

# Natural gas odorization

Daniel Tenkrat, Tomas Hlincik and Ondrej Prokes  
*Institute of Chemical Technology Prague  
Czech Republic*

## 1. Introduction

Natural gas is an odorless and colorless flammable gas. Natural gas odorization means operations involving addition of an odorant to gas to ensure characteristic odor of natural gas in order for people the odor to be distinctive and unpleasant so that the presence of gas in air in concentrations below the lower explosive limit (LEL) is readily detectable. By the odorant addition any physical or chemical property (except the smell) of natural gas cannot be changed. Generally speaking, in the process of natural gas delivering for both public and industrial use, odorization provides safety for those who use it.

Starting with the year 1807 when Pall-Mall in London was experimentally illuminated, the beginnings of gas industry in the European countries were exclusively associated with town gas. This gas, produced by carbonization of coal, contained mainly hydrogen and carbon monoxide. Besides other components, gas produced from coal contained a wide range of sulfur compounds which made it easily detectable in case of leaks and lent it the typical "gassy odor". With the development of the use of natural gas or gas produced by cracking of hydrocarbons or coal pressure gasification the need to odorize these gases became ever more evident.

Historically, first gas odorization was carried out in Germany in 1880's by Von Quaglio who used ethyl mercaptan for detecting gas leakages of blue water gas. However, the real begging of widespread odorization started in US in 1930's as a consequence of the New London's disaster.

Early in 1937, the New London school board cancelled their natural gas contract in order to save money. Instead, plumbers installed a tap into a residual gas line associated with oil production. This practice, while not explicitly authorized by local oil companies, was widespread in the area. The natural gas extracted with the oil was seen as a waste product and thus was flared off. Odorless and therefore undetectable natural gas had been leaking from the connection to the residual line and had built up inside an enclosed crawlspace which ran the entire length of the building. A spark is believed to have ignited the accumulated gas-air mixture leaving behind totally collapsed building and approximately 319 casualties (P&GJ, 2006).

As a consequence of this accident the use of odorants in USA and Canada was enacted. The currently applicable Federal Regulation, 49CFR, 192.625, "Odorization of Gas", requires a

combustible gas which is transmitted interstate or distributed to be odorized either with natural odorant which is present in that gas or by odorant addition so that at a concentration in air of one-fifth of the lower explosive limit, the gas is readily detectable by a person with a normal sense of smell. It means that the presence of natural gas at 1.26% in air must be detectable by smell.

Regulations in force in most European countries are similar (e.g. DVGW G280 in Germany), differing only in that there is a requirement for detectability of gas when 1/5 of lower flammable limit (LFL) is achieved. In practice, this represents 1% concentration of natural gas in the air. Used as an example may be Japan where natural gas used as CNG (compressed natural gas) must be detectable by smell whenever concentration in the air reaches 1.000ppm. In practice this represents the value of 0.1%.

## 2. Gas Odorants

As high quality natural gas replaced manufactured gas the need for odorization of this gas with little (if any) detectable smell arose. In beginnings, the "gassy odor" was supplied by cheap refinery and coke industry by products. However, these products varied in quality and were quite unreliable. After the World War II these by-products are being replaced by low molecular weight synthetic chemicals (such as mercaptans and sulfides) so that in 60's nearly all odorization of natural gas was performed either with pure or blended synthetic chemicals.

Modern gas odorants can be divided into two basic groups. The "classic" sulfur-based odorants which are further subdivided to alkyl mercaptans, alkyl sulfides and cyclic sulfides and new types of sulfur-free odorants based on acrylates which are being introduced to the market in recent years and have their special potential especially in environmental issues due to the zero sulfur dioxide emissions after gas combustion.

Basic requirements for odorants apply both to their physiological effects and on their physiochemical properties. Ideally odorants should have a characteristic "gassy odor". As for physiological properties these include in particular:

- Piercing, strong and unmistakable odor
- Odor must remain perceptible as long as the fault of technical equipment is detected and removed
- Odorant combustion must not produce toxic and irritating products

The most important physiochemical properties include:

- Odorants must be chemically stable, must not react with gas components, piping material, rust, etc.
- Must have high enough vapor pressure in order to avoid condensation at operating pressure
- Must not have a corrosive effect on gas equipment in concentrations used
- Must have a minimum tendency to soil adsorption during gas leaks from pipes
- Odorant smell must not be masked by the presence of higher hydrocarbons
- Odorants must not contain water and must not be diluted with water due to possible subsequent corrosion of the equipment.

The selection of the suitable odorant to be injected into natural gas grid is the key aspect of properly operated odorization system. Selecting the specific odorant involves knowledge of the chemical and physical characteristic of available odorants, properties of the gas to be odorized, the layout of the pipeline (e.g. soil properties, constructing material and pipeline condition), ambient conditions and also the recognition of smell of the local population.

## 2.1 Types of odorants

### Tetrahydrothiophene (THT)

THT is the sole representative of cyclic sulfides used in odorization of gas and is the archetype of "stand alone" odorants; due to poor soil permeability it is nevertheless used in blends with e.g. TBM. THT is most resistant to pipeline oxidation a due to its low odor impact it is difficult to over-odorize with this type of odorant. THT is slightly skin irritant and has a moderate narcotic effect.

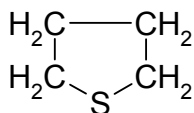


Fig. 1. Tetrahydrothiophene

Formula:  $C_4H_8S$   
 Molecular weight: 88.172  
 CAS reg. number: 110-01-0  
 Specific gravity: 1.000  
 Boiling point: 115 - 124 °C  
 Freezing point: -96°C  
 Flash point: -7 °C  
 Total sulfur content: 36.37 (Wt. %)

NFPA Ratings:



### Dimethyl sulfide (DMS)

DMS is characterized by good oxidation stability and good soil permeability. It is mainly used in blends with TBM, but thanks to its relatively high pressure of vapor in blends with DMS it is not quite suitable for vaporization type odorizers. DMS is a "garlic stinking" compound that causes nausea in higher concentrations. With its effect it first stimulates and then frustrates the nervous system.

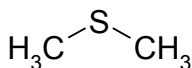


Fig. 2. Dimethyl Sulfide

Formula:  $C_2H_6S$   
 Molecular weight: 62.135  
 CAS reg. number: 75-18-3  
 Specific gravity: 0.8  
 Boiling point: 37 °C  
 Freezing point: -98°C  
 Flash point: -38 °C  
 Total sulfur content: 51.61 (Wt. %)

NFPA Ratings:



### Diethyl sulfide (DES)

DES has good oxidation stability, low odor threshold but its high boiling point is limiting for using in odorant blends.

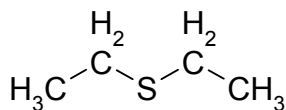


Fig. 3. Diethyl Sulfide

Formula:  $\text{C}_4\text{H}_{10}\text{S}$   
 Molecular weight: 90.188  
 CAS reg. number: 352-93-2  
 Specific gravity: 0.837  
 Boiling point: 90 °C  
 Freezing point: -100°C  
 Flash point: -9 °C  
 Total sulfur content: 35.55 (Wt. %)

NFPA Ratings:



### Methylethyl sulfide (MES)

MES has a good oxidation stability in pipelines and a vapor pressure similar with TBM and thus blends of TBM/MES are suitable for both vaporization and injection type odorizers. From the toxicological point of view MES has similar properties with NPM.

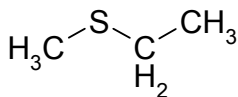


Fig. 4. Methylethyl Sulfide

Formula:  $\text{C}_3\text{H}_8\text{S}$   
 Molecular weight: 76.162  
 CAS reg. number: 624-89-5  
 Specific gravity: 0.8422  
 Boiling point: 65 - 67 °C  
 Freezing point: -106°C  
 Flash point: -15 °C  
 Total sulfur content: 42.10 (Wt. %)

NFPA Ratings:



### Ethyl mercaptan (EM)

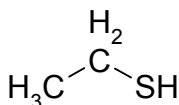


Fig. 5. Ethyl Mercaptan

Formula:  $\text{C}_2\text{H}_6\text{S}$   
 Molecular weight: 62.135  
 CAS reg. number: 75-08-1  
 Specific gravity: 0.839  
 Boiling point: 34 - 37 °C  
 Freezing point: -148 - -121°C  
 Flash point: -48 °C  
 Total sulfur content: 51.61 (Wt. %)

NFPA Ratings:



### Sec-butyl mercaptan (SBM)

SBM is one of the least used components in odorant blends. Originates as a by product or impurity in TBM manufacturing and is seldom used and only in low concentrations. This branched chain mercaptan has good oxidation stability but a relatively high boiling point.

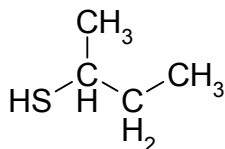


Fig. 6. Sec-butyl mercaptan

Formula:  $\text{C}_3\text{H}_8\text{S}$   
 Molecular weight: 90.188  
 CAS reg. number: 513-53-1  
 Specific gravity: 0.8299  
 Boiling point: 84 - 85 °C  
 Freezing point: -165°C  
 Flash point: -23 °C  
 Total sulfur content: 35.55 (Wt. %)

NFPA Ratings:



**Tert-butyl mercaptan (TBM)**

Typical "gassy odor", low odor threshold, high oxidation resistance (highest among mercaptans) and good soil penetration is what make TBM the most used component of gas odorants. The main disadvantage is its high freezing point which disables using TBM as a stand alone odorant and thus TBM has to be blended with other types of odorant.

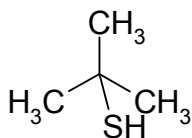


Fig. 7. Tert-Butyl Mercaptan

Formula:  $C_4H_{10}S$   
 Molecular weight: 90.188  
 CAS reg. number: 75-66-1  
 Specific gravity: 0.8002  
 Boiling point: 64 °C  
 Freezing point: 1°C  
 Flash point: <-29 °C  
 Total sulfur content: 35.55 (Wt. %)

NFPA Ratings:

**N-Propyl mercaptan (NPM)**

NPM has a low freezing point and a strong odor but is not used in high concentrations (typically 3-6%) due to its low oxidation stability. From the toxicological point of view it has a depressive effect on central nervous system.

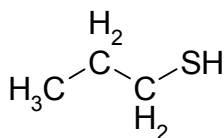


Fig. 8. N-Propyl mercaptan

Formula:  $C_3H_8S$   
 Molecular weight: 76.162  
 CAS reg. number: 107-03-9  
 Specific gravity: 0.8411  
 Boiling point: 67 - 68 °C  
 Freezing point: -113°C  
 Flash point: -21 °C  
 Total sulfur content: 42.10 (Wt. %)

NFPA Ratings:

**Isopropyl mercaptan (IPM)**

IPM is the second most resistant to oxidation from mercaptans, has a strong "gassy odor" and low freezing point. IPM is commonly used in blends with TBM in order to decrease the freezing point. In some cases IPM should be used as a stand alone odorant. IPM has similar toxicological effects with NPM.

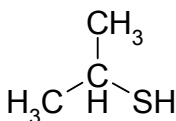


Fig. 9. Isopropyl mercaptan

Formula:  $C_3H_8S$   
 Molecular weight: 76.162  
 CAS reg. number: 75-33-2  
 Specific gravity: 0.8143  
 Boiling point: 53 °C  
 Freezing point: -113°C  
 Flash point: -34 °C  
 Total sulfur content: 42.10 (Wt. %)

NFPA Ratings:



### Methyl acrylate (MA)

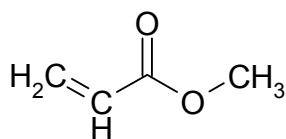


Fig. 10. Methyl acrylate

Formula:  $C_4H_6O$   
 Molecular weight: 86.0892  
 CAS reg. number: 96-33-3  
 Specific gravity: 0.9535 – 0.9574  
 Boiling point: 78 - 81 °C  
 Freezing point: -75°C  
 Flash point: -3 °C  
 Total sulfur content: - (Wt. %)

NFPA Ratings:



MA and EA are the main components (together with Methylethyl Pyrazine) of the sulfur-free odorant. They perform good permeability through soil (which is slightly lower in case of dry soil) and low odor threshold. Under certain circumstances they can be “washed out” from the gas stream particularly if hydrocarbon condensate occurs within the pipeline.

### Ethyl acrylate (EA)

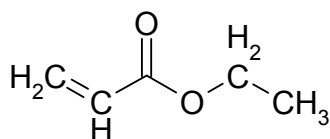


Fig. 11. Ethyl acrylate

Formula:  $C_5H_8O_2$   
 Molecular weight: 100.1158  
 CAS reg. number: 140-88-5  
 Specific gravity: 0.9  
 Boiling point: 99 - 100 °C  
 Freezing point: -72°C  
 Flash point: 8.3 °C  
 Total sulfur content: - (Wt. %)

NFPA Ratings:



## 2.2 Odorant blends

The odorants used today are typically a blend made and they fall into four main categories, which are:

- All mercaptan blends
- Mercaptan/ Alkyl sulfide blends
- Tetrahydrothiophene/mercaptan blends
- Acrylates blends (sulfur free).

The main reason for odorant blending is to reach specific properties of an odorant for use under different conditions or to improve some of its characteristic. A list of some common blends is given in table 1, other widespread odorants are e.g. Scintinel<sup>®</sup> odorants by Chevron Philips.

Blend Type	Composition	Specific density (20°C)	Boiling point [°C]	Flash point [°C]	Viscosity (20 °C) [cP]	Odor threshold
Alerton 88 Spotleak 1013	THT 100 %	1.000 (20°C)	115	<13	1.04	1 ppb
Alerton 452 Spotleak 1001	TBM 80 % DMS 20 %	0.816 (20°C)	50	<-32	0.52	0.1 ppb
Alerton 541	TBM 50 % DMS 50 %	0.830 (20°C)	36	<-34	0.41	N/A
Alerton 841 Penndorant 1005	THT 70% TBM 30 %	0.930 (20°C)	60	<-18	0.93	N/A
Alerton 841 P	THT 65 % TBM 35 %	0.931 (20°C)	65	<-20	0.92	N/A
Alerton 842	THT 95 % TBM 5%	0.991 (20°C)	65	<-4.4	0.98	N/A
Alerton 843	THT 85 % TBM 15 %	0.969 (20°C)	65	<-6.8	0.96	N/A
Alerton 1440	IPM 80 % NPM 10 % TBM 10 %	0.820 (20°C)	50	<-17	N/A	N/A
Spotleak 1007	TBM 80 % MES 20 %	0.815 (15.5°C)	63	<-18	0.55	0.1 ppb
Spotleak 1009	TBM 79 % IPM 15 % NPM 6 %	0.812 (15.5°C)	62	<-18	0.570	0.1 ppb
Spotleak 1039	THT 50 % TBM 50 %	0.904 (15.5°C)	67	<-12	N/A	N/A
Spotleak 1420	TBM 75 % DMS 25 %	0.825 (15.5°C)	54	<-18	0.49	0.1 ppb
Spotleak 1450	IPM 70% TBM 10 % DMS 10 % NPM 10 %	0.825 (15.5°C)	53	<-18	0.570	0.1 ppb
Spotleak 2323	TBM 50 % NPM 50 %	0.826 (15.5°C)	62	<-18	N/A	0.1 ppb
Gasodor S-free	Methyl acrylate 37.4 % Ethyl acrylate 60 % Methylethyl pyrazine 2.5 %	0.930 (20°C)	<130	<5	N/A	N/A

Table 1. Basic properties of common odorant blends (Sources: Arkema; Symrise)

### 3. Odorizing systems

In the odorization process an essential step is to select the right tool in this case a suitable odorizing system. From the technical point of view odorizers should be divided into two basic groups according to the system in which odorants are introduced into the gas stream which are:

- Chemical vaporization
- Chemical injection.

Vaporization based systems rely on diffusion of odorant into a flowing natural gas stream. Examples of vaporization systems are wick odorizers and bypass type systems. The main advantage of these odorizers is their simplicity however they are generally suitable for low and stable gas flows.

The injection type systems rely on direct injection of an odorant which is stored away from the pipeline directly into the flowing stream. These systems are generally used for wide range of flow rates.

### 3.1 Wick odorizers

Odorization by means of wick odorizers is one of the oldest and simplest methods. It is based on free evaporation of the odorant from the wick into the gas stream. It was and is still used for odorization of small amounts of gas. The device consists of a storage tank with odorant into which the wick extends through a hole. The other end of the wick is placed directly in the stream of fuel gas. Dosage was controlled only by setting the size of the wick. The disadvantage of the original device was that during low gas flow gas could be over odorized and vice versa the intensity of odorization could be insufficient during high gas flow.

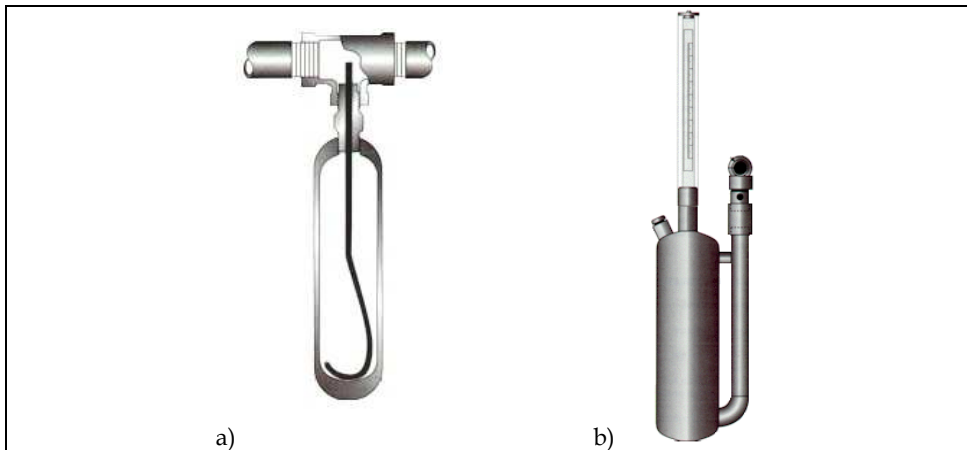


Fig. 12. Non-adjustable (a) and adjustable (b) wick odorizer [Source: King tool company]

### 3.2 By-pass systems

Due to its simplicity this method of odorization was widely used. By strangling the mainstream of natural gas in the pipeline (by means of an orifice, Venturi tube, slide or ram pipe with sideways cant embedded into gas stream) difference of pressures is reached so that partial flow of fuel gas proportional to the mainstream of fuel gas passes through the tank with odorant above its surface, saturates with odorant vapors and returns to main gas stream. Odorant dosage can be changed by changing the strangling of fuel gas mainstream. The device was used for fuel gas odorization up to the flow of 10 000 m<sup>3</sup>/h.. These devices are suitable for both local odorization and additional odorization of fuel gas in central odorization.



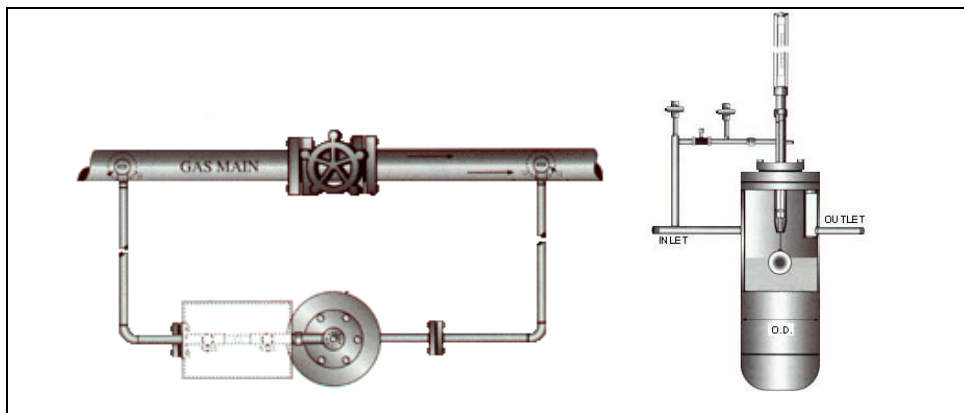


Fig. 13. Bypass odorizer [Source: King tool company]

### 3.3 Pulse Bypass

The operating principal of Pulse Bypass Odorization is to use higher pressure gas supply from the transmission line to introduce odorant vapors into a lower pressure feeder or distribution line. This is accomplished by diverting or bypassing un-odorized natural gas through an odorant filled tank to mix with odorant vapors. Odorization occurs when the odorant saturated bypass gas is returned to the down stream line. A signal from a meter interface switch is received to actuate the pulse bottle solenoid valve.

### 3.4 Bourdon Tube

In these rarely used odorizers the amount of odorant injected is controlled by a bourdon tube activated by a differential-pressure transmitter which senses the gas flow across an orifice plate in the pipeline.

### 3.5 Drip systems

This system was used for the odorization of high amounts of low-varying stream of fuel gas with stable temperature and pressure. Odorant dripping into fuel gas stream was controlled by a needle valve and monitored through a peep-hole. This type of odorization device required regular supervision because of frequent clogging of the needle valve due to variation of viscosity, density or odorant deposits.

In recent years Smart Drip systems appeared on the market. It is an odorization system composed of age old proven drip technology combined with modern measurement, computational processing, and feedback control electronics. The result is a precision dispensing system capable of supplying odorant over a wide range of natural gas flow rates.

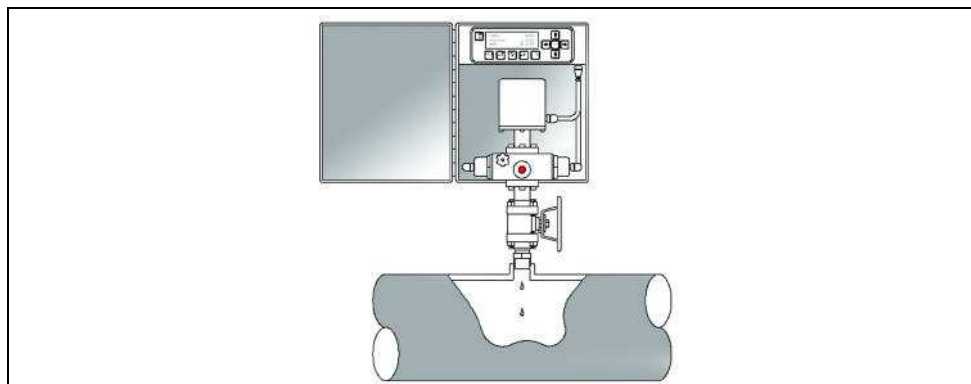


Fig. 14. Smart drip system (Source: Z systems, Midland, TX)

A conventional gravity feed drip odorization system was modified by adding electrically operated valves. The valves are pulsed on and off with a duty cycle sufficient to permit the required mass of odorant flow through a drip tube. The duty cycle and rate of valve operation is controlled to follow changes in gas flow and changes in head pressure resulting from varying levels in the run tank. The drip tubes are contained within a stainless steel measurement chamber equipped with optical interrupters sending electrical pulse signals with each drop of odorant dispensed. Drop size is dependent on the mass (weight) of the drop, surface tension of the fluid, and surface area of the drip tube tip. Surface tension is weakly dependent on fluid temperature, requiring a simple linear adjustment. Therefore the only variable required to calibrate drop mass is odorant temperature, which may be assumed to be the ambient temperature of the drip chamber. This methodology of odorant metering is more direct than measuring volume and converting to mass.

### 3.6 Electrically or pneumatically driven pump

Odorant is brought into the pipeline with flowing fuel gas by means of a dosage pump. The pump is controlled by an electronic system on the basis of gas flow data. Devices of this design are suitable for gas flow rates above 5000 m<sup>3</sup>/h and allow for accurate dosage. In simpler devices with built-in gas meter the energy required for dosage pump drive was discharged from fuel gas mainstream and the dosage pump was driven by gas meter rotational movement. Thus the appropriate odorant dose was also controlled.

Another system uses a diaphragm proportioning pump. Depending on a real flow of gas, impulses from gas meters, or counters actuate a pump by way of electronics of the equipment. A diaphragm proportioning pump which is controlled by a microprocessor and powered by a magnet injects the adjusted quantity of odorizing liquid by injection apparatus to the gas flow. Through a primary tank the pump sucks in the odorizing liquid from the exchangeable tank.

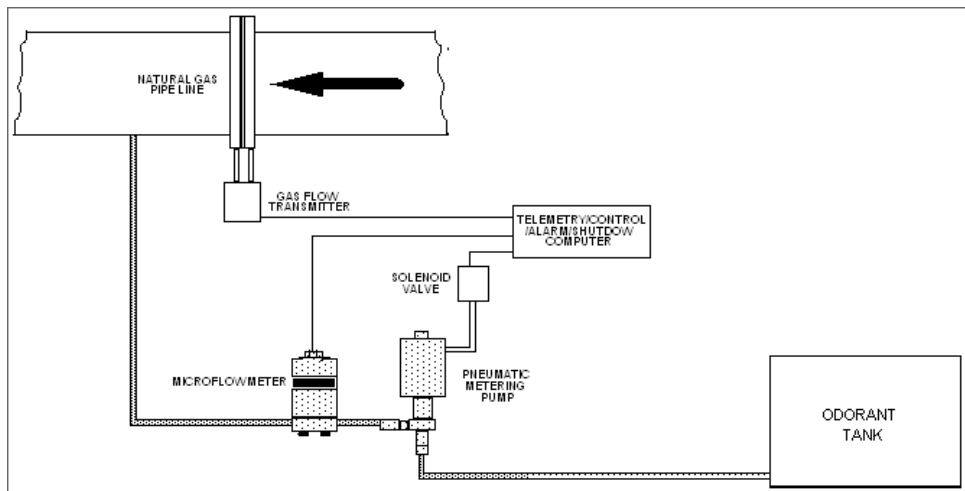


Fig. 15. Scheme of an odorant injection system (Source: DEA Engineering)

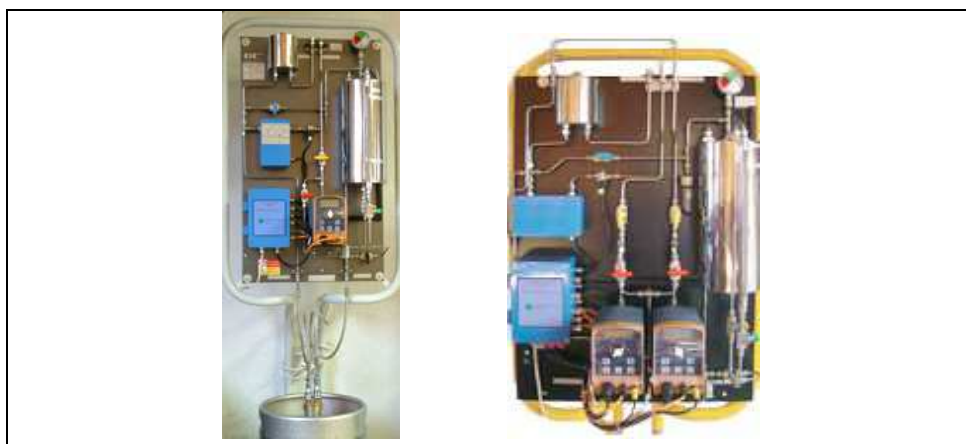


Fig. 16. Odorization device with a diaphragm proportioning pump (Source: Gascontrol)

#### 4. Odorization monitoring

The main task of natural gas odorization is to ensure such operating condition when natural gas in every part of the distribution grid fulfils the requirement of a „warning odor level“.

In case of a gas leakage the warning odor level (see table 2.) must be reached until the 20% of lower explosive/flammable limit (LEL/LFL) is reached. Odorisation level can be verified by:

1. The odorization level control - which can be done by olfactometry in selected points on distribution grid or by means of questionnaires at selected representative sample of customers. In both cases indirect indicators are taken into account so that both forms are considered to be subjective methods.

2. Odorant concentration measurement - in natural gas can be estimated continuously or discontinuously in selected points on grid. In this case particular concentration of odorant in NG is measured. This is so called objective method.

The most important task is to estimate optimal odorant concentration. For calculating the safety-relevant, minimum odorant concentration necessary to reach the warning odor level (grade 3, see table 2), an experimentally determined  $K$ -value is used.

Minimal odorant concentration represents the odorant content in natural gas ( $\text{mg}\cdot\text{m}^{-3}$ ) which fulfills the requirement for creating warning odor level - grade 3.

Estimation of the minimal odorant concentration is determined by:

- $K$ -value ( $\text{mg}\cdot\text{m}^{-3}$ ) which represents the minimal concentration of an odorant in natural gas-air mixture which reliably ensures the warning odor level,
- lower explosive/flammable limit (LEL/LFL) -expressed by vol. % of natural gas in air,
- and from the requirement to evoke the warning odor level before one fifth (i.e. 20 %) of LEL/LFL of natural gas in air is reached.

Minimal odorant concentration  $c_n$  can be estimated according to the following formula:

$$c_n = \frac{100 \cdot K}{0.2 \cdot \text{LEL}} \quad (\text{mg} \cdot \text{m}^3). \quad (1)$$

$K$ -values are obtained by olfactometry measurements using defined sample of population. Typical  $K$ -values of commonly used odorants are 0.08 for tetrahydrothiophene, 0.03 for mercaptans and  $0.07 \text{ mg}\cdot\text{m}^{-3}$  for the GASODOR S-free odorant.

Odor intensity is the extent of odor perception which is by the odor evoked. Commonly the odor intensity is evaluated as an odorization level. List of odorization levels can be found in the table 2.

Odorization Level (grade)	Olfactory perception	Comment
0	Odor not detected	-
1	Very low intensity	Odor threshold
2	Weak odor	-
3	Mean odor	Warning odor level
4	Strong odor	-
5	Very strong odor	-
6	Extremely strong odor	Upper limit of intensity

Table 2. Odorization levels

#### 4.1 Subjective odorization control

By subjective odorization control odorant concentration is tested primarily with the use of electronic instruments. These instruments all employ the use of the human nose to determine the gas in air mixture at which an individual can detect the smell of odorant. These quantitative olfactory tests are commonly called “sniff test”.

There are only several manufacturers of such units. Some of them are e.g. the DTEX made by YZ Systems, the Odorometer made by Bacharach, and the Heath Odorator (see Fig. 17.)

All three units are designed to mix gas and air and move them to a sniffing chamber. The air is drawn in through each unit, and mixed with gas. The technician smells the gas and air mixture, gradually raising the level of gas in the mixture until he or she detects an odor of gas.

The Bacharach Odorometer was the first device designed to monitor odor levels and is still available today. The Odorometer uses a rotameter (balls floating up and down on the air stream created by opening the gas stream). The results of a test are read off of the bottom of the balls and compared to a chart on the unit door prepared for each Odorometer.



Fig. 17. Bacharach ODOROMETR (a) YZ Industries DTEX (b) and Heath Consultants ODORATOR

The Heath Odorator is another unit designed to test for odor intensity. First step with this device is to zero the unit following the instructions printed on the side of the box. Next opening the gas valve while positioning your nose above the sniff chamber until the odor intensity reaches the threshold level. Push the display button and copy down the reading.

Again with your nose above the sniff chamber, open the valve until the odor intensity reaches a readily detectable level. After the readily detectable level is reached, you push the display button and read the display. Then compare the two display readings to the chart for correction on the side of the unit to get your test results.

To take a test with the DTEX the operator turns on the power and the unit puts itself through a series of self-diagnostic checks. After the operator logs on with a private password, he or she can choose to do a test at a pre-entered test location, or a new location can be entered via the keypad on the unit.

#### 4.2 Objective odorization control

The use of titrators, analyzers and chromatographs are several methods employed for quantitative sulfur analysis. A variety of detectors are used including lead acetate tapes, chemiluminescence, flame photometric and technologies with electro-chemical detectors. These instruments can be configured either for laboratory use or placed directly on the pipeline for real-time calculations. These instruments provide for real-time determinations of total sulfur and in many case individual mercaptan and sulfide component levels.

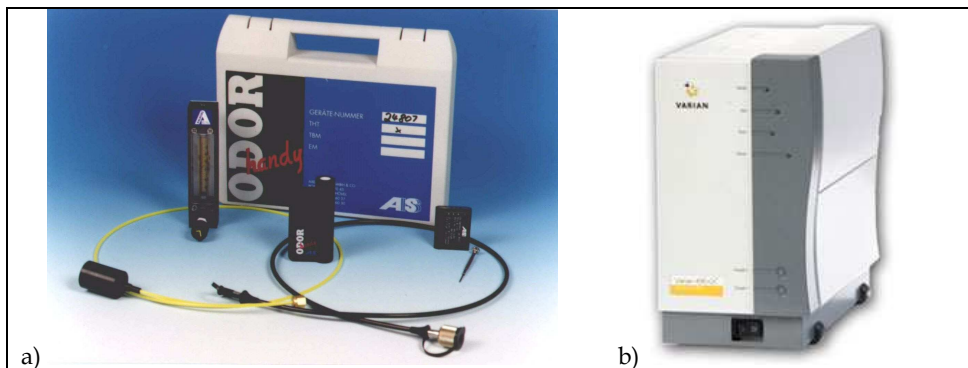


Fig. 18. Electro-chemical detector (a) and micro gas chromatography (b) for quantitative estimation of odorant concentrations

Although these “quantitative” methods of determining actual odorant concentrations in the gas stream does not meet the Federal requirement for odorant reporting (not only) under DOT 192.625 it does, however, provide another piece of information in terms of evaluating the overall effectiveness of the odorization program.

To determine the concentrations of Gasodor S-Free odorants a number of analyzers based on different principles may be used. Table 3 provides an overview of suitable analyzers.





	(Micro-)GC	IMS-Odor	$\mu$ IMS-Odor	CMS-Analyzer
Type				
Measuring principle	Chromatography	Ion Mobility Spectrometry	Ion Mobility Spectrometry	Colorimetric Chemical
Application	Stationary, mobile	Stationary	Mobile	mobile
Measuring range [mg/m <sup>3</sup> ]	>1.5	4 - 23	0 - 23	3 -30

Table 3. Equipment suitable for sulfur free odorant monitoring (Source: Graf 2007)

### Impact odorization

Impact (temporarily increased) odorization which is sometimes performed is a targeted, one, two or threefold increase in the dosage of odorant into fuel gas compared to standard operating condition. Its aim is to verify the technical condition of gas distribution and gas supply facilities, usually before the winter season. It is advisable that public in the area where impact odorization is to be carried out be alerted.

## 5. Preodorization and odor fade

When a new pipeline is constructed preodorization must be carried out. When gas with odorant is injected into the new pipeline absorption and reaction between the pipeline inner wall and the odorant occurs during the passage of this gas mixture through the pipeline. Gas at the exit from the pipeline is then odorless and may pose a serious security risk

If a new steel pipe is ready, the porous inner wall of the pipe contains metal oxides (rust) which react with the odorant; in reaction with TBM disulfides may for example form which are less odorous than TBM proper. Therefore the steel pipe must be clean and free of oxides, otherwise it could happen that the exiting gas is odorless and may pose a potential risk. This effect occurs even when plastic pipes are used and this phenomenon must be given increased attention when putting the pipeline into operation. In order to ensure sufficient security to end users the new line must be saturated with odorant prior to its commissioning. This is done by overodorizing the gas entering the new line. The process of pipeline preodorization and saturation with odorant is often referred to as "pickling".

Used for gas pipeline preodorization and pickling are three basic methods:

1. Injection of highly odorized gas (more than 40 ppm of odorant).
2. Slugging, i.e. pouring a bulk amount of liquid odorant directly into the pipeline and letting the pipe "pickle" for a prolonged period without any flow through the pipe.
3. Continuous injection of controlled dosage of liquid odorant into the gas stream flowing through the pipe.

### **Odor Fade**

Even though odorant is added to natural gas, contractors should not rely solely on the sense of smell to determine if natural gas is present in the ambient air of a work space. This is because it may be possible that:

- Some individuals suffer an impaired sense of smell (chronic or transient) and cannot detect the odorant;
- The odorant can at times be disguised by other odors present on the job site or naturally occurring in the environment;
- Some individuals who have worked around natural gas odorant for an extended period of time may suffer from odor fatigue and may be unable to recognize the presence or change in odor levels; and
- In some rare cases, odor fade (loss of odorant) may occur making it difficult to detect the presence of natural gas in the air. In general, odor fade occurs when physical and/or chemical processes cause the level of odorant in the gas to be reduced. Odor fade can occur in both existing pipe and new installations but is most likely to occur in new steel pipe of larger diameters and longer lengths. Odorant fade can also occur in plastic pipe and in smaller and/or shorter pipe installations.

## **6. Odorants decontamination**

Although odorization systems are designed as leakage-free systems odorant may still leak in current operation e.g. due to an accident or improper handling. Recommended methods of odorant disposal may be divided into three areas according to the quantity and nature of odorant to be disposed.

When disposing smaller amounts of odorants and in order to remove the repulsive smell of spilled odorant the smell is eliminated by means of absorption of spilled odorant in chips impregnated with special oil and masked by a suitable pleasantly smelling substance such as ALAMASK THT-X, ALAMASK VET, ALDOR 1052, PLANAROME 877, or by using PENNCOVER.

For cleaning barrels and tanks from odorants a solution of 2 kg of calcium hypochlorite in 50 l of water with addition of hydrogen peroxide is used. This solution must be left to work 2 – 3 days and is sufficient to clean one 200 l barrel. The residue from cleaning barrels and the barrels proper must be disposed of separately as hazardous waste.

When disposing larger odorant leakages the odorant must first be drained by appropriate binding substances (peat, diatomaceous earth, sawdust, cleaning wool) and the soil soaked

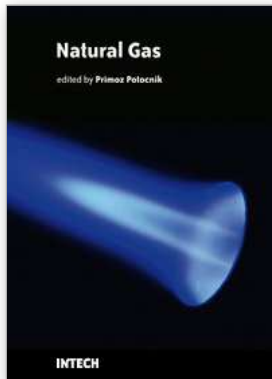


with odorant together with soaked binding substance must be stored in closable containers. These containers must be disposed of separately as hazardous waste. This means disposal in special equipment intended for this purpose. The location where odorant spilled may be decontaminated by oxidizing means, either by 1.5% solution of sodium hypochlorite (bleaching process), or by 5% solution of potassium permanganate

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## Natural Gas

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The contributions in this book present an overview of cutting edge research on natural gas which is a vital component of world's supply of energy. Natural gas is a combustible mixture of hydrocarbon gases, primarily methane but also heavier gaseous hydrocarbons such as ethane, propane and butane. Unlike other fossil fuels, natural gas is clean burning and emits lower levels of potentially harmful by-products into the air. Therefore, it is considered as one of the cleanest, safest, and most useful of all energy sources applied in variety of residential, commercial and industrial fields. The book is organized in 25 chapters that cover various aspects of natural gas research: technology, applications, forecasting, numerical simulations, transport and risk assessment.

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### InTech Europe

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
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### InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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