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**Natural gas — Determination of sulfur
compounds using gas chromatography**

*Gaz naturel — Détermination des composés soufrés par
chromatographie en phase gazeuse*

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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 19739 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

This first edition of ISO 19739 cancels and replaces ISO 6326-2:1981 and ISO 6326-4:1994, of which it constitutes a technical revision.

This corrected version of ISO 19739:2004 incorporates the following corrections:

- page 2, 3.2: a prime has been added to the second R in the formula and the description in parenthesis;
- page 2, 3.3: a prime has been added to the second R in the formula and the description in parenthesis;
- page 7, 9 b): the name of the molecule has been corrected to 2-methylpropane-2-thiol;
- pages 20, 31, 43 and 44: the footnotes have been corrected to read "...this International Standard...";
- page 22, D.3.4.2: the temperature has been changed to 293 K;
- page 43: the name of the molecule has been corrected to 2-methylpropane-2-thiol;
- other minor editorial rectifications.

Introduction

Sulfur compounds may 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, etc.) and the requirements of the determinations (e.g. required uncertainty, measurement at the drilling head, clean-up plant or in transmission pipes).

In order to enable its user to choose the most appropriate method for his/her particular needs and perform the measurements under the best conditions, this International Standard gives the requirements needed to perform a sulfur analysis.

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Natural gas — Determination of sulfur compounds using gas chromatography

WARNING — Some sulfur compounds can constitute a serious health hazard.

1 Scope

This International Standard specifies the determination of hydrogen sulfide, carbonyl sulfide, C₁ to C₄ thiols, sulfides and tetrahydrothiophene (THT) using gas chromatography (GC). Depending on the method chosen from those given in the annexes, the application ranges for the determination of sulfur compounds can vary, but whichever of the methods is used, the requirements of this International Standard apply.

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 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

ISO 6141, *Gas analysis — Requirements for certificates for calibration gases and gas mixtures*

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

ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method*

ISO 10715:1997, *Natural gas — Sampling guidelines*

ISO 14532:2001, *Natural gas — Vocabulary*

3 Terms and definitions

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

3.1

alkane thiol

alkyl mercaptan

organic sulfur compound with the general formula R-SH (where R is the alkyl group), either naturally present or added as an odorant to natural gas

[ISO 14532:2001, definition 2.5.3.3.1]

EXAMPLE Methanethiol (MeSH), ethanethiol (EtSH), 2-methylpropane-2-thiol (tert-butylmercaptan TBM).

3.2

alkyl disulfide

organic sulfur compound with the general formula R-S-S-R' (where R and R' are alkyl groups)

[ISO 14532:2001, definition 3.5.3.3.3]

3.3

**alkyl sulfide
thioether**

organic sulfur compound with the general formula R-S-R' (where R and R' are alkyl groups), either naturally present or added as an odorant to natural gas

[ISO 14532:2001, definition 3.5.3.3.2]

EXAMPLE Dimethyl sulfide (DMS), diethyl sulfide (DES).

3.4

**carbonyl sulfide
COS**

sulfur compound found in natural gas, which contributes to the total sulfur content

[ISO 14532:2001, definition 3.5.3.3.4]

3.5

chromatographic resolution

column efficiency characteristic describing the degree of separation of two adjacent peaks in gas chromatography

[ISO 14532:2001, definition 2.5.3.4.6]

NOTE The resolution is measured as twice the distance between the maximum of the named peaks divided by the sum of the intercepts on the baseline made by tangents drawn to the peaks at half the height.

3.6

**cyclic sulfide
thioether**

cyclic organic sulfur compound with one sulfur atom incorporated in a saturated hydrocarbon ring

EXAMPLE Tetrahydrothiophene (thiophane or thiacyclopentane, THT), i.e. C₄H₈S, which is added as an odorant to natural gas.

[ISO 14532:2001, definition 2.5.3.3.6]

3.7

**hydrogen sulfide
H₂S**

colourless, toxic gas with an odour similar to rotten eggs

[ISO 14532:2001, definition 2.5.3.3.8]

3.8

normal reference conditions

reference conditions of pressure, temperature and humidity (state of saturation) equal to 101,325 kPa and 273,15 K for a dry, real gas

[ISO 14532:2001, definition 2.6.1.3]

3.9**standard reference conditions**

reference conditions of pressure, temperature and humidity (state of saturation) equal to 101,325 kPa and 288,15 K for a dry, real gas

[ISO 14532:2001, definition 2.6.1.4]

3.10**total sulfur**

total amount of sulfur found in natural gas

[ISO 14532:2001, definition 2.5.3.3.17]

NOTE The total amount of sulfur may be determined by an analytical method not differentiating between individual sulfur compounds.

3.11**working reference gas mixture****WRM**

working standard gas mixture

gas mixture whose component quantity levels have been validated by direct comparison with a secondary standard gas mixture (CRM)

[ISO 14532:2001, definition 2.5.3.5.2.3]

3.12**secondary standard gas mixture**

gas mixture whose component quantity levels have been validated by direct comparison with a PSM

[ISO 14532:2001, definition 2.5.3.5.2.2]

3.13**primary standard gas mixture****PSM**

gas mixture whose component quantity levels have been determined with the utmost accuracy and can be used as a reference gas for determining the component quantity levels of other gas mixtures

[ISO 14532:2001, definition 2.5.3.5.2.1]

4 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 measured by comparison with calibration or reference gases. The gas being used for calibration and the sample gas shall be analysed with the same measuring system under the same set of conditions

5 Apparatus

5.1 Gas chromatograph, containing injection device, oven, regulation system for temperature control and pressure, detector.

5.2 Chromatographic columns, with column tubing made of a material inert to sulfur compounds (see 6.4), and a stationary phase able to separate the sulfur compounds to be analysed in order that the resolution between two adjacent peaks shall not be less than 1,5.

NOTE 1 See Annex A for a list of chromatographic columns mostly used in sulfur analysis.

NOTE 2 The absence of chromatographic separation between COS and H₂S will lead to an error in total sulfur amount calculation.

5.3 Detectors for detecting sulfur compounds:

- sulfur-specific,
- multi-specific (respond to halogen, sulfur), and/or
- general detectors.

See Annex B for descriptions of suitable detectors.

NOTE 1 Separation problems on a column could be solved by using a sulfur-specific detector, as hydrocarbons will not be seen by it.

NOTE 2 Matrix effects can occur in sulfur analysis with certain methods/detectors.

NOTE 3 Sulfur response can be affected by quenching effects produced by hydrocarbons.

NOTE 4 Many detectors use an excited state of a molecule or atom to detect sulfur. An atom or molecule with one electron shifted from its normal orbit to another (more energetic) is said to be excited. When it relaxes, returning to its normal state, the electron falls back to its normal orbit emitting a photon. The energy of this photon is relative to the difference in energy between the orbits. The wavelength of the photon is specific for each excited state. So, if photons of different wavelength are separated (by a filter, monochromator, diffraction prism, etc.), the amount of specific photons can be measured.

6 Sampling

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 place demands on the sampling procedure to ensure that the sulfur compounds in correct quantity reach the analytical detector.

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 have replicate stable analytical results within the acceptable standard deviation of the analyser. Purge time needed will depend on the type and concentration of the sulfur compound, materials of construction in gas contact and the gas flow through the sample loop.

6.1 Safety precautions

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

6.2 Temperature control

When a cylinder of a calibration or sample gas mixture arrives at the place of use, ensure that the cylinder temperature is kept above the condensation temperature (as stated on the certificate). If condensation may have occurred during transportation or storage, store the cylinder at ambient temperature in a horizontal position for at least 7 days. Rolling of the cylinder will lower the homogenisation time.

Always store both calibration and sample gases at the same suitable temperature.

To reduce any adsorption of low concentration levels of sulfur compounds when using the calibration gas or a sample, the transfer lines from the cylinder and the bypass injection valve should be heated (to, for example, 90 °C).

6.3 Construction materials

The presence of sulfur compounds in the calibration or sample gas makes the choice of materials of construction in the pressure reduction device, the transfer line, the sample loop and the separation column very important. The general considerations of ISO 10715 should always be followed.

6.4 Cleanness

When a calibration or sample gas cylinder is to be connected to a gas system, always inspect visually the connection on the cylinder valve outlet. Carefully clean out any dirt, dust or particles with a dust-free cloth. Any trace of humidity is to be purged out with dry inert gas.

Make sure that all transfer lines are free of dirt, rust, grease or other particles. Change all tubing/fittings if there is any suspicion of impurities. Particle filters may be helpful, but they shall only contain material proposed in ISO 10715.

6.5 Installation of the calibration gas cylinder

The installation of a calibration gas cylinder and use of the certified gas mixture is dependent on the method by which a gas sample is taken and is to be analysed/compared. To minimise the surface in gas contact, it is important to connect the calibration gas as near as possible to the injection point. One principle for the connection of a calibration gas cylinder in direct sampling is shown in ISO 10715:1997, Annex A.

6.6 Pressure control

As described for the sample handling in ISO 10715, very often a pressure reduction device is required in order to feed the calibration and sample gas to an analyser. Normally, this is a reduction valve connected directly or close to the calibration and sample gas cylinder. Only use a pressure regulator made of the material approved by the producer of the calibration gas mixture.

To further minimise any adsorption effects, a fine regulating needle valve (made in approved material) could be connected directly to the cylinder valve. Be sure that the certified pressure range of this valve suits that of the total system and that no local or national safety regulation prohibits such an arrangement.

Never use a calibration gas mixture with a total pressure lower than that recommended on the certificate. If no recommendation is stated, stop using the mixture if the total pressure is lower than 10 % of the certified filling pressure.

Always use the same reduced pressure when injecting the calibration mixture and the natural gas sample. Control the purge flow by a needle valve, not by adjusting the reduction pressure valve.

If several calibration gases with different concentrations of the sulfur compounds are used, it is very important to always use the same needle valve for the same calibration gas mixture. Be aware of the need to change needle valves to different concentration levels.

6.7 Purging of reduction valve and transfer lines

Due to the strong tendency of sulfur compounds to adsorb to different materials of construction, it is important to purge all surfaces (which are in contact with the gas) from the cylinder valve to the injection point. Using a pressure-reducing valve mounted directly onto the cylinder valve connection, the purging should include a number of "fill and empty" cycles as described in ISO 10715. A good practice is also to connect the total transfer line from the reducing valve to vent and include the purge all the way through the sample loop.

When analysing calibration gases with different concentration levels, always flush the transfer lines and the valves with dry N₂ in order to avoid memory effects.

6.8 Flow control

As stated in ISO 10715, turbulent flow is advantageous in a sampling system. The flow rate of the calibration gas with 3,175 mm (1/8 in) tubing should at least be 80 ml/min to 100 ml/min. When purging a calibration gas for analytical comparison with natural gas samples, the flow rate should be the same as the sample gas flow rate.

With light gases like H₂ or He in the calibration gas mixture, it may be of importance that the purge flow rate of calibration gas mixtures is never below 10 ml/min, in order to avoid separation effects of lighter versus heavier gases (effusion).

Stopping of flow just before injection of the standard/sample is the best way to minimize differences in the injected gas volumes due to back-pressure variations. However, be aware of any change in atmospheric pressure during the total analysis.

6.9 Diffusion control

Any leakage caused by diffusion of air-in or gas mixture out should be avoided by using pressure regulators with non-permeable membranes.

Be aware that using polymer types of tubing in gas transfer lines may cause problems related to diffusion of humidity from the environmental air.

6.10 Automation and sequences of sampling

With repeated injections and in order to get stable response from each sulfur compound in calibration and sample gas mixtures, a programmable automatic gas sampling valve should be installed and used. Normally, the tendency is that, due to adsorption phenomena, the peak from some sulfur compounds increases during the first injections, but after a few repeated injections the peak areas become more and more stable. The number of repeated injections required is to be defined based on achieved areas from each sulfur compound.

Repeated injections of the same calibration mixture before and after comparison analysis with one or more samples gives a good indication of any drift in the detector response during the total analytical time.

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7 Calibration

Perform regular calibration using working standard gas mixtures certified in accordance with ISO 6143 or permeation devices according to ISO 6145-10. The working standard gas mixtures shall contain appropriate number and concentrations of sulfur compounds in methane or natural gas depending upon the detector characteristics (e.g. hydrocarbon quenching). A certificate of mixture according to ISO 6141 should always be available with the cylinder.

NOTE 1 Sulfur compounds at low concentrations in gas mixtures are easily lost by sorption or reaction. The preparation of such mixtures requires that extreme care be taken with the cleanliness of the surfaces of cylinders and of tubing used for transfer, with the purities of the components used, particularly the matrix gas, and with the preparation procedure. Stability of the mixture can be demonstrated by regular repeat analyses of the contents, using as reference a dynamically prepared mixture of similar composition. A demonstrated history of preparation of mixtures which have been successfully assessed for stability is the best form of assurance for the user.

NOTE 2 Another problem with diffusion is caused by connecting reduction valves to the cylinders. The air contained in the reduction valve will diffuse into the cylinder when the cylinder valve is opened while the reduction valve is still closed. The oxygen will, for example, oxidize mercaptans to disulfides.

8 Analysis

Perform quantitative analysis and determine the mass concentration and uncertainty budget of the different sulfur compounds in natural gas in accordance with ISO 6143.

Be aware of the special adsorption and/or chemical problems that can occur with the handling of sulfur gas components. Repeated injections of the same working reference gas mixture before and after comparison analysis may give an indication of any drift due to sulfur adsorption during the total analytical time.

9 Performance characteristics required for sulfur analysis

The performance characteristics required for sulfur analysis were determined from a proficiency test performed by seven laboratories in different countries. The following two mixtures — given here with their compound/IUPAC name and mass concentration expressed in milligrams per cubic metre (under normal reference conditions) — were analysed.

a) Mixture 1

- Hydrogen sulfide (H₂S): 3 mg/m³
- Methane (CH₄): matrix

b) Mixture 2

- Carbonyl sulfide (COS): 5 mg/m³
- Methanethiol (MeSH): 5 mg/m³
- Ethanethiol (EtSH): 5 mg/m³
- 2-Methylpropane-2-thiol (TBM): 6 mg/m³
- Diethyl sulfide (DES): 10 mg/m³
- Tetrahydrothiophene (THT): 25 mg/m³
- Methane (CH₄): matrix

The seven laboratories used different methods and calibration gases. The data obtained are given in Table 1.

Table 1 — Performance characteristics for sulfur analysis

Compound	Mass concentration (sulfur compound in methane) mg/m ³ (norm. ref. cond.)	Achievable repeatability (absolute) mg/m ³ (norm. ref. cond.)	Achievable repeatability (relative) %	Proficiency agreement (relative) %
H ₂ S	3	0,1	3	25
COS	5	0,1	2	15
MeSH	5	0,1	2	10
EtSH	5	0,2	4	30
TBM	6	0,4	7	25
DES	10	0,2	2	20
THT	25	1,0	4	20

Proficiency agreement values quoted in Table 1 were calculated based on z -scores as defined in Reference [5] (see 4.1, 4.2, 4.3), and are the limits between which two laboratories shall be able to achieve a result of analyzing a known standard using different methods and calibration gases. The two laboratories analyze a standard of known mass concentration of 25 mg/m^3 of THT. If their results lie within the range of 19 mg/m^3 and 31 mg/m^3 , then they are comparable, i.e. $25 \text{ mg/m}^3 \pm 5 \text{ mg/m}^3$ (20 % of the proficiency agreement given in Table 1) $\pm 1 \text{ mg/m}^3$ (4 % of the achievable repeatability given in Table 1).

The repeatability shown in Table 1 was calculated in the following way: two times the standard deviation based on $n-1$ values (95 % confidence interval, see ISO 5725-2), free of outliers (see ISO 5725-2:1994, 7.3.4.1), assuming a normal distribution calculated with 5 analyses.

10 Test report

The test report shall include at least the following information:

- a) reference to this International Standard and the analytical method used;
- b) sample identification including
 - time/date of the sampling,
 - sample point/stream (location), and
 - cylinder identification (for spot sampling);
- c) reference to the calibration system used;
- d) sample mass concentration, including the number of digits appropriate to the certificate of WRM and size of error, including the result of uncertainty calculation;
- e) comments, including
 - any deviation from specified procedure, and/or
 - problems concerning the sample;
- f) date of analysis, name of laboratory and signature of analyst.