission spectroscopy
AES
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 document 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), $\rho_{(20\ °C)}$ = 1,41 g/ml; 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), $\rho_{(20\,^{\circ}C)}$ = 1,16 g/ml; 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	Molecular formula	Cyclic siloxanes	Molecular formula
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 to 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 solution (only trace level of HF is acceptable) with Si mass concentration of 10 000 µg/ml and relative expanded uncertainty (coverage factor k = 2) 0,5 %. This concentration is used in the example of the Si standard solution preparation in 5.6.3.

Certified Si stock 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.

5.6.3 Si standard solution.

The target Si mass fraction is ρ(Si) ≈ 100 mg/kg. Weigh empty 50 ml plastic volumetric flask using analytical balance (6.3). Add around 10 ml of 2 % nitric acid (mass fraction). Accurately pipette 0,5 ml of stock solution (5.6.2) and add it to the plastic volumetric flask. Dilute with 2 % nitric acid (mass fraction) to volume. Weigh full plastic volumetric flask and calculate the concentration of silicon.

Store the solution in plastic volumetric flask or similar vessel of silicon free material properly stoppered at room temperature or refrigerated (~5 °C). The solution is stable for at least two weeks if stored properly.

5.6.4 Si calibration solutions.

Gravimetrically prepare a minimum of five calibration solutions in accordance with expected silicon concentration in the collected sample.

As an example proceed as follows for the Si mass fraction range from 10 µg/kg to 200 µg/kg.

Weigh empty 100 ml (or 200 ml) plastic volumetric flasks.

Pipette 10 µl; 20 µl; 50 µl; 75 µl; 100 µl; 150 µl; and 200 µl; respectively of silicon standard solution (5.6.3) into 100 ml one-mark plastic volumetric flask that was empty-weighted and prefilled with around 10 ml - 20 ml of 2 % nitric acid (mass fraction). Dilute with 2 % nitric acid (mass fraction) to volume. Weigh full plastic volumetric flask and calculate the concentration of silicon.

The Si mass fraction in the calibration solutions is 10 µg/kg; 20 µg/kg; 50 µg/kg; 75 µg/kg; 100 µg/kg; 150 µg/kg and 200 µg/kg respectively.

Calculate the uncertainty of the mass fractions of the calibration solutions. Check what the contributions are of the combination of shared effects, such as the uncertainty of the concentration of the stock solution and the calibration of the pipette. If these effects account for more than 40 % of the uncertainty budget, then calculate the dilution factors and their associated uncertainties. Then the concentrations of these standards are substantially correlated.

5.6.5 Solution for wavelength calibration control.

Perform wavelength check using solution containing assorted elements covering the wavelength range of the instrumentation used provided by the manufacturer prior to daily calibration of the instrument for the analysis of silicon. This solution is usually provided as concentrate that needs to be diluted prior to the analysis in accordance with the manufacturer's instructions. Wavelength calibration control test result shows if the optical settings of the instrument are appropriate, and if the readings of the emission

lines for each individual element correspond to the instrumental settings when selecting the analytical wavelengths for the analyte of interest.

NOTE The solution for wavelength calibration control is usually provided by the manufacturer of the equipment.

5.7 Quality control.

5.7.1 Blanks.

Three types of blanks are used during the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess any contamination from the sample preparation procedure and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

5.7.1.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards; in this case it is 2 % nitric acid (mass fraction). The calibration blank should be stored in a plastic container as samples.

5.7.1.2 The laboratory reagent blank should contain all the reagents in the same volumes as used in the processing of the samples. The laboratory reagent blank shall be carried through the same entire preparation scheme as the samples including sample derivatization. This type of blank should be prepared at least every time new reagents are used.

5.7.1.3 The rinse blank is prepared by acidifying reagent water to the same concentrations of nitric acid as used in the calibration blank and stored in a convenient manner.

5.7.1.4 Labware blank – pure methane gas free from silicon used as blank gas sample to test the cleanliness of labware used.

5.7.2 Instrument performance check i.e. wavelength calibration control sample (5.6.5).

5.7.3 Calibration Control Sample (CC).

A calibration control sample shall be used for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The CC shall be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. It can be either ready standard solution obtained from a different supplier, or at least from a different lot, or it can be prepared gravimetrically using pure $(NH_4)_2SiF_6$ salt. The concentration of the silicon in the CC solution should be near to expected concentration of silicon in the sample or at the middle of calibration range. A fresh solution should be prepared prior to the analysis and stored in plastic container as samples.

5.7.4 Derivatization control sample (DC).

A derivatization control sample shall be used for initial and periodic verification of the completeness of the derivatization process. For this purpose pure siloxane compounds are used. For example, L2 and D4 siloxanes represent linear and cyclic siloxanes found in biomethane matrices. Other siloxanes may be used as well. The DC is prepared by accurately pipetting appropriate amount of siloxane with previously calculated mass of silicon contained, and adding this amount to the aliquot of nitric acid thus simulating the absorbance procedure. The solution of siloxane(s) is then subjected to derivatization by adding appropriate amount of hydroxide solution and hydrofluoric solution. The DC should be stored in a plastic container as sample. Concentration of the silicon in DC shall be within the calibration range and can be adjusted by dilution if needed.

5.7.5 Reference gas mixture of siloxanes in methane with certified silicon content, over the mass concentration range of 0,1 mg/m³ to 0,5 mg/m³.

Certified reference gas mixtures containing different siloxanes and combinations of siloxanes in methane are available with certified siloxane amount fractions. These amount fractions can be converted to a total silicon concentration, but it should be noted that the total silicon in the mixture may differ, i.e. be higher due to siloxane impurities that are present as non-certified siloxanes. Such gas mixtures are suitable for assessing the recovery of the sampling and derivatization.

ISO 14912 shall be used for the conversion of amount fractions to concentrations, including the associated uncertainties.

6 Apparatus

6.1 Sampling and derivatization equipment.

An outline of the equipment for the sampling of gas is given in Figure 1. The apparatus consists of a gas flow meter and an impinger train containing absorbent (concentrated nitric acid) to capture gaseous siloxanes. A thermometer shall be used if the laboratory has no controlled ambient temperature within ±3 °C. If gas flow meter used is not equipped with the embedded ambient pressure sensor providing data for normalization to standard reference conditions of 273,15 K and 101,325 kPa, a barometer shall be used to measure atmospheric pressure during collection of the gas. Using the measured temperature and pressure, volumes and concentrations shall be converted to appropriate standard reference conditions.

All tubing, gaskets and seals used to for passing of the sample gas, as well as the impingers and derivatization vessels and stirring rod shall be made of plastic polymer silicon free.

The sampling and sample derivatization described in this document refers to the laboratory equipment and conditions. Specialized sampling equipment may be used that allows the absorption of siloxane from the gaseous medium in the field if the described requirements are met.

Field sampling/absorption and derivatization were not covered by the study during the development of this standard. In the case of the development of equipment that enables field sampling and derivatization, it shall be validated in terms of applicability and minimize and avoid any losses. To generate the best results, it is recommended to perform sampling/absorption and derivatization procedures in the laboratory.

6.1.1 Gas flow meter with temperature sensor, calibrated with methane, operating range: 0 ml/min - 20 ml/min with the software readout of normalized values for the volume of gas.

Methane calibrated gas flow meters are commercially available, which is applicable for biomethane matrix. If a flow meter is used to read the flow of different biogas gas matrices, a calibration shall be performed on the actual medium, i.e. a correction of sampled gas volume in relation to the composition of the biogas.

6.1.2 Gas cylinder with gas pressure regulator.

Pressure regulator suitable to deliver low outlet pressure (just above the atmospheric pressure) in order to achieve low but measurable gas flow and slow release of gas from the cylinder to keep gas bubbles longer in the liquid absorbent to increase the absorption efficiency of siloxanes.

NOTE There are studies available on different types and treatments of cylinders especially for different concentrations of siloxanes in methane and biogas. Refer to the manufacturer's instructions in terms of the applicability of the cylinder type for the application in question.

6.1.3 Digital or manual automatic pipettes, adjustable volume 1 ml to 5 ml, and 10 µl to 200 µl with silicon free tips.

6.1.4 Plastic gas bubblers/impingers with tubing, 20 ml to 50 ml capacity with stoppers, silicon free.

6.1.5 Plastic vessels for the derivatization, 200 ml capacity with stoppers, heat durable.

6.1.6 Stirring rod, plastic, silicon free.

6.1.7 Laboratory fume hood with constant ventilation EX design.

6.2 MWP/ICP-AES instrument.

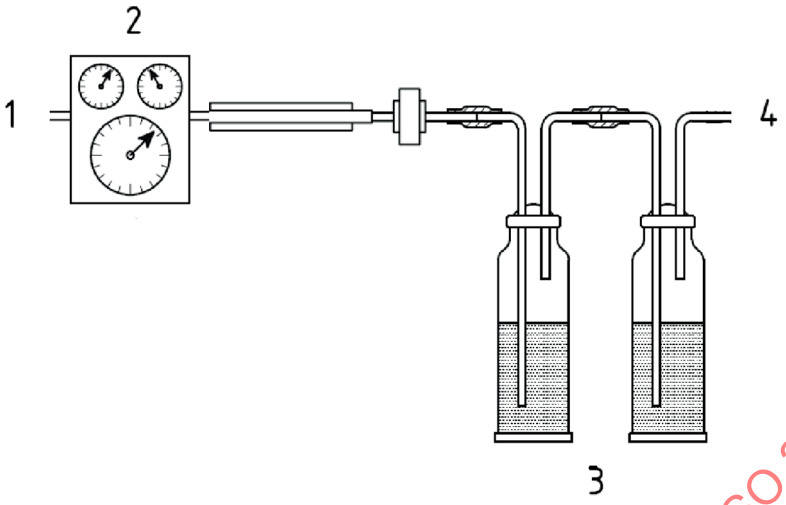
Microwave plasma (MWP)/ Inductively coupled plasma (ICP) atomic/ionic emission spectrometer with inert (HF) sample introduction system including nebulizer and inert (HF) torch, capable of measuring silicon emission lines [250,590 nm; 251,432 nm; 251,611 nm (the most sensitive line); 288,158 nm] with a minimum optical resolution 0,05 nm and capable of background correction.

6.3 Analytical balance, capable of weighing to the nearest 0,01 mg.

7 Sampling

Sampling of biomethane/biogas shall be conducted in accordance with ISO 10715. Only sampling containers (cylinders) that show minimal adsorption of siloxanes shall be used.

The sampling procedure refers to the sampling from pressurized gas cylinder equipped with gas pressure regulator (6.1.2) displaying the pressure inside the cylinder as well as the outlet pressure. Gas regulator is airtight connected to the gas flow meter with plastic silicon free tubing ensuring measurement of gas flow and volume released. Gas flow meter is connected with the same type of plastic silicon free tubing with two to three serially connected gas bubblers/impingers (6.1.4) containing absorbent media – concentrated nitric acid (5.1.1).



Key

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

Figure 1 — Sampling of silicon from biomethane/biogas

Check for gas leaks on the fittings of cylinder/gas flow meter system using soapy water. Apply a soap-and-water solution to each connection in the gas lines. Turn on the gas and look for bubbles. If bubbles form, tighten the fitting slightly with a pipe wrench and recheck. Be sure to wipe off the previously applied soap-and-water solution and apply the solution again.

The opening of the tube through which the gas is being introduced in the bubblers shall be immersed in the absorbent. Adjust the volume of the absorbent accordingly. If 50 ml gas bubblers are used, this volume should not be smaller than 7,5 ml. In order to ensure quantitative sampling, bubblers are equipped with stoppers (rubber or some similar adhesive elastic material) airtight with PFTE tape. The whole sampling setting consisting of serially connected bubblers and gas flow meter should be placed in fume hood, especially the exhaust on the last bubbler in line, releasing the excess gas.

If a longer sampling time (>5 h) is applied, care shall be taken to evade evaporation of the absorbent to prevent the gas delivering tube from emerging above the absorbent surface.

Sampling flow should be kept constant at approximately 10 cm^3/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. In order to ensure as accurate sampling as possible, keep the gas flow low and constant for the whole sampling time. In order to ensure reasonable duration of the sampling, the total volume should be in the range of 2 dm^3 to 20 dm^3 of gas.

Absorbing liquid from both gas bubblers shall be quantitatively transferred to plastic silicon free derivatization vessel.

All plastic parts of the sampling equipment (tubes and vessels) shall be washed with ultra-pure 2 % nitric acid (mass fraction) before use. Labware is initially rinsed and then kept submerged for at least eight hours using this medium. Rinse the dishes thoroughly with water (5.3) and air dry in clean environment before use. Check the cleanliness of the labware by occasional performance of blank

analysis (5.7.1.4) performing the described analytical procedure with pure methane, free from silicon, as gas sample.

The efficiency of the sampling procedure can be assessed using a reference gas mixture of siloxane in methane or in biogas matrix, depending on the application, with certified silicon content. Efficiency data should be considered when estimating bias and combined measurement uncertainty of the calculated results. Estimated absorbance efficiency is 80 % to 100 % for lower concentrations and 60 % to 100 % for higher concentrations of silicon (see Scope).

8 Derivatization

Absorbent media from the bubblers after the sampling is quantitatively transferred to derivatization vessel (6.1.5). Rinsing of the bubblers/tubing for the purpose of quantitative transfer of the content is performed with a small volume (several ml) of an absorbent media (5.1.1). Derivatization vessels shall be accurately weighed empty with corresponding stoppers.

Add 8 mol/l to 10 mol/l sodium or potassium hydroxide solution (5.2.1) dropwise until slightly basic pH is reached. Calculate the volume of hydroxide solution needed to neutralize the nitric acid in absorbent and add couple of drops in excess. After basic pH of the solution is reached, immediately add appropriate volume of concentrated hydrofluoric acid (5.2.2) dropwise until acidic pH value of around 3,5 is reached. After acidic pH of the solution is reached add water (5.3) to dilute the sample matrix (usually one third of the total volume). Total volume depends on the volume of absorbent used. It should be taken into account prior sampling that derivatization vessels are of required volume.

Heat durable derivatization vessels shall be used (6.1.5). If water cooling is to be applied, special care shall be taken to avoid contamination of the derivatization vessel with water.

Use pH indicator strips (5.5) to check the pH of the solution throughout the derivatization procedure by placing one drop of the homogenized solution on the strip using plastic stirring rod.

Accurately weigh derivatized sample by subtracting the mass of the solution with the vessel with the mass of empty vessel recorded. Samples shall be further diluted to obtain silicon concentration within calibration range.

The same procedure is applied when reference gas mixture (5.7.5) is used as control sample. Calculate the expected mass of silicon collected and check the recovery by reading the sample as unknown.

9 Analytical procedure

9.1 Set-up of the equipment

The data processing unit of the ICP/MWP spectrometer is used to establish a measuring programme in which the intensities of the silicon emission lines 250,590 nm, 251,611 nm (most sensitive line) and 288,158 nm are measured in the same sample simultaneously or within very short timeframe. After ignition allow ISP/MWP torch at least 15 min to stabilize before use. Aspirate the rinse blank solution (5.7.1.3) through the system for at least 20 min prior analysis to minimise carry over interferences from the tubing.

Calibrate the optical detection system by performing wavelength control check (5.6.5). If the check passes continue with the analysis. If the check is not satisfactory, perform the same procedure again until desired result is obtained.

Upon selection of the silicon emission lines to be measured, optimize the nebulizer pressure and viewing position for the particular analysis. This check shall 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.

Follow the manufacturer's instructions in terms of recommendations for optimization of individual parameters of the instrument system and analysis. This can include, e.g., the choice of axial or radial

view for ICP-type instruments, blank subtraction and emission peak integration parameters, system stability tests, frequency of stability check readings for emission values, etc.

9.2 Calibration line

Prepare calibration sequence by obtaining instrument responses for each of the calibration standards (5.6.4). After the sample introduction system has been appropriately flushed with rinse blank, aspirate calibration solutions including calibration blank (5.7.1.1) in ascending order of concentration. Record emission intensities for each selected wavelength against concentration.

Use the method of ISO 6143 to obtain the analysis function. Confirm the linearity of the instrument by visual inspection of the residuals of the data points about the analysis function.

If the concentrations of the calibration standards are correlated (5.6.4), then either

— calculate the covariances between the concentrations and provide these to the regression software supporting ISO 6143, or

— use the dilution factors and their standard uncertainties to obtain the analysis function in accordance with ISO 6143, and

— calculate the concentration of the sample by using the dilution factor and the concentration of the stock solution (see 9.3)

Follow the manufacturer's instructions when selecting instrument method parameters. The number of readings of the standard solutions should be a minimum of seven to allow monitoring of the stability of readings under repeatability conditions.

9.3 Analysis of unknown and QC samples

Prepare the analysis sequence for unknown samples and QC samples in the following order: calibration blank, laboratory reagent blank, unknown sample(s), derivatization control sample (DC), calibration blank, calibration control sample (CC), rinse blank solution.

After each measuring series of at least five to ten measurements, re-analyse the calibration blank and calibration control sample to check whether the calibration curve is still valid.

If the silicon content in the unknown sample solutions exceeds the range of validity of the calibration curve, dilute the measuring solution accordingly with calibration blank (2 % nitric acid mass fraction).

Follow the manufacturer's instructions when selecting instrument method parameters. The number of readings of the unknown and QC sample solutions should be a minimum of seven to allow monitoring of the stability of readings under repeatability conditions.

10 Calculation

Establish the calibration function by linear regression using the data obtained from the measurement of the calibration solutions.

Calculate the mass fraction of silicon $\rho(\mathrm{Si})$ expressed in mg/kg in the liquid derivatized sample including any dilutions prior to readings, as given by Formula (1):

$$\rho(\mathrm{Si}) =_{x} (\mathrm{Si}) \cdot D \tag{1}$$

where

$\rho(\mathrm{Si})$ is the mass fraction of silicon in liquid sample, expressed in mg/kg;