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

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



Reference number  
ISO 13734:2013(E)

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2. [www.iso.org/directives](http://www.iso.org/directives)

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received. [www.iso.org/patents](http://www.iso.org/patents)

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

The committee responsible for this document is ISO/TC 193, *Natural gas*.

This second edition cancels and replaces the first edition (ISO 13734:1998), which has been technically revised. It also incorporates the Corrigendum ISO 13734:1998/Corr.1:1999.

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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 the volume fraction in air of 4 % to 5 %.



# Natural gas — Organic components used as odorants — Requirements and test methods

## 1 Scope

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

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3007:2005, *Petroleum products and crude petroleum — Determination of vapour pressure — Reid method*

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

ISO 4256:1996, *Liquefied petroleum gases — Determination of gauge vapour pressure — LPG method*

ISO 4626:1980, *Volatile organic liquids — Determination of boiling range of organic solvents used as raw materials*

ISO 14532, *Natural gas — Vocabulary*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14532 (in particular [3.1](#) to [3.4](#)) and the following apply.

### 3.1 odorization

addition of odorants, normally intensely smelling organic sulfur compounds, to natural gas (normally odourless) to allow the recognition of gas leaks by smell at very low concentration (before a build up to a dangerous gas in air concentration can occur)

Note 1 to entry: Adapted from ISO 14532.

Note 2 to entry: Natural gas is normally odourless. The addition of an odorant to the gas fed into the distribution system for safety reasons permits the detection of the gas by smell at very low concentrations.

### 3.2 odorant

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

[SOURCE: ISO 14532]

**3.3**

**odour character**

type of sensation of an odour

[SOURCE: ISO 14532]

Note 1 to entry: Odour character is a qualitative parameter.

**3.4**

**odour intensity**

strength of odour perception

[SOURCE: ISO 14532]

**3.5**

**threshold concentration**

concentration at which an individual has a probability of 0,5 in perceiving the odour

Note 1 to entry: To detect an odour does not imply that this odour may be identified.

**3.6**

**odour intensity curve**

relationship between odour intensity and odorant concentration in air

Note 1 to entry: The odour intensity can only be determined by the human olfactory organ.

**3.7**

**diluent**

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

**3.8**

**cloud point**

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

## **4 Requirements**

### **4.1 Recommendations of an effective odorant**

Gas odorants should meet the following general recommendations:

- a) The gas odorant should have a strong odour at very low concentration.
- b) The odour character of the odorant needs to be unpleasant, distinctive and not confusable with other frequently occurring odours so that it is unmistakably associated with a gas leak.
- c) The odour character should be the same at different dilutions of natural gas with air.
- d) The odorant should be sufficiently stable during storage and when mixed with natural gas.
- e) The volatility of the odorant should be high enough so that the odorant does not appreciably condense under the conditions (temperature and pressure) existing in the pipeline system.
- f) Evaporation of the gas odorant should not appreciably leave residues.
- g) The odorant should be useable at low temperatures, when required.
- h) The combustion of the odorant should not leave significant solid deposits.
- i) The addition of the odorant to natural gas should not make the resulting gas harmful.



These general recommendations should be assessed against the specific conditions of use of the odorant (conditions of the natural gas transportation grid, odorization installation, type of odorant, composition of the gas).

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 i), other, non-sulfurous odorants have been developed and are available.

## 4.2 Composition of odorants

The mass fraction of the declared chemical product in the undiluted odorant shall be at least 95 %. The composition of the odorant, and where applicable the dilution range, shall be declared by the producer or distributor. It shall be stable over the maximum shelf time as declared by the manufacturer.

In sulfur containing odorants, the mass fraction of sulfides (thioethers) or secondary or tertiary mercaptans (thiols) shall be at least 80 %. Primary mercaptans are more easily oxidized than secondary or tertiary mercaptans.

For non-sulfurous odorants based on acrylates, care shall be taken e.g. by use of an appropriate additive to avoid polymerisation.

## 4.3 Cloud point

The cloud point of the undried odorant, to be determined in accordance with [6.4](#), shall be below -30 °C.

## 4.4 Phase properties

### 4.4.1 Boiling point

The boiling point of the components of the odorants and diluent, measured in accordance with [6.5](#), shall not be higher than 130 °C.

### 4.4.2 Vapour pressure curve

The vapour pressure curve of the odorant and eventually the diluent shall be given. It shall be determined in accordance with [6.5](#).

## 4.5 Evaporation residue

The mass fraction of the evaporation residue, to be determined in accordance with [6.6](#), shall be less than 0,2 %.

## 4.6 Insoluble matter

Odorants shall not contain any visible insoluble matter, to be determined in accordance with [6.7](#).

## 4.7 Solubility in water

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.

## 5 Handling and transport

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

Appropriate personnel protective equipment, as specified in the safety data sheet, shall be used when handling odorants. The safety data sheet shall also give information about safe handling, transport and storage.

## 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 material safety data sheet (MSDS) conforming to the requirements of the country of use;
- 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. Any gas-chromatographic method giving sufficient component separation and detection may be used.

### 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 °C, the test jar is removed from the jacket quickly, without disturbing the sample, and inspected for cloudiness.

### 6.5 Determination of phase properties

The boiling point of compounds used as odorants shall be measured in accordance with ISO 4626.

The vapour pressure curve shall be determined either in accordance with ISO 3007 or, for odorants applicable for the odorization of liquefied petroleum gases (LPG), in accordance with ISO 4256.

### 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 strongly recommended that PTFE (polytetrafluoroethylene) or other non-reactive/non-absorptive material 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 connecting the outlet of the cold trap or absorber to a vacuum pump and replacing the gas inlet tube by a fine capillary to avoid retardation of ebullition. Flush the capillary with an inert gas, for example nitrogen, to avoid the oxidation of mercaptans.

When all visible odorant has been evaporated, close the stopcocks, dry the flask carefully, allow it to return to room temperature and weigh ( $m_{E(1)}$ ). Then continue the evaporation for 15 min under the abovementioned conditions. Continue the weighing and evaporation until the difference in mass between the last two weighings ( $m_{E(n+1)} - m_{E(n)}$ ) 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:

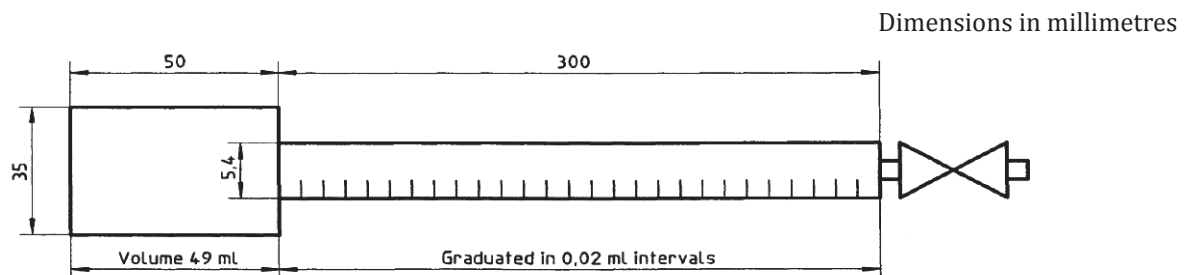
$$R = \frac{m_{E(n+1)} - m_0}{m_1 - m_0} \times 100$$

## 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**

Keep the cylinder horizontal in a thermostatically controlled water bath at a temperature of 10 °C ± 1 °C for 24 h. Then measure again the volume of the odorant in the graduated part of the cylinder ( $V_2$ ) and calculate the solubility  $S$  to the nearest 0,1 %, from the following equation:

$$S = \frac{V_1 - V_2}{V_1} \times 100$$

## 7 Labelling and documentation

### 7.1 Labelling

Odorant containers shall be clearly marked in accordance with the applicable safety and transport regulations. The markings will normally include:

- a) the name and/or registered trade mark of the producer of the odorant;
- b) the designation and composition of the odorant;

- c) safety and handling instructions conforming to the requirements of the country of use (e.g. hazard classification).

## **7.2 Documentation**

The supplier of the odorant shall provide each user of the odorant (e.g. a gas distribution company) with a (material) safety data sheet and additional documentation giving information about:

- the odour intensity curve of the odorant including the detection threshold of the odorant determined in accordance with ISO standards (when and if such standards are published);
- storage conditions that will preserve the olfactory, physical and chemical properties of the odorant;
- compatibility of the liquid odorant with materials it may be in contact with before vaporization;
- indication of the odorant stability under pipeline conditions;
- indication of the odorant stability in the ground and with water;
- indication of the reactivity of the vaporized odorant with pipeline materials including seals.

The origin of this information (i.e. experimental procedure, source of data) shall be given. It is also possible to express this information relatively to a well-known odorant such as THT.

## Annex A (informative)

### Properties of odorants

#### A.1 Odorant components

The components of commonly used odorants are almost exclusively sulfur containing organic compounds which comply with the basic recommendations listed in [Clause 4](#). They 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.  $(CH_3)_3C-SH$ .

A number of non-sulfur products have been proposed for gas odorant, for instance, norbornene and derivatives, acrylates, pentanones, pyrazine aldehydes and mixtures of those. So far, only few of these products are in use, based on acrylates.

#### A.2 Properties of sulfurous odorants

##### A.2.1 Olfactory properties

Mercaptans and sulfides are used as natural gas odorants because of their strong and characteristic odour. Compared to other compounds of the class of sulfides, e.g. the simple alkyl sulfides such as dimethylsulfide, methylethylsulfide and diethylsulfide, the cyclic sulfide tetrahydrothiophene (THT) (thiacyclopentane) shows higher odour intensity. Mercaptans possess the highest odour intensity.

##### A.2.2 Physical and chemical properties

Among the physical properties of odorants, the volatility, closely related to the boiling point, is the most important. To avoid condensation low-boiling components are preferred. When used in evaporation odorizers, the differences between the boiling points of the odorant components in mixtures should be small.

It is not recommended to use tert.-butylmercaptan (TBM) as a single component odorant because of its high freezing point. At low temperatures, TBM would not be sufficiently vaporized and thus not be detected.

Sulfides are chemically more stable than mercaptans. Mercaptans may be oxidized by iron oxide (rust) to disulfides. Iron oxide also acts as a catalyst for the oxidation of mercaptans by oxygen [e.g. when LPG<sup>1)</sup>-air mixtures are used for peak shaving]. By this reaction mercaptans are transformed into disulfides, which have significantly lower odour intensity and also a different odour character. Tertiary mercaptans (e.g. TBM) are more resistant to oxidation than secondary mercaptans (e.g. iso-propylmercaptan) and secondary mercaptans are more resistant than primary mercaptans. Mixtures of branched and unbranched mercaptans are more easily or more quickly oxidized than pure branched mercaptans.

For the odorization of pipeline gas, it is preferable to use sulfides and branched mercaptans. Mercaptans are normally used as mixtures with sulfides. However, examples of pure products used as odorants are THT and secondary butylmercaptan (SBM).

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1) LPG = liquefied petroleum gas

When starting gas distribution through new gas lines or when changing the odorant, it may take some time to reach the required odorant concentration at the end of the line. This may result from the odorant being sorbed on the pipe wall, by pipe dust, rust and incrustations or by gas condensates (odour fading). The degree of sorption depends on several factors, for example the condition of the pipe grid, the pressure, the temperature, the flow velocity and the physicochemical properties of odorants.

Odorized gases leaking from gas lines in the ground may lose odorants by sorption in the soil. Higher boiling odorants such as THT will more likely be adsorbed than lower boiling odorants such as TBM. Mercaptans may be oxidized by soil containing iron oxide to less odoriferous but more strongly sorbed disulfides. Sorption and oxidation of odorants may vary with moisture content and the type of soil. Degradation of odorants by micro-organisms may also occur.

### **A.3 Physical and chemical data of pure sulfur compounds**

Some data of the most widely used sulfur compounds used as odorants pure or in a mixture are listed in [Table A.1](#).

**Table A.1 — List of chemical and physical properties of pure sulfur compounds**

| Sulfur compound   | Formula  | Molar mass<br>g/mol | Boiling point<br>°C | Freezing point<br>°C | Density<br>(at 20 °C) g/cm <sup>3</sup> |
|---|--|---------------------|---------------------|----------------------|---|
| Sulfides (thioether)  |  |                     |                     |                      |   |
| Dimethyl sulfide (DMS)  | CH <sub>3</sub> SCH <sub>3</sub>                     | 62,14               | 37,3                | -98,3                | 0,848 3                                 |
| Methyl ethyl sulfide (MES)  | CH <sub>3</sub> SC <sub>2</sub> H <sub>5</sub>       | 76,16               | 66,7                | -105,9               | 0,842 2                                 |
| Diethyl sulfide (DES)   | (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S      | 90,19               | 92,1                | -103,9               | 0,836 2                                 |
| Tetrahydrothiophene (THT)   | C <sub>4</sub> H <sub>8</sub> S                      | 88,17               | 121,0               | -96,1                | 0,998 7                                 |
| Mercaptans (thiols)   |  |                     |                     |                      |   |
| Methylmercaptan (MM) <sup>a</sup><br>(methanethiol)   | CH <sub>3</sub> SH                                   | 48,11               | 5,9                 | -123                 | 0,866 5                                 |
| Ethylmercaptan (EM) <sup>c</sup><br>(ethanethiol)   | C <sub>2</sub> H <sub>5</sub> SH                     | 62,14               | 35,1                | -147,8               | 0,831 5 <sup>b</sup>                    |
| n-Propylmercaptan (NPM)<br>(1-propanethiol)   | C <sub>3</sub> H <sub>7</sub> SH                     | 76,16               | 67 to 68            | -113,3               | 0,841 1                                 |
| iso-Propylmercaptan (IPM)<br>(2-propanethiol)   | (CH <sub>3</sub> ) <sub>2</sub> CHSH                 | 76,16               | 52,6                | -130,5               | 0,814 3                                 |
| n-Butylmercaptan (NBM)<br>(1-butanethiol)   | C <sub>4</sub> H <sub>9</sub> SH                     | 90,19               | 98,5                | -115,7               | 0,841 6                                 |
| sec.-Butylmercaptan (SBM)<br>(2-butanethiol)  | CH <sub>3</sub> CH(SH)C <sub>2</sub> H <sub>5</sub>  | 90,19               | 85                  | -165                 | 0,829 5                                 |
| iso-Butylmercaptan (IBM)<br>(2-methylpropane-1-thiol)   | (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> SH | 90,19               | 88,5                | < -70                | 0,835 7                                 |
| tert.-Butylmercaptan (TBM)<br>(2-methylpropane-2-thiol)   | (CH <sub>3</sub> ) <sub>3</sub> CSH                  | 90,19               | 64,3                | -0,5                 | 0,794 3 <sup>b</sup>                    |
| Values taken from the <i>Handbook of Chemistry and Physics</i> , 87th ed., CRC Press, Boca Raton, Florida, USA.                     |  |                     |                     |                      |   |
| <sup>a</sup> Not used for natural gas odorization, but may naturally occur in natural gas.  |  |                     |                     |                      |   |
| <sup>b</sup> Value at 25 °C.  |  |                     |                     |                      |   |
| <sup>c</sup> Generally applied as odorant for LPG only but may occur in natural gas after conditioning involving propane or butane. |  |                     |                     |                      |   |

#### A.4 Properties of non-sulfurous odorant

Some data of the most widely used non-sulfur compounds used as odorants pure or in a mixture are listed in [Table A.2](#).

**Table A.2 — Physical data of non-sulfur odorant compounds of odorants in use**

| Odorant         | Formula   | Molar mass<br>g/mol | Boiling point<br>°C | Freezing point<br>°C | Density<br>(at 20 °C) g/cm <sup>3</sup> |
|-----------------|---|---------------------|---------------------|----------------------|---|
| Methyl acrylate | C <sub>2</sub> H <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>               | 86                  | 80                  | -75                  | 0,956                                   |
| Ethyl acrylate  | C <sub>2</sub> H <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> | 100,12              | 100                 | -72                  | 0,922                                   |

NOTE Acrylates present a smell different to that of sulfurous odorants. Furthermore some caution is to be taken when switching from one to the other as they may not readily fulfil [4.1 b](#)).



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