
**Natural gas — Organic sulfur compounds
used as odorants — Requirements and test
methods**

*Gaz naturel — Composés organiques soufrés utilisés comme odorants —
Prescriptions et méthodes d'essai*

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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.

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.

International Standard ISO 13734 was prepared by Technical Committee ISO/TC 193, *Natural gas*.

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Introduction

Processed natural gas received from suppliers normally has little or no odour. For safety reasons, natural gas is therefore odorized to permit the detection by smell of the gas at very low concentrations in air.

NOTE — It is a common requirement that natural gas in air be readily detectable by smell at a concentration of 20 % of the lower flammability limit (LFL). The LFL of natural gas is normally taken as a volume content in air of 4 % to 5 %.

Odorants used for the odorization of natural gas need to meet several basic requirements:

- a) They need to have an intense odour.
- b) The odour needs to be distinctive and not confusable with other frequently occurring odours.
- c) The odour needs to be unpleasant but not too obnoxious. The odour character needs to be the same at different dilutions of natural gas with air.
- d) The odorized gas must not be toxic or an irritant at the concentration levels at which the odorant is employed and the addition of the odorant must not lead to the production of significant levels of harmful combustion products.
- e) The odorant needs to be volatile, and sufficiently stable in the gas phase and during storage. It must not form deposits on burners and safety devices.

Experience in many countries has shown that these basic requirements are best met by organic sulfur compounds — sulfides (thioethers) and mercaptans (thiols) — with boiling points below 130 °C. Since primary mercaptans are easily oxidized to disulfides which have a much lower odour intensity, mercaptan-based odorants need to predominantly contain secondary and tertiary mercaptans.

While it has been established that the above sulfur compounds fulfil the basic requirements listed above under a) to e), the suitability of other compounds (e.g. non-sulfur compounds) should not be precluded, provided they meet these basic requirements.

Natural gas — Organic sulfur compounds used as odorants — Requirements and test methods

1 Scope

This International Standard specifies requirements and test methods for organic sulfur compounds suitable for odorization of natural gas and natural gas substitutes for public gas supply, hereafter referred to as odorants.

2 Normative reference

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

ISO 3015:1992, *Petroleum products — Determination of cloud point.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 odorant

an intensely smelling organic chemical or combination of chemicals added to natural gas at low concentration and capable of imparting a characteristic and distinctive (usually disagreeable) warning odour so gas leaks can be detected at concentrations below their lower flammability limit

NOTE — Currently commercially used odorants belong to the following classes of substances:

- a) alkyl sulfides (alkyl thioethers)
 - symmetrical sulfides, e.g. $C_2H_5-S-C_2H_5$
 - asymmetrical sulfides, e.g. $CH_3-S-C_2H_5$
- b) cyclic sulfides (cyclic thioethers), e.g. C_4H_8S
- c) alkyl mercaptans (alkane thiols)
 - primary mercaptans, e.g. C_2H_5-SH
 - secondary mercaptans, e.g. $(CH_3)_2CH-SH$
 - tertiary mercaptans, e.g. $(CH_3)_3C-SH$

3.2

diluent

an organic liquid, normally consisting of paraffinic hydrocarbons, used to reduce the concentration of an odorant to a suitable level at which the solution may be injected into the natural gas

3.3

cloud point

the temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under specified conditions

[ISO 3015:1992]

4 Requirements

4.1 Composition

The mass content of organic sulfur compounds in the undiluted odorant when determined in accordance with 6.3 shall be equal to or higher than 95 %. At least 80 % of the mass content of these sulfur compounds shall consist of sulfides (thioethers) or secondary or tertiary mercaptans (thiols). The composition of the odorant, and where applicable the dilution range, shall be declared by the producer or distributor.

NOTE — Primary mercaptans — especially methyl and ethyl mercaptan — are more easily oxidized than secondary or tertiary mercaptans by traces of oxygen in the gas and by iron oxide, e.g. in the form of pipe dust. It is therefore recommended that the content of primary mercaptans in odorants be minimized.

4.2 Cloud point

The cloud point of the undried odorant, when determined in accordance with 6.4, shall be below $-30\text{ }^{\circ}\text{C}$.

4.3 Boiling point

The boiling points of the odorant and diluent, when determined in accordance with 6.5, shall not be higher than $130\text{ }^{\circ}\text{C}$.

4.4 Evaporation residue

The mass content of the evaporation residue, when determined in accordance with 6.6, shall be less than 0,2 %.

4.5 Insoluble matter

Odorants shall not contain any visible insoluble matter, when determined in accordance with 6.7.

4.6 Solubility in water (optional requirement)

When the odorant is added to water in the way specified in 6.8, less than 2 % by volume of the odorant shall be soluble. This optional requirement is valid for wet distribution systems.

5 Handling and transport

When delivered, odorants shall be accompanied by a safety data sheet conforming to the requirements of the country of use.

6 Tests

6.1 Test sample

For type approval and control tests, the producer or supplier shall deliver at least 0,5 l of a representative sample of the liquid odorant to a qualified test laboratory, acceptable to both producer and purchaser.

6.2 Test documentation

The following documentation shall be provided by the producer or supplier:

- a) a safety data sheet conforming to the requirements of the country of use;
- b) complete details of the composition of the odorant.

6.3 Determination of composition

The composition of the odorant shall be determined by gas-chromatographic analysis on a 50 m methyl silicone capillary column (internal diameter 0,2 mm) with a carrier gas (H₂ or He) at a flow rate of 1,8 ml/min and a split ratio of 1:30. The initial temperature shall be 35 °C; after 10 min, the temperature shall be raised at a rate of 7 °C/min to 250 °C and kept at this temperature.

For the detection of sulfur and non-sulfur compounds (diluent or impurities), a non-sulfur-specific detector — e.g. a flame ionization detector (FID) or a thermal-conductivity detector (TCD) — shall be used. The response functions of the various sulfur compounds shall be determined with calibration mixtures prepared from pure components. The concentrations of impurities which cannot be identified shall be calculated on the basis of the response factor for *n*-hexane.

The retention times of the relevant sulfur compounds in relation to the retention time of tetrahydrothiophene (THT), which is about 15 min, are given in table 1, which also lists the boiling points.

Any gas-chromatographic method giving equivalent, or better, component separation and detection may be used. In cases of dispute, the above-mentioned method shall be used.

A sulfur-specific detector may additionally be used to differentiate between sulfur and non-sulfur components.

6.4 Determination of cloud point

The cloud point shall be determined in accordance with ISO 3015 except that, contrary to the method specified in that standard, cloud formation by water shall be taken into account; therefore the sample shall be neither filtered nor dried. The test jar in its jacket is directly immersed in bath No. 4 specified in table 2 of ISO 3015:1992 having the temperature range –52 °C to –49 °C. When the temperature of the

odorant has reached $-30\text{ }^{\circ}\text{C}$, the test jar is removed from the jacket quickly, without disturbing the sample, and inspected for cloudiness.

6.5 Determination of boiling point

The boiling points of sulfur compounds used as odorants are listed in table 1. Boiling points of paraffinic-hydrocarbon diluents may be found in the literature given at the bottom of table 1.

Table 1 — Relative gas-chromatographic retention times and boiling points of relevant sulfur compounds

| Sulfur compound | Formula | Relative retention time ¹⁾ | Boiling point $^{\circ}\text{C}$ ²⁾ |
|--|---|---------------------------------------|--|
| methyl mercaptan (methanethiol) | CH_3SH | 0,232 | 6,2 |
| ethyl mercaptan (ethanethiol) | $\text{C}_2\text{H}_5\text{SH}$ | 0,280 | 35 |
| dimethyl sulfide (dimethyl thioether) | CH_3SCH_3 | 0,291 | 37,3 |
| isopropyl mercaptan (2-propanethiol) | $(\text{CH}_3)_2\text{CHSH}$ | 0,324 | 52,5 |
| <i>tert.</i> -butyl mercaptan (2-methyl-2-propanethiol) | $(\text{CH}_3)_3\text{CSH}$ | 0,350 | 64,2 |
| <i>n</i> -propyl mercaptan (1-propanethiol) | $\text{C}_3\text{H}_7\text{SH}$ | 0,392 | 67 to 68 |
| methyl ethyl sulfide (methyl ethyl thioether) | $\text{CH}_3\text{SC}_2\text{H}_5$ | 0,393 | 66,6 |
| <i>sec.</i> -butyl mercaptan (2-butanethiol) | $\text{CH}_3\text{CH}(\text{SH})\text{C}_2\text{H}_5$ | 0,515 | 85 |
| isobutyl mercaptan (2-methyl-1-propanethiol) | $(\text{CH}_3)_2\text{CHCH}_2\text{SH}$ | 0,558 | 88,7 |
| diethyl sulfide (diethyl thioether) | $(\text{C}_2\text{H}_5)_2\text{S}$ | 0,640 | 92,1 |
| <i>n</i> -butyl mercaptan (1-butanethiol) | $\text{C}_4\text{H}_9\text{SH}$ | 0,686 | 98,4 |
| tetrahydrothiophene (tetramethylene sulfide) | $\text{C}_4\text{H}_8\text{S}$ | 1,000 | 121,1 |
| <i>n</i> -pentyl mercaptan (1-pentanethiol) | $\text{C}_5\text{H}_{11}\text{SH}$ | 1,060 | 126,6 (613 mbar) |

1) The retention times are given relative to tetrahydrothiophene (THT) which has a retention time of about 15 min under the conditions given in 6.3.

2) *Handbook of Chemistry and Physics*, 67th Edition, CRC Press, Boca Raton, Florida, USA (1986-1987).

6.6 Determination of evaporation residue

Insert a gas inlet tube equipped with a stopcock into one neck of a two-necked round-bottomed flask with a volume of about 25 ml so that the tube extends nearly to the bottom of flask. Close off the other neck with a gas outlet tube also equipped with a stopcock. It is recommended that PTFE (polytetrafluoroethylene) jackets are used to seal the ground-glass connections instead of grease and stopcocks with PTFE plugs. Weigh the assembly to an accuracy of better than 1 mg (m_0). Using a pipette or syringe, transfer about 5 ml of the odorant into the flask. Weigh the closed flask (m_1) to determine the mass of the odorant sample.

Connect the gas inlet tube to a supply of inert gas, e.g. nitrogen, to avoid the oxidation of mercaptans. Connect the gas outlet to a cold trap or an absorber filled with activated charcoal to trap the evaporated odorant. Evaporate the odorant by passing a stream of inert gas at about 20 ml/min through the flask, which is heated in a water bath at a temperature of about 20 °C to 30 °C below the boiling point of the odorant. For odorants with high boiling points, the determination can be accelerated by reducing the pressure. This is done by replacing the gas inlet tube by a capillary.

When all visible odorant has been evaporated, close the stopcocks, dry the flask carefully, allow it to return to room temperature and weigh (m_{E1}). Then continue the evaporation for 15 min under the above-mentioned conditions. Continue the weighing and evaporation until the difference in mass between the last two weighings ($m_{E(n+1)} - m_{En}$) is less than 1 mg. Calculate the evaporation residue R from the last value ($m_{E(n+1)}$) and the mass of the sample used, to the nearest 0,01 %, from the following equation:

$$R = \frac{m_{E(n+1)} - m_0}{m_1 - m_0} \times 100$$

6.7 Visual examination for solids or suspended matter

Take a sample of about 20 ml of the odorant in a normal test tube of about 15 mm internal diameter and inspect it after shaking and again after a settling time of 15 min, against a light source, for insoluble material.

6.8 Determination of solubility in water

Add 5 ml of the odorant to 50 ml of a 10 % solution of sodium chloride in water in a graduated glass cylinder (see figure 1) with a ground-in plug. Measure the volume of the odorant in the graduated part of the cylinder with the cylinder in the upright position (V_1).

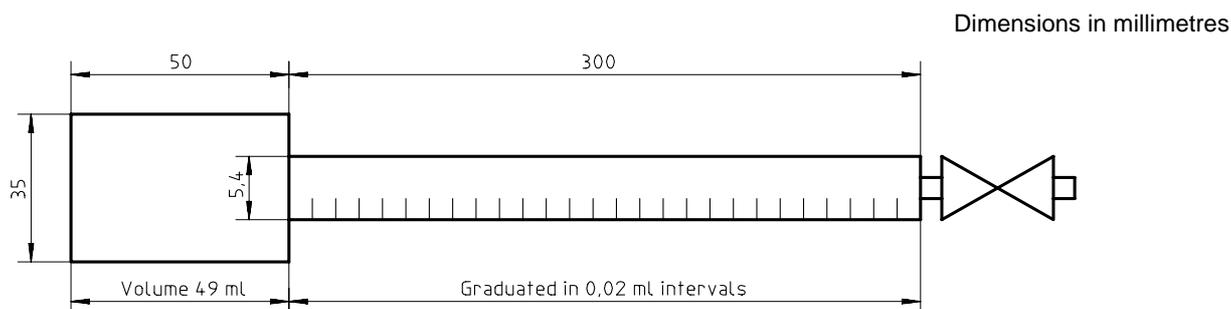


Figure 1 — Cylinder for solubility determination