TECHNICAL SPECIFICATION

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Natural gas — Guidelines for odorizing gases

Gaz naturel — Lignes directrices pour odoriser les gaz

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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 3.

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.

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of normative document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

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An ISO/PAS or ISO/TS is reviewed after three years with a view to deciding whether it should be confirmed for a further three years, revised to become an International Standard, or withdrawn. In the case of a confirmed ISO/PAS or ISO/TS, it is reviewed again after six years at which time it has to be either transposed into an International Standard or withdrawn.

Attention is drawn to the possibility that some of the elements of this Technical Specification may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TS 16922 was prepared by Technical Committee ISO/TC 193, *Natural gas*.

Annex A of this Technical Specification is for information only.

Introduction

Processed natural gas normally has little or no odour. For safety reasons distributed natural gas should therefore be odorized, to permit the detection of the gas by smell.

Natural gas — Guidelines for odorizing gases

1 Scope

This Technical Specification gives the guidelines for the methods and odorants to be used in the odorization of natural gas.

This Technical Specification also specifies the general requirements for odorants, the physical and chemical properties of commonly used sulfur-containing odorants, the principles for the determination of odour intensity, the odorization technique (including handling and storage of odorants) and the control of odorization of natural gas.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this Technical Specification. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this Technical Specification are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5492, *Sensory analysis — Vocabulary*

ISO 10715, *Natural gas — Sampling guidelines*

ISO 13734, *Natural gas — Organic sulfur compounds used as odorants — Requirements and test methods*

ISO 14532, *Natural gas — Vocabulary*

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

3 Terms and definitions

For the purposes of this Technical Specification, the terms and definitions given in ISO 5492 and ISO 14532 and the following apply.

3.1 General

The following general definitions apply to the human ability for sensation, awareness and intensity of odour perception.

3.1.1
odour perception
awareness of the effect of volatile substances by the olfactory organ

3.1.2
odour character
type of sensation of an odour

NOTE Odour character is a qualitative parameter.

3.1.3
odour intensity
strength of odour perception

3.1.4
terminal threshold
saturation
minimum value of an intense sensory stimulus above which no difference in intensity can be perceived

[ISO 5492]

3.1.5
sensory fatigue
form of sensory adaptation in which a decrease in sensitivity occurs

[ISO 5492]

3.1.6
addition of odours
masking of odours
result of the odour intensity of a mixture of odoriferous compounds being higher or lower than the odour intensity of each odorant present at the same concentration as in the mixture

NOTE The odour character may be changed by the addition or masking of odours.

3.2 Specific definitions for the gas odorants

3.2.1
olfactory degree
unit of measure of the odour intensity in accordance with the general law established by Weber, Fechner and Stevens and is proportional to the logarithm of the odorant concentration

NOTE Various scales have been proposed for expressing the odour intensity of substances. The gas industry refers frequently to the scale proposed by Sales (see Table 1). It refers to trained persons.

Table 1 — Odour intensity and corresponding sensation

Odour intensity olfactory degrees	**Sensation**
0	No odour
0,5	Very feeble odour (limit of odour perception)
1	Feeble odour
2	Medium odour (alert level)
3	Strong odour
4	Very strong odour
5	Maximum odour (upper limit of perception)

3.2.2
detection threshold
odorant concentration which has a probability of 0,5 of being detected by a person or by 50 % of the population

NOTE To detect an odour does not imply that this odour may be identified.

3.2.3
identification threshold
odorant concentration which has a probability of 0,5 of being identified under test condition by a person or by 50 % of the population

3.2.4
alert level
by convention a medium odour of olfactory intensity degree 2 on the Sales scale

3.2.5
odour intensity curve
gives the correlation of odour intensity versus odorant concentration in air

NOTE The odour intensity of an odorant for natural gas or a gas can only be determined by human olfactory organ.

4 General recommendations for natural gas odorants

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 (condition of the natural gas transportation grid, odorization installation, type of odorant, composition of the gas).

Requirements for organic sulfur compounds used as natural gas odorants are specified in ISO 13734.

5 Typical odorants

5.1 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. $(CH_3)_2$CH-SH;
- tertiary mercaptans, e.g. $(CH_3)_3$C-SH.

5.2 Properties of sulfurous odorants

5.2.1 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, for example 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.

5.2.2 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 as evaporation odorizers, the differences between the boiling points of the odorand 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, TMB 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[1)]–air mixtures are used for peak shaving[2)]]. 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 *sec*-butylmercaptan.

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 physico-chemical 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 microorganisms may also occur.

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1) LPG = liquefied petroleum gas

2) Peak shaving is a load management tool that reduces energy costs by replacing expensive energy used during peak operating hours with inexpensive energy which is produced on-site.

5.3 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 2. Specific requirements for commonly used natural gas odorants and the appropriate test methods are specified in ISO 13734.

Table 2 — List of chemical and physical properties of pure sulfur compounds

Sulfur compound	Formula	Molar mass g/mol	Boiling point °C	Freezing point °C	Density (at 20 °C) g/cm³
Sulfides (thioether)					
Dimethyl sulfide (DMS)	CH_3SCH_3	62,14	37,3	−98,3	0,848 3
Methyl ethyl sulfide (MES)	$CH_3SC_2H_5$	76,16	66,7	−105,9	0,842 2
Diethyl sulfide (DES)	$(C_2H_5)_2S$	90,19	92,1	−103,9	0,836 2
Tetrahydrothiophene (THT)	C_4H_8S	88,17	121,0	−96,1	0,998 7
Mercaptans (thiol)					
Methylmercaptan (MM)[a] (methanethiol)	CH_3SH	48,11	5,9	−123	0,866 5
Ethylmercaptan (EM) [a] (ethanethiol)	C_2H_5SH	62,14	35,1	−147,8	0,831 5[b]
n-Propylmercaptan (NPM) (1-propanethiol)	C_3H_7SH	76,16	67 to 68	−113,3	0,841 1
iso-Propylmercaptan (IPM) (2-propanethiol)	$(CH_3)_2CHSH$	76,16	52,6	−130,5	0,814 3
n-Butylmercaptan (NBM) (1-butanethiol)	C_4H_9SH	90,19	98,5	−115,7	0,841 6
sec-Butylmercaptan (SBM) (2-butanethiol)	$CH_3CH(SH)C_2H_5$	90,19	85	−165	0,829 5
iso-Butylmercaptan (IBM) (2-methylpropane-1-thiol)	$(CH_3)_2CHCH_2SH$	90,19	88,5	< −70	0,835 7
tert-Butylmercaptan (TBM) (2-methylpropane-2-thiol)	$(CH_3)_3CSH$	90,19	64,3	−0,5	0,794 3[b]

Values taken from the *Handbook of Chemistry and Physics*, 80th ed., CRC Press, Boca Raton, Florida, USA.

[a] Not used for natural gas odorization, but may naturally occur in natural gas.

[b] Value at 25 °C.

5.4 General remarks on odorant behaviour

Liquid odorants may cause severe swelling or even dissolution of organic materials such as plastics, elastomeric seals and lubricants. Therefore in odorization equipment and for joints close to the point where the liquid odorant is injected into the line, only sealing materials should be used which are compatible with liquid odorants (e.g. fluorocarbon elastomers).

However, the low odorant concentrations used for odorization of natural gas and thus their low partial pressures do not compromise the integrity of plastic pipes, seals or diaphragms in gas transportation, distribution and utilization.