FINAL DRAFT
International Standard

ISO/FDIS 2611-1

Analysis of natural gas — Biomethane — Determination of halogenated compounds —

Part 1: HCl and HF content by ion chromatography

Analyse du gaz naturel — Biométhane — Détermination des composés halogénés —

Partie 1: Détermination de la teneur en HCl et HF par chromatographie ionique

ISO/TC **193**/SC **1**

Secretariat: **NEN**

Voting begins on:
2024-01-04

Voting terminates on:
2024-02-29

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/FDIS 2611-1:2024(en)

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Published in Switzerland

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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 document 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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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).

A list of all parts in the ISO 2611 series can be found on the ISO website.

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

A method for measuring hydrogen chloride (HCl) and hydrogen fluoride (HF) in biomethane is described based on the absorption of these components on an alkali-impregnated quartz fibre filtre. The anions chloride and fluoride are then analysed by ion chromatography with conductimetric detection. The concentrations are expressed in equivalent hydrochloric acid and hydrofluoric acid at appropriate reference conditions.

Analysis of natural gas — Biomethane — Determination of halogenated compounds —

Part 1:
HCl and HF content by ion chromatography

1 Scope

This document specifies a method for the determination of the concentration hydrochloric acid (HCl) and hydrofluoric acid (HF) in biomethane, after absorption on an alkali-impregnated quartz fibre filtre or in a sorbent trap, by ion chromatography (IC) with conductimetric detection.

The method is applicable to biomethane for concentration levels for HCl from 0,07 mg/m^3 to 35 mg/m^3 and for HF from 0,07 mg/m^3 to 20 mg/m^3.

Unless stated otherwise, all concentrations in this document are given under standard reference conditions (see ISO 13443). Other conditions can be applied.

This method is also applicable to biogas. This method is intended to support conformity assessment of biomethane and biogas according to specifications, such as the EN 16723 series.

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 6974-1, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 1: General guidelines and calculation of composition*

ISO 6974-2, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 2: Uncertainty calculations*

ISO 6974-3, *Natural gas — Determination of composition and associated uncertainty by gas chromatography — Part 3: Precision and bias*

ISO 6976, *Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition*

ISO 10304-1, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

ISO 14532, *Natural gas — Vocabulary*

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 terminology 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
analyte
element, ion or substance to be determined by an analytical method

[SOURCE: EN 16687:2015, 4.1.11]

4 Symbols and abbreviated terms

4.1 Symbols

Symbol	Description	Unit
$\rho_{(x)}$	Concentration of gaseous hydrogen chloride or hydrogen fluoride in biomethane	µg/m^3
$\rho_{(x-)}$	Concentration of ions chlorides or fluorides	µg/l
M(x-)	Molar mass of ions chlorides or fluorides	g/mol
M(x)	Molar mass of hydrogen chloride or hydrogen fluoride	g/mol
$m_{(x)}$	Mass of gaseous chlorides or fluorides collected	µg
V_S	Volume of extract solution	l
V_{gas}	Volume of the gas sampled	m^3
q_V	Volume flow rate of the gas during sampling	ml/min
p_0	Pressure at reference conditions	kPa
p_{gas}	Pressure at sampling conditions	kPa
t	Sampling time	min
T_0	Temperature at reference conditions	K
T_{gas}	Temperature at sampling conditions	K
Z	Compressibility factor	1

4.2 Abbreviated terms

CD	conductimetric detector
HCl	Hydrochloric acid
HF	hydrofluoric acid
HPLC	high-performance liquid chromatography
IC	ion chromatography
SI	international system of units

5 Principle

Hydrochloric acid (HCl) and hydrofluoric acid (HF) contained in biomethane are trapped on an alkali-impregnated quartz fibre filter. The adsorbed inorganic halides are eluted by aqueous extraction with a sonification step.

NOTE Where “biomethane” is written, it is implied that it also covers biogas.

The instrumental analysis of chlorides and fluorides in the extracts is performed by ion chromatography with a conductimetric detector (CD).

When using CDs, it is essential that the eluents show a sufficiently low conductivity. For this reason, CDs are usually combined with a suppressor device (cation exchanger), which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

6 Reagents and consumables

Use only reagents of recognized analytical grade. Weigh the reagents with a relative expanded uncertainty of ±1 % (k = 2) of the nominal mass, unless stated otherwise.

6.1 Water

The water used in this method shall comply with grade 1 in accordance with ISO 3696.

6.2 Aqueous solutions

Sodium carbonate solution, Na_2CO_3 with a mass concentration of 50 g l^{-1}.

Sodium bicarbonate solution, $NaHCO_3$ with an amount-of-substance concentration of 0,002 4 mol l^{-1}.

6.3 Chloride and fluoride stock standard solutions

The solutions shall have a mass concentration of ρ_X = 1 000 mg l^{-1} ± 10 mg l^{-1} (k = 2) each.

Single anion and mixed anion stock solutions with adequate and required specification are commercially available. These solutions are stable for several months. Solutions used shall have certified concentrations with acceptable metrological traceability and a stated uncertainty.

6.4 Chloride and fluoride standard solutions

Depending on the concentrations expected, prepare single or mixed standard solutions of chloride and fluoride concentrations from the stock standard solution (6.3). Store the standard solutions in polyethene bottles.

The equipment used (e.g. balances, volumetric glass ware) shall be calibrated or checked for performance. The calculation of the concentration(s) of the standard solution(s) shall include the evaluation of the measurement uncertainty associated with the concentration.

NOTE Guidance on the evaluation of measurement uncertainty is given in Reference [3].

For example, a chloride and fluoride mixed standard solution, ρ_X= 10 mg l^{-1} each is obtained by pipetting using a volumetric pipette of 1,0 ml of each of the stock standard solutions (6.3) into a 100 ml volumetric flask and filling the flask up to the volume with water (6.1).

These solutions shall be stored in the dark between 2 °C to 8 °C in polyethene bottles and shall be used until one week after preparation.

6.5 Chloride and fluoride calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (6.4) to prepare, e.g. 5 to 10 calibration solutions distributed as evenly as possible over the working range. The working range shall be wide enough to allow interpolation of the concentrations of the envisaged extracts prepared from samples of biomethane (see Clause 9).

EXAMPLE For the range 0,05 mg l^{-1} to 0,5 mg l^{-1}: Pipette using a calibrated micropipette, into a series of 20 mL volumetric flasks, the following volumes: 100 µl, 200 µl, 300 µl, 400 µl, 500 µl, 600 µl, 700 µl, 800 µl, 900 µl or 1 000 µl of the standard solution (6.4) and dilute to volume with water (6.1).

The nominal concentrations of the anions in these calibration solutions are: 0,05 mg l^{-1}, 0,1 mg l^{-1}, 0,15 mg l^{-1}, 0,2 mg l^{-1}, 0,25 mg l^{1}, 0,3 mg l^{-1}, 0,35 mg l^{-1}, 0,4 mg l^{-1}, 0,45 mg l^{-1} or 0,5 mg l^{-1}, respectively.

Prepare the calibration solutions on the day of use.

6.6 Blank

Fill a volumetric flask (e.g. 100 ml flask) with water (6.1).

6.7 Eluents

Degas all water used for eluent preparation. To minimize the growth of bacteria or algae, prepare eluents freshly if the current ones are older than 3 days.

The choice of eluent (for example, potassium hydroxide, KOH) depends on the chosen column. Consult the documentation of the column or seek advice from the column supplier. The chosen combination of separator column and eluent shall meet the resolution requirements stated in 7.2.

6.8 Quartz filters

Quartz fibre filters suitable for gas sampling of acidic gases of an appropriate diameter in a sampling cassette with a pore size of 2,5 µm.

6.9 Syringe filters

Nylon syringe filter with a diameter of 0,45 µm.

6.10 Sorbent tubes

Activated silica gel cartridges, specially cleaned, suited for active air (gas) sampling. Particle size: 20 mesh - 40 mesh.

7 Apparatus

Usual laboratory apparatus, and, in particular:

7.1 Ion chromatography system

In general, it consists of the following components (see Figure 1):

— eluent reservoir, and degassing unit,

— metal-free HPLC pump,

— precolumn, if necessary,

— separator column, with the specified separating performance (7.2),

— conductimetric detector (CD),