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Stationary source emissions — Manual method for the determination of the methane concentration using gas chromatography

Émissions de sources fixes — Méthode manuelle pour la détermination de la concentration en méthane par chromatographie en phase gazeuse

Reference number
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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 International Standards 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 25139 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Introduction

Methane (CH_4) is a gas of relevance to the climate ("greenhouse gas") and contributes directly to the atmospheric greenhouse effect. The emissions of methane originate from natural sources and those due to human activity. Significant sources are, for example, cattle breeding, cultivation of rice, extraction and transport of natural gas, and landfills. Other important sources contributing to emissions of methane are, for example, composting plants, the use of biogas and natural gas, and biomass firings. This International Standard specifies a method of measurement for the determination of methane emissions from stationary sources.

Stationary source emissions — Manual method for the determination of the methane concentration using gas chromatography

1 Scope

This International Standard specifies a manual method for the determination of the concentration of methane emissions from stationary sources.

This International Standard specifies an independent method of measurement, which is validated for mass concentrations up to 1 500 mg/m^3.

NOTE 1 An independent method of measurement is used for such purposes as calibration or validation of permanently installed measuring systems.

NOTE 2 An “independent method of measurement” is termed “standard reference method (SRM)” in EN 14181[5].

2 Normative references

The following referenced documents are indispensable for the application 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 9169, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

EN 15267-3, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
reference gas
⟨air quality⟩ gas of known, reliable and stable composition

NOTE In the context of this International Standard, a reference gas is used to calibrate the gas chromatograph.

3.2
interferent
interfering substance
⟨air quality⟩ substance present in the air mass under investigation, other than the measurand, that affects the response

[ISO 9169:2006, 2.1.12]

3.3
mass concentration
⟨stationary source emissions⟩ concentration of a substance in an emitted waste gas expressed as mass per volume

NOTE Mass concentration is often expressed in milligrams per cubic metre.

[ISO 25140:2010[3], 3.14]

3.4
uncertainty (of measurement)
parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008[4], 2.2.3]

3.5
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008[4], 2.3.1]

4 Symbols and abbreviated terms

AMS automatic measuring system

FID flame ionization detector

FKM fluoro rubber

GC gas chromatograph

PE polyethylene

PET poly(ethylene terephthalate)

PLOT porous layer open tubular

PTFE polytetrafluoroethylene

QA/QC quality assurance and quality control

A peak area

e_j residual at mass concentration level γ_j

f_{GC} GC calibration factor

k slope of the calibration line

L limit of detection

$m_{H_2O,v}$ mass of water vapour

M_{CH_4} molecular mass of methane (16 g/mol)

M_{H_2O}	molecular mass of water (18 g/mol)
n	number of measurements
s_r	repeatability standard deviation
S_{GC}	GC signal
$S_{GC,cal}$	GC signal in response to the reference gas applied
V_0	volume of the dry gas sampled
V_m	standard molar volume (22,4 l/mol)
x_i	ith measured value
$\overline{x}$	average of the measured values x_i
$\overline{x}_j$	average of the measured values at mass concentration level γ_j
$\gamma_{CH_4,s}$	methane mass concentration at standard conditions of temperature and pressure
$\gamma_{CH_4,(H_2O)_0}$	methane mass concentration at reference conditions of water vapour (dry gas)
γ_{CH_4,O_2}	methane mass concentration at reference conditions of oxygen
γ_j	jth mass concentration level
$\rho_{H_2O,v}$	density of water vapour
$\varphi_{CH_4,cal}$	methane content, as a volume fraction, of the reference gas applied during calibration
$\varphi_{CH_4,o}$	methane content, as a volume fraction, at operating conditions
φ_{H_2O}	water vapour content, as a volume fraction, in the waste gas
$\varphi_{O_2,m}$	measured oxygen content, as a volume fraction, in the waste gas
$\varphi_{O_2,ref}$	reference oxygen content, as a volume fraction

5 Principle

The sample gas is extracted from the waste gas duct via a sampling system and pumped into a gas-sampling bag or canister. A portion of the sample is taken off from the gas-sampling bag or canister and introduced into a gas chromatographic system. After separation on a packed or capillary column, methane is determined by means of a flame ionization detector.

6 Equipment

6.1 Sampling system

The sampling system shall allow for the extraction of the sample gas from the waste gas duct. It consists in principle of:

— sampling probe;

— particle filter;

— sample gas cooler;

— sample gas flow meter;

— sample gas pump;

— vacuum pump, if necessary;

— gas-sampling vessel (bag, glass tube or canister), or direct sampling loop to the GC.

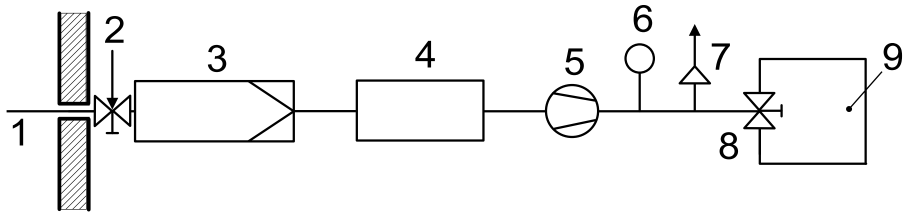
Several sampling techniques are suitable such as:

— use of gas-sampling bags with upstream pump (see Figure 1);

— use of evacuated gas-sampling vessels made of glass or canisters made of corrosion-resistant materials (e.g. stainless steel) with upstream pump (see Figure 2);

— use of the “lung principle” with the gas-sampling bag placed in an evacuated container;

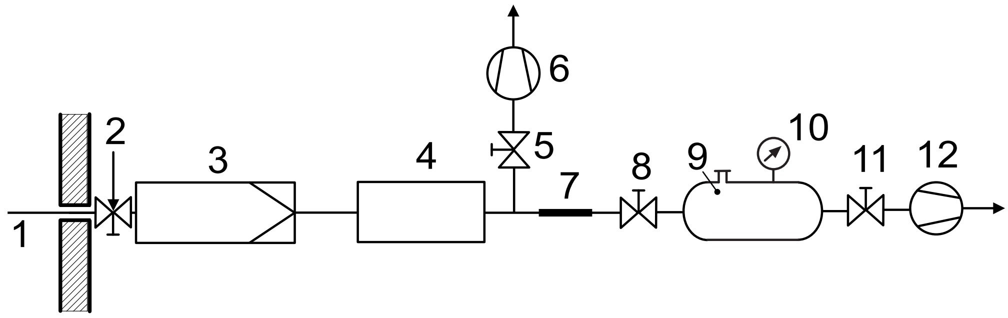
— use of a sampling system as shown in Figure 1 but with the gas-sampling bag replaced by a sampling line directly connected to the loop sampling system of the GC.



Key

1 sampling probe, heated (if necessary)
2 valve for introducing test gases
3 particle filter, heated
4 sample gas cooler or permeation dryer
5 sample gas pump
6 flow meter
7 bypass valve for purging the sampling system
8 sampling bag valve
9 gas-sampling bag

Figure 1 — Example of a sampling system with gas-sampling bag



Key

1 sampling probe, heated (if necessary)
2 valve for introducing test gases
3 particle filter, heated
4 sample gas cooler or permeation dryer
5 control valve
6 sample gas pump
7 throttle element
8 shut-off valve
9 gas-sampling vessel or canister
10 temperature and pressure measuring device
11 shut-off valve
12 vacuum pump (if necessary)

Figure 2 — Example of a sampling system with evacuated gas-sampling vessel

The sampling line shall be as short as possible. The sampling line shall be installed so as to descend to the cooler. Condensation shall be avoided at any point of the sampling system.

The sampling system shall meet the following requirements:

— the sampling probe shall be a tube made of stainless steel or glass, which can be heated to 150 °C, if necessary, equipped with a device (e.g. a valve) for introducing test gases;

— the dust filter shall be a quartz fibre or ceramic filter in a filter housing and shall be heatable to 150 °C, if necessary;

— the sampling line shall be made of stainless steel or polytetrafluoroethylene (PTFE) and shall be heatable to 150 °C, if necessary;

— the sample gas cooler or permeation dryer shall be suitable for a flow rate up to 1 l/min;

— the sample gas pump shall be gas-tight with adjustable flow rate (up to 1 l/min), and shall be heatable, if necessary;

— vacuum pump for evacuating the gas-sampling vessel down to a residual pressure of 10 hPa to 20 hPa;

— connecting pieces for components of the sampling apparatus shall be made of an inert tubing material, e.g. PTFE or fluoro rubber (FKM);

— the flow meter with control valve shall be suitable for measuring the sampling flow rate;

— the gas-sampling vessel shall be gas-tight (e.g. a plastic bag with closable filler nozzle or canister of corrosion-resistant materials equipped with valves) with a volume of 5 l to 30 l;

— all components of the sampling system shall be made of corrosion-resistant material;

— all components upstream the cooler shall withstand a temperature of 150 °C, if necessary.

Suitable materials for the storage of methane samples are aluminium-coated polyethylene (PE) and poly(vinyl fluoride). Sample storage in gas-sampling bags made from these materials for at most 10 days is possible without significant methane losses, in aluminium-coated PE bags even longer.