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Natural gas — Determination of sulfur compounds —

Part 1 : General introduction

Gaz naturel — Détermination des composés soufrés —

Partie 1 : Introduction générale

Reference number
ISO 6326-1 : 1989 (E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 6326-1 was prepared by Technical Committee ISO/TC 158, *Analysis of gases.*

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

— *Part 1: General introduction*

— *Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds*

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

— *Part 4: Determination of individual sulfur compounds by gas chromatography with a flame photometric detector*

— *Part 5: Lingener combustion method*

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Introduction

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, thiols (mercaptans), tetrahydrothiophene (THT), etc.] and the purposes of the determinations (required accuracy, measurement at the drilling head 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 gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

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

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Natural gas — Determination of sulfur compounds —

Part 1 : General introduction

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

1 Scope

This part of ISO 6326 gives a brief list 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 concentration range for which the method is suited is indicated and the sensitivity and precision of each method is given. It should enable the user to judiciously select the proper method for the application being considered. The determination of sulfur compounds can be carried out in three ways:

— the determination of total sulfur;

— the determination of individual sulfur compounds;

— the determination of a specific group of sulfur compounds.

The available standardized methods for the determination of sulfur are:

— Wickbold combustion method: for total sulfur (ISO 4260);

— Lingener combustion method: for total sulfur (ISO 6326-5);

— Gas chromatography with electrochemical detector: for individual sulfur compounds (ISO 6326-2);

— Gas chromatography with flame photometric detector: for individual sulfur compounds (ISO 6326-4);

— Potentiometry: for hydrogen sulfide, carbonyl sulfide sulfur, and mercaptan sulfur (ISO 6326-3).

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

To carry out the analysis, reference should be made to the specific methods, which are described in detail in ISO 4260 and the other parts (2 to 5) of ISO 6326.

NOTE — In all parts of ISO 6326, 1 m³ of gas is expressed at normal conditions (0 °C; 101,325 kPa).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 6326. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6326 are encouraged to investigate the possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 4260 : 1987, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method.*

ISO 6326-2 : 1981, *Natural gas — Determination of sulfur compounds — Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds.*

ISO 6326-3 : 1989, *Natural gas — Determination of sulfur compounds — Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry.*

ISO 6326-4 : —[1], *Natural gas — Determination of sulfur compounds — Part 4: Determination of individual sulfur compounds by gas chromatography with a flame photometric detector.*

ISO 6326-5 : 1989, *Natural gas — Determination of sulfur compounds — Part 5: Lingener combustion method.*

1) To be published.

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

Determination	Method	Concentration range (sulfur content in mg/m^3)	Reference
Total sulfur	Wickbold combustion method Lingener combustion method	1 to 20 000 0,5 to 1 000	ISO 4260 ISO 6326-5
Hydrogen sulfide (H_2S)	Gas chromatography with electrochemical detection Potentiometry Gas chromatography with flame photometric detection	0,1 to 100 ⩾ 1 0,1 to 30	ISO 6326-2 ISO 6326-3 ISO 6326-4
Carbonyl sulfide (COS)	Gas chromatography with flame photometric detection Potentiometry	0,1 to 30 ⩾ 1	ISO 6326-4 ISO 6326-3
Tetrahydrothiophene (THT)	Gas chromatography with electrochemical detection Gas chromatography with flame photometric detection	0,1 to 100 0,1 to 30	ISO 6326-2 ISO 6326-4
Mercaptan sulfur	Potentiometry	⩾ 1	ISO 6326-3
Individual mercaptans	Gas chromatography with electrochemical detection Gas chromatography with flame photometric detection	0,1 to 100 0,1 to 30	ISO 6326-2 ISO 6326-4
Individual thiophenes	Gas chromatography with flame photometric detection	0,1 to 30	ISO 6326-4
Individual organic sulfides and disulfides	Gas chromatography with electrochemical detection[1)] Gas chromatography with flame photometric detection	0,1 to 100 0,1 to 30	ISO 6326-2 ISO 6326-4

1) After adaptation.

3 Sampling

Mainly due to their reactivity, the structure of sulfur compounds can change under the influence of humidity, oxygen and ultraviolet radiation.

To minimize adsorption phenomena in sampling cylinders, on-line sampling and testing of the gas to be analysed is recommended, especially if minor constituents are to be determined.

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

— at atmospheric pressure in a silanised glass vessel, equipped with polytetrafluoroethylene plugs, 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.

NOTE — The majority of sulfur compounds are very reactive. That is why specific materials should be used for storage and transport: silanised glass, stainless steel lined with polytetrafluoroethylene, sputter anodised and silanised aluminium, polytetrafluoroethylene and fluorelastomers.

4 Methods for determination of total sulfur content

4.1 Wickbold combustion method (ISO 4260)

4.1.1 Scope

The method may be applied to products having sulfur contents in the range of 1 mg/m^3 to 20 000 mg/m^3 and is particularly suitable for gases with total sulfur contents less than 300 mg/m^3.

4.1.2 Principle

The natural gas is supplied to the burner of an oxy-hydrogen flame, where the sulfur compounds are burnt 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 titrations (see table 2).

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;

b) the type of titration used in the determination.

The reproducibility is of the order of 60 % to 20 % for sulfur contents between 1 mg/m^3 and 10 mg/m^3 and 20 % to 12 % for higher contents (see figure 5 of ISO 4260 : 1987, where values were not determined on gas samples).

4.2 Lingener combustion method (ISO 6326-5)

4.2.1 Scope

The method may be used for determining the total sulfur content in natural gas. The sulfur content may be in the range from 0,5 mg/m^3 to 1 000 mg/m^3.

4.2.2 Principle

A given volume of gas is burnt 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.

With a total sulfur content of 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 (see table 2).

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 contents 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 chromatographic method using an electrochemical detector (ISO 6326-2)

5.1.1 Scope

The method is intended for the analysis of natural gas containing odoriferous sulfur compounds (hydrogen sulfide, methyl to butyl mercaptans and tetrahydrothiophene) in the range of 0,1 mg/m^3 to 100 mg/m^3. Organic sulfides and disulfides can also be determined, after adaptation of the analytical conditions. The method is not suitable for the determination of carbonyl sulfide.

5.1.2 Principle

The odoriferous sulfur compounds are separated in a gas chromatograph with a column containing 30 % (*m*/*m*) silicone oil and 30 % (*m*/*m*) dinonylphthalate on chromosorb W[1] support. The sulfur compounds are subsequently oxidized in an electrochemical cell by a chromium oxide solution and detected by means of the potential difference between the platinum electrodes.

5.1.3 Results and precision

After calibration of the instruments with reference mixtures, this method allows the determination of odoriferous sulfur compounds with a precision of about 10 % for each constituent.

5.2 Gas chromatographic method with flame photometric detection (ISO 6326-4)

5.2.1 Scope

The method describes the determination of individual sulfur containing compounds in natural gas: hydrogen sulfide, carbonyl sulfide and odorants. The method is suitable for sulfur compounds having sulfur contents in the range 0,5 mg/m^3 to

Table 2 — Detection limits and precision data of the methods for the determination of the sulfur compounds in natural gas

Method	Determination	Concentration range mg/m^3	Precision %
Wickbold combustion method	Total sulfur	1 to 10 > 10	60 to 20 20 to 12
Lingener combustion method	Total sulfur	10 to 1 000	12
Gas chromatography			
— electrochemical detection	All S compounds, except COS	0,1 to 100	10
— flame photometric detection	All S compounds	0,1 to 30	10
Potentiometry	H_2S	1 to 10	20
	Mercaptan sulfur	1 to 20	20
	COS sulfur	1 to 30	15

1) Chromosorb W is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 6326 and does not constitute an endorsement by ISO of this product.

50 mg/m^3. Larger concentrations of hydrogen sulfide (up to 5 000 mg/m^3) cannot be quantitatively measured, but other sulfur compounds in such samples can be quantified.

5.2.2 Principle

The compounds are separated using a temperature programmed column of Porapak QS[1] and measured with a sulfur-selective FDP. Potentially interfering hydrocarbons are also separated from the sulfur compounds. Some sulfur compounds are not completely resolved from others. Identification can be aided by selective scrubbing of the sample to remove types of sulfur compound.

5.2.3 Results and precision

Depending on the application chosen, this method allows the determination of:

— hydrogen sulfide, mercaptans, sulfides, disulfides and thiophenes;

— carbonyl sulfide, even in the presence of a large excess of hydrogen sulfide;

with a precision of about 10 % for each constituent.

The repeatability of the method, as a relative value, is of the order of 10 % for all components.

5.3 Potentiometric method (ISO 6326-3)

5.3.1 Scope

The method can be used for the determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur in natural gas in the concentration range equal to or above 1 mg/m^3.

5.3.2 Principle

Hydrogen sulfide and mercaptans are absorbed in a 35 % (*m*/*m*) potassium hydroxide solution; carbonyl sulfide is absorbed in a downstream 5 % (*m*/*m*) alcoholic monoethanolamine solution. The quantity absorbed by each solution is determined by potentiometric titration with silver nitrate solution.

5.3.3 Results and precision

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

1) Porapak QS is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 6326 and does not constitute an endorsement by ISO of this product.

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