

GAS ODORANTS – SAFE HANDLING, HEALTH, AND ENVIRONMENT

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INTRODUCTION

Thiols (mercaptans), alkyl sulfides (dimethyl sulfide and methyl ethyl sulfide), and cyclic sulfides, such as tetrahydrothiophene, have been widely used in the odorization of natural and liquefied petroleum gas due to the fact that natural gas does not possess an odor. Mercaptans, for example, have proven to be very effective in odorizing because of their low odor threshold and therefore, immediate impact on the olfactory system (Roberts, 1993).

Although, gas odorants are characterized as having a “low” hazard potential regarding health effects, their unique physical chemical properties such as, high flammability, require that they be handled safely.

The objective of this paper is to provide an overview of the human health and environmental concerns associated with gas odorants, to recommend safe handling and personal monitoring, and to discuss the impact of regulatory changes associated with the chemical management of these chemicals.

REGULATORY PERSPECTIVE

Gas odorant blends are subject to various regulations. Some of the regulations include; the Toxic Substances Control Act (TSCA), Office of Environmental Health Hazard Assessment (OEHHA) Proposition 65, and Registration, Evaluation, and Authorization of Chemicals in Europe (EU Reach), to name a few. Table 1 summarizes some of the regulatory status of chemicals used in gas odorant blends.

In the United States, the Occupational Safety and Health Administration (OSHA), within the Department of Labor, administers the implementation of the Federal Right-to-Know (RTK) laws embodied under 29 CFR 1910.1200. This particular regulation covers hazard communication. As a result, chemical producers and importers are required to provide Material Safety Data Sheets describing any associated hazards of chemicals per the directives of 29 CFR 1910.1200. On March 26, 2012, OSHA issued a final ruling announcing a modification of the current Hazard Communication Standard (HCS) to conform to the provisions of the United Nations (UN) Globally Harmonized System (GHS) of the Classification and Labeling of Chemicals moving away from a performance based standard. The United Nations Committee of Experts on the Transport of Dangerous Goods formally adopted GHS in 2002 (Hazard Communication 2012). The goal of the GHS is to provide a set of harmonized criteria to classify chemicals according to their health and physical hazards. Under the revised HCS (also referred to as HazCom 2012), changes involve the use of “signal” words (i.e. Danger or Warning), pictograms, hazard and precautionary statements (Refer to fig. A). This information will be required for both the material safety data sheet (now called Safety Data Sheet (SDS)) and labels. More importantly, this final ruling should improve the quality and consistency of hazard information provided by chemical producers and importers (OSHA 2012).

PHYSICAL AND HEALTH HAZARDS

Flammability

Gas odorants are considered flammable under OSHA HazCom, U.S. Department of Transportation (DOT), and Canadian WHMIS (Workplace Hazardous Materials Information System). They are characterized as having a very low flashpoint (typically below 0°F). Gas odorants are stable and can travel a considerable distance to a source of ignition and flash back. The burning of “neat” gas odorants can lead to the formation of combustion by-products that include sulfur and carbon oxides. These by-products are known to cause acute adverse health effects; therefore, when handling odorants one should maintain all the precautions applicable.

Health Hazard

Below is an overview describing the health hazards associated with individual components of gas odorant blends as defined by OSHA HazCom 2012. The revised (HCS) describes health hazards attributed to chemicals as having the following characteristics: acute toxicity, corrosion (skin and eye), irritation (skin and eye), skin and respiratory sensitizers, mutagenicity, carcinogenicity, reproductive toxicity, target organ systemic toxicity (single or repeated exposure), and aspiration hazard.

Acute Toxicity

One must first recognize that not all “odorants” are created equal. Mercaptans, for example, are generally described as having a “low” hazard potential. Chemicals described as such are determined on the basis of a battery of acute toxicological studies (i.e. acute lethality, skin/eye irritation, skin sensitization, etc.). With the exception of Ethyl, Isopropyl and Normal Propyl Mercaptan, Mercaptans are not considered harmful based on studies looking at acute lethality. Mercaptans except for Ethyl, which may cause serious eye damage, may also be slightly or irritating to the eye and skin. (Please refer to Table 2 for a summary of the hazard data). Similar studies have been conducted on Dimethyl Sulfide (DMS), Methyl Ethyl Sulfide (MES) and Tetrahydrothiophene (THT). Adverse effects such as severe eye irritation in rabbits were reported (e.g. MES and THT), but, again, acute lethality studies indicate these substances are not considered harmful with the exception of THT. In regards to the potential for skin allergies associated with gas odorants, mercaptans have been identified as positive for skin sensitization in guinea pig and mice studies.

Acute oral toxicity studies conducted on these chemicals suggest that values of >2000 mg/kg-body weight are not expected to be harmful. However, this is not true for Ethyl, Normal and Isopropyl Mercaptan and Tetrahydrothiophene as studies infer these chemicals are in fact harmful for acute oral toxicity. In addition, accidental ingestion of gas odorants can cause an aspiration hazard leading to the inflammation and possible fluid accumulation in the lungs.

Dermal acute toxicity studies conducted on gas odorants surmise that gas odorants are not expected to be harmful through the skin. For example, lethal doses for dermal exposure report values of >2000 mg/kg-body weight.

Given inhalation is the most likely route of exposure when dealing with gas odorants, several inhalation studies have been conducted using experimental animals. Various lethal concentration (LC₅₀) studies commissioned indicate gas odorants are considered to have a low hazard potential with the exception of Ethyl Mercaptan. Exposures via inhalation at exceedingly higher concentrations above the odor threshold value (low ppb) have been described as having the following effects; central nervous system depression (characterized by headache, nausea, dizziness, vomiting, and unconsciousness) along with respiratory irritation. The effects described above have been documented in animal studies as well as instances where occupational workers, either in confined spaces or during accidental releases, were exposed without adequate ventilation and/or breathing personal protective equipment.

Sub-Chronic and Chronic Toxicity

Prolonged or repeated exposure studies conducted on gas odorants have been determined for individual components using experimental animals. For mercaptans, inhalation studies have been performed for tert-Butyl Mercaptan (TBM) and Secondary Butyl Mercaptan (SBM). TBM administered orally, reported hematological effects slight in nature with no indication of any associated adverse clinical or histopathological effects and centrilobular hepatocellular hypertrophy was likely an adaptive response. The non-observed adverse effect level (NOAEL) for this study is 50 mg/kg bw/day (based on decreased body weight in females dosed at 200 mg/kg bw/day). Inhalation studies conducted on TBM reported effects in the kidneys of males but were considered to be rat-specific with no relevance for human risk assessment. The non-observed adverse effect concentration (NOAEC) for systemic toxicity was determined to be ≥ 196 ppm (721 mg/m³). An inhalation study reported for SBM showed effects to erythrocytes, kidneys, liver, and nasal turbinates in rats. The lowest observed adverse effect concentration (LOAEC) is 1.488 mg/L (403.4 ppm or 1488 mg/m³) and the NOAEC is 0.367 mg/L (99.6 ppm or 367 mg/m³) (Kim *et al.* 2009). It is important to note concentrations used in these studies are orders of magnitude above the odor threshold and would not typically be expected to be encountered in an occupational setting.

Similar studies have also been conducted on sulfides, such as Dimethyl sulfide (DMS) and Tetrahydrothiophene (THT). For example, studies on DMS reported no treatment related effects in male and female rats from daily exposures to oral doses of 2.5, 25 and 250 mg /kg bw/day for 14 weeks. The endpoints examined included body weights, clinical signs, food and water

consumption, hematology and clinical chemistry, kidney function tests, and pathologic examinations including microscopic (Butterworth *et al.*, 1975). The NOAEL was 250 mg/kg bw/day. As for THT, rats were exposed by whole-body to 0, 50, 275 or 1500 ppm (180, 990 or 5410 mg/m³, purity at least 99%) six hours per day, five days per week for 13 weeks. The analytical concentrations were reported as 51, 236 or 1442 ppm (184, 852 or 5201 mg/m³). Symptoms observed such as irritation (lacrimation, salivation, eyes closed) were seen with increasing concentrations. These were more frequently pronounced at concentrations starting at 236 ppm. Hematological parameters showed small differences compared to the control animals, but these were not considered toxicologically significant, with exception of the increase of white blood cells and lymphocytes at 1442 ppm. There was also a slight but not toxicologically significant increase in pH urine in females at 1442 ppm. Macroscopic examination and determination of organ weights provided no abnormal findings. Although a minimal increase in liver weights was observed in females exposed to 1442 ppm, the effect was not considered toxicologically relevant. In addition, histopathological examinations were performed on the lungs of all animals and on some other tissues of the control and 1442 ppm dose group. This also included tissues from the nasal cavity (rostral and caudal) as well. There was free blood reported in the sinuses of one male animal at the 1442 ppm dose group and sinusoidal free blood in one female of the control group. These changes were considered random. The NOAEC for the local irritation was 51 ppm (183 mg/m³) and the NOAEC for systemic effect was 1442 ppm (5191 mg/m³) (Hardy, 1988).

Reproductive/Developmental/Carcinogenicity

Potential adverse effects on reproductive and development in experimental animals have also been investigated for individual components of gas odorant blends. Findings from various studies suggest adverse effects are not expected. Regarding the carcinogenicity of gas odorants, there are currently no studies available, however, a combination of *in vitro* and *in vivo* screening assays have been conducted on individual components. Screening assays are useful in that they provide some indication about a chemical's potential to interact with the basic building blocks of life "DNA - Deoxyribonucleic acid" and disrupt normal cellular homeostasis. Overall, the weight of evidence suggests gas odorant blends are not expected to cause cancer.

Occupational Exposure Limits

Occupational Exposure Limits (OELs) have been proposed by many organizations in numerous countries for more than 50 years. The primary intent of developing an OEL is to establish a limit value that would serve to protect workers in an occupational setting from airborne contaminants (Paustenbach, 2000). In the United States, OELs have been developed by many groups which include; the American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values® (TLVs), Recommended Exposure Limits (REL), developed by the National Institute for Occupational Safety and Health (NIOSH) of the U.S. Department of Health and Human Services, the Workplace Environmental Exposure Levels (WEEL™), now transferred to the Occupational Alliance for Risk Science (OARS) managed by Toxicology Excellence for Risk Assessment (TERA), and recommendations put forward by local, state or federal agencies. More importantly, there is the Permissible Exposure Limits (PELs) developed by the Department of Labor and enforced by OSHA.

Looking through the body of literature one will find OELs developed for individual components of gas odorants. (Please refer to Table 3). In most cases, the basis for the OEL has been to protect against upper respiratory irritation. For mercaptans, such as Ethyl, OELs were developed to protect not only against upper respiratory irritation, but impairment to the central nervous system (ACGIH, 2001). It is, however, important to note the OEL values for mercaptans are typically orders of magnitude above the reported odor threshold value. For example, the odor threshold value for Ethyl mercaptan is 0.00035 ppm (Turk *et al.*, 2000).

Occupational Exposure

Exposure to gas odorants in occupational and non-occupational settings is expected to be limited. This is partly due to the fact they exhibit a very "strong" repulsive odor, and also that handling is usually conducted in closed systems. One important factor when dealing with gas odorants to consider is the potential for odor fatigue (olfactory adaptation). Odor fatigue is defined as a decrement in sensitivity to an odorant due to an adaptation to the stimulus (Turk *et al.*, 2000). As a result, the perception of the intensity of the odorant is altered and it is not uncommon to exhibit both a loss of sensitivity and decrease in perception of odorants.

Non-occupational exposures primarily occur during the consumption of gas odorants, which occurs during the burning of natural gas. This type of exposure, usually in the ppb – ppm range, is rare and generally occurs when a leak develops. Because of their repulsive odor, prolonged exposures leading to adverse health effects are usually mitigated. Another source

of exposure to gas odorants occurs when the pilot of the gas stove is turned on before there is a flame. These types of exposures are minimal and not a cause for concern. In the event of an accidental release, odorants are expected to dissipate quickly into the atmosphere.

AIR SAMPLING

Air sampling for mercaptans can be done with instrumentation in real-time or by methods which require laboratory analysis.

Sampling in the field to get precise and accurate readings at levels relevant to the low OEL's of mercaptans is not as easy as sampling for other types of chemical agents in the workplace. Portable photoionization devices (PID's) are commercially available to sample work spaces in real time, but the ionization potential for the compound being sampled for must be known so an applicable correction factor can be applied. This correction factor is necessary since most PID's are calibrated to isobutylene. The PID should be one that reads in the parts per billion (ppb) range in order to provide that precision and accuracy that would benefit in the assessment of exposures in the workplace. PID's cannot differentiate mercaptans from other gases that may be in the work environment so the readings may not reflect only the mercaptan levels, but may also display the levels of other chemicals present. Therefore, the chemical with the lowest OEL should be referenced until more specificity can be obtained. Overall PID's are good tools, but have limitations.

Chemical sensor technology developed for direct reading of hydrogen sulfide compounds can be useful for detecting and quantifying mercaptan compounds but as with the PID there is a lack of specificity. Some detector units are able to suppress or automatically subtract measured hydrogen sulfide from other sulfide compounds and can be calibrated to THT, TBM and methanethiol (MeSH), as well as other reduced sulfides such as Dimethyl Disulfide (DMDS) and DMS. This technology allows chemical sensors to achieve better quantification of mercaptan but user knowledge of the anticipated compound proportions remains essential to evaluating atmospheres.

Detector tubes are available for performing "grab samples" in the field from various manufacturers. Availability is good for most commonly used mercaptan odorants. The use of detector tubes is appropriate for estimating exposure conditions and may be used to support other sampling and analytical methodologies. However, analytical error of the detector tubes is typically 20-30%.

Laboratory sampling is recommended for better accuracy and precision. Sampling in the lab is performed by using an active sampling pump train, which involves a calibrated pump, tubing, tube holder, and the adsorbent or absorbent media. For mercaptans sampling, NIOSH (National Institute of Occupational Safety and Health) method 2542 should be used, which is a modified method of OSHA method 26, to capture ethyl and n-butyl mercaptan as well as methyl mercaptan. In order to obtain accurate results, the media should be sent to an American Industrial Hygiene Association (AIHA®) accredited laboratory or equivalent, in accordance with laboratory instructions. Some accredited industrial hygiene laboratories also have evacuated canisters available to collect samples of most mercaptan odorants for analysis by means of OSHA method PV2120. Reports generated by the laboratory should be reviewed by someone experienced in the field of industrial hygiene.

SAFE HANDLING

Respiratory Protection

Where respiratory protection is used in the workplace, a formal respiratory protection program must be established in accordance with the Occupational Safety and Health Administration (OSHA) Respiratory Protection Standard (29 CFR 1910.134). Where other authorities having jurisdiction enforce standards more stringent than the OSHA standard, then the state or local standards should be used instead.

A written respiratory protection program should follow accepted industrial hygiene practices. Respiratory protection can only be selected once workplace contaminants and their concentrations have been identified and quantified. Only respirators certified by NIOSH for the specific agent and exposure level are appropriate for mercaptans using applicable occupational exposure limits. Because actual conditions vary from one worksite to another, selection of the most appropriate respirator will depend on the specific working conditions and should be made only by a respiratory protection program administrator in consultation with the vendor of the respiratory protection selected by the employer.

Employers must use the OSHA assigned protection factors listed in Table 4 (or applicable local, state or federal law) to select a respirator that meets or exceeds the required level of employee protection.

Maximum use concentration (MUC) means the maximum atmospheric concentration of a hazardous chemical from which an employee can be expected to be protected when wearing a respirator, and it is determined by the assigned protection factor of the respirator or class of respirators and the occupational exposure limit of the hazardous substance. The MUC can be determined mathematically by multiplying the assigned protection factor specified for a respirator by the required applicable permissible exposure limit, short-term exposure limit, or ceiling limit (OSHA PEL, ACGIH® TLV®, OARS WEEL™, NIOSH REL or manufacturers OEL). When no exposure limit is available for a hazardous chemical, an employer must determine an MUC on the basis of relevant available information and informed professional judgment.

Skin Protection

Glove selection for maximum protection should include laminate film gloves in combination with another appropriate type of protective glove. If the chance of chemical exposure is low, a leather glove can be used, and if exposure occurs, the gloves can be properly disposed of. If exposure is expected, then a neoprene or butyl chemical resistant glove should be selected. For splash protection, laminate sleeves, aprons, coats, or full encapsulating suits should be used based upon a proper PPE hazard selection as per OSHA 29 CFR 1910.132.

Spill Response Procedures

The most effective method for mitigating the risk of odorant loss during storage and transfer is to have proper procedures and training in place. These procedures should include the following: preventive measures that are strictly followed and continually reviewed to ensure best practices are in place to minimize the chance of a vapor release. Since a product or vapor release is at the highest risk during transportation and transfer, it is imperative to have spill response procedures in place for both incidental and major accidents.

Contain/Confine the Spill

A spill or leak of mercaptans will result in an obnoxious odor that must be dealt with immediately to avoid personnel and complaints from surrounding communities. If a release occurs in an open area, shut off all ignition sources immediately. In the leak is within confined spaces, such as within odorant injections sites, evaluate possible sources of ignition and follow facility procedures. Please note when in confined spaces the concentration of odorant can become relatively high quickly and one can be overwhelmed if personal protective equipment is not in use.

A spill can generally be contained using a catch bucket below a drip which is filled with a masking/neutralizing agent or diking. Release into watersheds should also be avoided. Environmental fate and aquatic toxicology studies commissioned on various odorant blend components indicate some chemicals can be persistent and highly toxic to aquatic species.

Absorb the Spill

Once a spill is contained, the next-step is to minimize dissipation of odors and absorb the gas odorant. A variety of materials can be used to quickly reduce vapors emitted as well as contain the spill. For example, commercial powder absorbents, pads, kitty litter, clay, sand, dirt, or sawdust can be utilized. Large spills can be controlled with aqueous film forming foam (AFFF) and re-applied continually, as necessary. Absorbents should be removed and placed in proper waste disposal containers or plastic bags to further contain the odor. In circumstances where the prior measures cannot be utilized, plastic sheets or tarps can be applied over the absorbents used to clean the spill.

Neutralize and Mask the Odor

Chemical oxidation is a very effective method for neutralizing mercaptans. The most commonly used materials are household liquid bleach (5% Sodium Hypochlorite), Hydrogen Peroxide (3%), and live bacteria. *Under no circumstances should a concentrated amount of oxidizer be used to mitigate a mercaptan spill.* Oxidation reactions are exothermic and can cause ignition.

Neutralization with bleach or peroxide is fast and efficient. These types of products are most effectively used to clean up contaminated areas after the spill has been absorbed and removed. Please note, the neutralizing agent, absorbent pads, and other related items (i.e. rags) must be treated as hazardous materials. Bacterial solutions containing enzymes that naturally

degrade gas odorants are also effective, however colder temperatures can reduce the degradation of gas odorants or render them inactive.

Finally, masking agents are used to camouflage the mercaptan odor. These products do not chemically react with the mercaptans, but are a highly fragrant chemical in the family of Terpenes. They are most effectively used to mask any minor vapor releases during product transferring or breaking hose connections (Eilerts *et al.*, 2005).

Disposal of materials

Absorbents, rags, gloves, or pads used to clean or adsorb odorants should be placed in proper containers and disposed of according to governmental requirements by certified hazardous material contractors.

CONCLUSION

Gas odorants are necessary for odorizing natural gas. They possess a low hazard potential and their odor threshold impact on the olfactory system makes them ideal for warning against gas leaks. When working with gas odorants one must be cautious of their high flammability and need for containment. Release of odorants should be avoided at all costs and if encountered, appropriate risk mitigating measures should be employed immediately. Workers should minimize exposures to gas odorants during their normal day-to-day routines with the use of monitoring and personal protective equipment when working with these materials.

Regulatory List	Ethyl Mercaptan (EM)	Isopropyl Mercaptan (IPM)	Propyl Mercaptan (NPM)	tert-Butyl Mercaptan (TBM)	Secondary Butyl Mercaptan (SBM)	Dimethyl Sulfide (DMS)	Methylethyl Sulfide (MES)	Tetrahydro thiophene (THT)
CAS#	75-08-1	75-33-2	107-03-9	75-66-1	513-53-1	75-18-3	624-89-5	110-01-0
NTP list of Carcinogens	NO	NO	NO	NO	NO	NO	NO	NO
IARC list of carcinogens	NO	NO	NO	NO	NO	NO	NO	NO
California Prop 65	NO	NO	NO	NO	NO	NO	NO	NO
SARA 313	NO	NO	NO	NO	NO	NO	NO	NO
CERCLA CFR 302.4	NO	NO	NO	NO	NO	NO	NO	NO
DOT Marine Pollutant	YES	NO	NO	NO	NO	NO	NO	NO
MA RTK	YES	YES	YES	YES	YES	YES	NO	NO
NJ RTK	YES	YES	YES	YES	YES	YES	NO	YES
PA RTK	YES	NO	NO	YES	YES	YES	NO	NO
HPV	YES	YES	YES	YES	YES	YES	NO	YES
Canada CEPA	NO	NO	NO	NO	NO	NO	NO	NO

NTP: National Toxicology Program
 IARC: International Agency for Research on Cancer
 DOT: U.S. Department of Transportation
 SARA: Superfund Amendments and Reauthorization Act
 CERCLA: Comprehensive Environmental Response, Compensation, and Liability Act
 MA: Massachusetts Right to Know
 NJ: New Jersey Right to Know
 PA: Pennsylvania Right to Know
 HPV: High Production Volume Chemical (includes Extended and Evergreen Programs)
 CEPA: the *Canadian Environmental Protection Act, 1999* (CEPA 1999)

TABLE 1. Regulatory Overview of Chemicals used in Gas Odorant Blends.

SCENTINEL* T-50, 54 GAL DRUM

Contains: Tetrahydrothiophene(110-01-0) t-Butyl Mercaptan(75-66-1)

Net weight: 405 LB

Gross weight: 458 LB

Signal Word: Danger Flash point: 59 °F (15 °C) Material: 1024725

Emergency Contact Information Health: 866.442.9628 (North America) / 1.832.813.4984 (International)

Transport: CHEMTREC 800.424.9300 or 703.527.3887(int'l) /Asia: +800 CHEMCALL (+800 2436 2255) China:+86-21-22157316 / EUROPE: BIG +32.14.584545 (phone) or +32.14583516 (telefax) / South America SOS-Cotec Inside Brazil: 0800.111.767 Outside Brazil: +55.19.3467.1600

Hazard Statements: H225: Highly flammable liquid and vapor. H315: Causes skin irritation. H317: May cause an allergic skin reaction. H319: Causes serious eye irritation.
Precautionary Statements: P210: Keep away from heat/sparks/open flames/hot surfaces. No smoking. P233: Keep container tightly closed. P240: Ground/bond container and receiving equipment. P241: Use explosion-proof electrical/ ventilating/ lighting/ equipment. P242: Use only non-sparking tools. P243: Take precautionary measures against static discharge. P261: Avoid breathing dust/fume/gas/mist/vapors/spray. P264: Wash skin thoroughly after handling. P272: Contaminated work clothing must not be allowed out of the workplace. P280: Wear protective gloves/ eye protection/ face protection. P303 + P361 + P353: IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse skin with water/shower. P305 + P351 + P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. P333 + P313: If skin irritation or rash occurs: Get medical advice/ attention. P337 + P313: If eye irritation persists: Get medical advice/ attention. P362: Take off contaminated clothing and wash before reuse. P370 + P378: In case of fire: Use dry sand, dry chemical or alcohol-resistant foam for extinction. P403 + P235: Store in a well-ventilated place. Keep cool. P501: Dispose of contents/ container to an approved waste disposal plant.



THIS CONTAINER IS FOR PACKAGING AND TRANSPORT OF CAPTIONED PRODUCT. USE CONTAINER FOR INTENDED PURPOSE ONLY. Do not use pressure to empty any container unless specified, or it may rupture with explosive force, which may cause injury or death. Empty containers retain product residue (solid, liquid, and/or vapor) and can be dangerous. Empty containers should be completely drained, properly sealed, and promptly returned to a re-conditioner, or properly disposed of.

CHEVRON PHILLIPS CHEM CO LP
Main Warehouse
SPUR 119 EAST
BORGER, TX 79007
USA



See SDS: 100000013852 or 387280 for further details regarding safe use of this product.

NON-RETURNABLE CONTAINER

FIGURE A. Example of changes to the revised Hazardous Communication Standard (HazCom 2012) related to the use of signal words, pictograms and hazard/precautionary statements for labels.

Chemical	Oral LD ₅₀ mg/kg bw	Dermal LD ₅₀ mg/kg bw	Inhalation LC ₅₀ PPM	Irritation Eye/Skin		Sensitizer
EM	682	> 2000	4420	Causes Serious Eye Damage	Slightly	Yes
NPM	1790	> 2000	> 1820	Slightly	Slightly	Yes
IPM	> 2000 - <5000	> 2000	> 5917	Slightly	Slightly	Yes
TBM	4729	> 2000	26,643	Causes Serious Eye Irritation	Slightly	Yes
DMS	> 2000	> 2000	40,250	Slightly	Non- irritating	Not expected
MES	> 5000	> 2000	> 6988	Causes Serious Eye Irritation	Slightly	Not expected
THT	1850	> 2000	6270	Causes Serious Eye Irritation	Irritating	Not expected

LD₅₀ (Lethal Dose) or LC₅₀ (Lethal Concentration) is the dose at which 50% of the test population dies. Greater than symbol (>) listed for inhalation studies indicates an LC₅₀ was not determined at the concentration(s) evaluated. Data presented in the table was developed by members of a consortium.

TABLE 2. Summary of Acute Hazards Reported for Chemicals used in Gas Odorant Blends.

Organization	ACGIH® TLV®	OSHA PEL	NIOSH REL	MAK
Chemical				
Ethyl Mercaptan	0.5 ppm (1.3 mg/m³)	10 ppm (C) (25 mg/m³)	0.5 ppm (C) (1.3 mg/m³) (C)	N/A
Normal Propyl Mercaptan	N/A	N/A	0.5 ppm (C) (1.6 mg/m³) (C)	N/A
Dimethyl Sulfide	10 ppm (25 mg/m³)	NA	N/A	N/A
Tetrahydro thiophene	N/A	N/A	N/A	50 ppm (180 mg/m³)

Ceiling (C): The concentration that shall not be exceeded during any part of the working exposure.

TWA: Time weighted average exposure concentration for a conventional 8-hour (TLV®, PEL or up to a 10-hour (REL)) workday and a 40-hour workweek.

OSHA PELs: U.S. Occupational Safety and Health Administration Permissible Exposure Limits

NIOSH RELs: U.S. National Institute for Occupational Safety and Health Recommended Exposure Limits. RELs represent a time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek.

MAK: Federal Republic of Germany Maximum Concentration Values in the Workplace

N/A: indicates not available

TABLE 3. Occupational Exposure Limits Established for Chemicals used in Gas Odorant Blends.

<u>Air Purifying Respirators</u>	<u>APF</u>
• Half facepiece (maintenance-free and dual cartridge)	10
• Full facepiece	50
<u>Powered Air Purifying Respirators</u>	
• Loose-fitting facepiece (e.g., L-501, Airstream™)	25
• Half facepiece	50
• Full facepiece, helmet, or hood	1000
<u>Supplied Air Respirators (airline)</u>	
• Continuous Flow	
–Loose-fitting facepiece	25
–Half facepiece	50
–Full facepiece, helmet, or hood	1000
• Pressure Demand with Full facepiece	1000
• Pressure Demand Airline with Escape SCBA. unknown and IDLH atmospheres	10,000
• Pressure Demand SCBA unknown and IDLH atmospheres	10,000

APF: Assigned Protection Factor
IDLH: Immediately Dangerous to Life or Health

TABLE 4. OSHA Assigned Protection Factors for Various Respirators.

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