BRITISH STANDARD

BS EN ISO
6326-1:2009

Natural gas — Determination of sulfur compounds

Part 1: General introduction (ISO 6326-1:2007)

ICS 75.060

BSI
British Standards

National foreword

This British Standard is the UK implementation of EN ISO 6326-1:2009. It is identical to ISO 6326-1:2007. It supersedes BS 3156-11.4.1:1994 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/15, Natural Gas and Gas Analysis.

A list of organizations represented on this committee can be obtained on request to its secretary.

The flame photometric detector is available from most manufacturers of chromatographs, both laboratory and process units, and is applicable to any sulfur compounds. By contrast, the electrochemical detector is available from a single supplier and is operated under completely different conditions in order to measure carbonyl sulfide to those used for all other sulfur compounds.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

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Foreword

The text of ISO 6326-1:2007 has been prepared by Technical Committee ISO/TC 193 “Natural gas” of the International Organization for Standardization (ISO) and has been taken over as EN ISO 6326-1:2009.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 2010, and conflicting national standards shall be withdrawn at the latest by January 2010.

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Endorsement notice

The text of ISO 6326-1:2007 has been approved by CEN as EN ISO 6326-1:2009 without any modification.

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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.

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ISO 6326-1 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This second edition cancels and replaces the first edition (ISO 6326-1:1989), which has been technically revised due to the replacement of ISO 6326-2:1981 and ISO 6326-4:1994 by ISO 19739:2004, *Natural gas – Determination of sulfur compounds using gas chromatography*, which gives the requirements needed to perform a sulfur analysis by gas chromatography. This second edition also provides a general introduction to ISO 19739.

ISO 6326 consists of the following parts, under the general title *Natural gas — Determination of sulfur compounds*:

— *Part 1: General introduction*

— *Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry*

— *Part 5: Lingener combustion method*

Introduction

Sulfur compounds can occur naturally in natural gas and remain as traces after treatment, or they may have been injected deliberately to allow subsequent olfactory detection for safety reasons.

The standardization of several methods for the determination of sulfur compounds in natural gas is necessary in view of the diversity of these compounds [hydrogen sulfide, carbonyl sulfide, tetrahydrothiophene (THT), etc.] and the requirements of the determinations (required uncertainty, measurement at the well head, at clean-up plant or in the transmission pipes, etc.).

In order to enable the user to choose the method most appropriate to his needs and to perform the measurements under the best conditions, ISO 6326 has been prepared in several parts.

This part of ISO 6326 gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

The other parts of ISO 6326 and ISO 19739 describe in detail the various standardized methods.

INTERNATIONAL STANDARD **ISO 6326-1:2007(E)**

Natural gas — Determination of sulfur compounds —

Part 1: General introduction

WARNING — The majority of sulfur compounds are extremely toxic and thus present a serious health hazard if handled without precautions.

1 Scope

This part of ISO 6326 gives a brief description of standardized methods that can be used for the determination of sulfur compounds in natural gas.

The principle of each method is described generally, the range of concentrations for which the method is suitable is indicated, and the analytical range and precision of each method is given. It should enable the user to select judiciously the proper method for the application being considered. Sulfur analysis is performed in order to determine

a) total sulfur,

b) sulfur contained in specific groups (e.g. thiol sulfur),

c) individual sulfur compounds, and

d) specific groups of sulfur compounds.

The standardized methods available in the field of sulfur analysis are

— the Wickbold combustion method: for total sulfur determination (ISO 4260),

— the Lingener combustion method: for total sulfur determination (ISO 6326-5),

— gas chromatography: for determination of individual sulfur compounds (ISO 19739), and

— potentiometry: for determination of hydrogen sulfide, carbonyl sulfide and thiol compounds (ISO 6326-3).

Other methods for the determination of sulfur compounds are available but are not considered here. Table 1 gives an overview of the standardized methods which can be used for the determination of total sulfur, hydrogen sulfide, carbonyl sulfide, tetrahydrothiophene, thiol sulfur, individual thiols, individual thiophenes, individual organic sulfides and disulfides.

Table 1 — Methods for the determination of sulfur compounds in natural gas

Determination	Method	Concentration range [a] mg/m^3	Reference
Total sulfur	Wickbold combustion method	1 to 20 000	ISO 4260
	Lingener combustion method	0,5 to 1 000	ISO 6326-5
Hydrogen sulfide (H_2S)	Potentiometry	$\geqslant$ 1	ISO 6326-3
	Gas chromatography	0,1 to 100 (or 0,5 to 600 depending on the detector used)	ISO 19739
Carbonyl sulfide (COS)	Gas chromatography	0,1 to 30	ISO 19739
	Potentiometry	$\geqslant$ 1	ISO 6326-3
Tetrahydrothiophene (THT)	Gas chromatography	0,1 to 100	ISO 19739
Thiol sulfur	Potentiometry	$\geqslant$ 1	ISO 6326-3
Individual thiols	Gas chromatography	0,1 to 100	ISO 19739
Individual thiophenes	Gas chromatography	0,1 to 100	ISO 19739
Individual organic sulfides and disulfides	Gas chromatography	0,1 to 100	ISO 19739

[a] For the determination of total sulfur, the sulfur content is expressed as milligrams of sulfur per cubic metre of gas. For the determination of sulfur compounds, the mass concentration of sulfur compounds is expressed as milligrams of sulfur compound per cubic metre of gas.

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 4260, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method*

ISO 6326-3, *Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry*

ISO 6326-5, *Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method*

ISO 10715, *Natural gas — Sampling guidelines*

ISO 16664, *Gas analysis — Handling of calibration gases and gas mixtures — Guidelines*

ISO 19739:2004, *Natural gas — Determination of sulfur compounds using gas chromatography*

3 Sampling

3.1 General

The sampling procedures are very important in the analysis of sulfur compounds. Sulfur compounds have a strong tendency to adsorb on to, or to chemically react with, different materials of construction. Low contents of sulfur compounds in samples and calibration gas mixtures put demands on the sampling procedure in order to ensure that the sulfur compounds in correct quantity reach the analytical device.

Carry out representative sampling in such a way that the sample represents the bulk of the gas at the time of sampling. Sampling and sample transfer shall be in accordance with ISO 10715.

Purge time should be long enough to obtain replicate stable analytical results within the acceptable standard deviation of the analyser. The purge time needed depends on the type and concentration of the sulfur compound, materials in contact with the gas, and the gas flow rate through the sample loop.

Sampling of the gas can be carried out in two different ways:

— at atmospheric pressure in a silanized glass vessel, equipped with polytetrafluoroethylene (PTFE) plugs [or a sampling bag made of material inert to sulfur compounds, such as polyvinylfluoride (PVF) or PTFE], which has been flushed with dilute hydrochloric acid, subsequently flushed with distilled water and dried; after the glass vessel is filled with the gas under study, it should be shielded from daylight;

— under pressure in a stainless steel or aluminium cylinder, if the sulfur content exceeds 50 mg/m^3.

3.2 Safety precautions

Safety precautions required in handling gas cylinders with pressurized flammable gas mixtures are described in ISO 10715. If a pressure regulator is to be connected to the cylinder, always use a regulator whose materials of construction are recommended by the producer of the calibration gas.

For other precautions and advice for the use, sampling and handling of gas mixtures containing sulfur compounds, see Clause 3 of ISO 19739:2004 and ISO 16664.

4 Methods for determination of total sulfur content

To carry out the analyses, reference should be made to the specific methods which are described in detail in ISO 4260, ISO 19739, ISO 6326-3 and ISO 6326-5.

4.1 Wickbold combustion method (ISO 4260)

4.1.1 Scope

This method is applicable to products having sulfur content on the order of 1 mg/m^3, and is particularly suitable for gases with total sulfur content in the range 1 mg/m^3 to 20 000 mg/m^3 and for distillates with total sulfur content of less than 300 mg/m^3.

4.1.2 Principle

The natural gas is supplied to the burner of a hydrogen-oxygen flame, where the sulfur compounds undergo combustion with a considerable excess of oxygen. The resulting sulfur oxides are converted into sulfuric acid by absorption in hydrogen peroxide solution.

Depending on the sulfur content of the sample, the sulfate ions in the absorption solution are determined by colorimetric, nephelometric, turbidimetric or conductometric titration (see Table 2).

Table 2 — Concentration range and precision data for methods of determination of sulfur compounds in natural gas

Method	Determination	Concentration range mg/m^3	Repeatability %
Wickbold combustion method	Total sulfur	1 to 10 > 10	10 to 15 5 to 7
Lingener combustion method	Total sulfur	10 to 1 000	6
Gas chromatography	COS All other S compounds	0,1 to 30 0,1 to 100	2 to 7
Potentiometry	H_2S Thiol sulfur COS sulfur	1 to 10 1 to 20 1 to 30	15 15 10

4.1.3 Results and precision

The total sulfur content of the sample is expressed in milligrams of sulfur per cubic metre of gas. The precision is a function of

a) the sulfur concentration of the gas, and

b) the type of titration used in the determination.

The repeatability for samples containing < 10 mg/m^3 ranges from 10 % to 15 % and the reproducibility ranges from 20 % to 30 %. The repeatability for samples containing > 10 mg/m^3 ranges from 5 % to 7 % and the reproducibility is 13 %.

4.2 Lingener combustion method (ISO 6326-5)

4.2.1 Scope

The method is suitable for the determination of the total sulfur content in natural gas. The method is applicable to gases with sulfur content in the range from 0,5 mg/m^3 to 1 000 mg/m^3.

4.2.2 Principle

A given volume of gas undergoes combustion with air at atmospheric pressure in a glass combustion apparatus. The resulting sulfur oxides are converted into sulfuric acid by absorption in hydrogen peroxide solution.

If the total sulfur content is more than 0,1 mg sulfur in the absorption solution, visual titration with an indicator can be chosen, whereas for lower concentrations, turbidimetric titration is preferable.

4.2.3 Results and precision

The total sulfur content of the sample is expressed in milligrams of sulfur per cubic metre of gas and rounded off to 0,5 mg/m^3 in the case of determination by visual titration and to 0,1 mg/m^3 in the case of determination by turbidimetric titration.

The reproducibility is about 12 % for sulfur content between 10 mg/m^3 and 1 000 mg/m^3.

5 Methods for determination of individual sulfur compounds or groups of sulfur compounds

5.1 Gas chromatography method (ISO 19739)

5.1.1 Scope

ISO 19739 specifies the determination of hydrogen sulfide, carbonyl sulfide, C_1 to C_4 thiols, sulfides and tetrahydrothiophene (THT) using gas chromatography (GC). Depending on the method chosen from those given, the application ranges for the determination of sulfur compounds can vary, but whichever of the methods given in the annexes is used, the requirements in the body of the standard apply.

5.1.2 Principle

All significant components or groups of components to be determined in a gaseous sample are physically separated by means of gas chromatography (GC) and their content measured by comparison with calibration or reference gases. The gas being used for calibration and the sample gas shall be analysed using the same measuring system under the same set of conditions.

5.1.3 Performance characteristics required for sulfur analysis

The performance characteristics required for sulfur analysis were determined for this method from a proficiency test performed by seven laboratories in different countries. The results obtained are shown in Table 1 of ISO 19739:2004.

5.2 Potentiometric method (ISO 6326-3)

5.2.1 Scope

The method can be used for the determination of hydrogen sulfide, thiol sulfur and carbonyl sulfide sulfur in natural gas in concentrations $\geqslant$ 1 mg/m^3.

5.2.2 Principle

Hydrogen sulfide and thiols (mercaptans) are absorbed in a 35 % (mass fraction) KOH solution. COS is absorbed in a 5 % (mass fraction) alcoholic monoethanolamine solution. The quantity absorbed by each solution is determined by potentiometric titration with silver nitrate solution.

5.2.3 Results and precision

The results are expressed in milligrams of hydrogen sulfide, thiol sulfur and carbonyl sulfide sulfur per cubic metre of gas. The reproducibility is about 20 % for hydrogen sulfide content up to 10 mg/m^3 and thiol sulfur content up to 20 mg/m^3; for carbonyl sulfide sulfur content up to 30 mg/m^3 it is on the order of 15 %.

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