

Workplace Health and Safety Bulletin



Reduced Sulphur Compounds: Focus on Thiols

Thiols, once known as mercaptans, are a family of organic chemicals that contain sulphur. Thiols are included in the group of chemicals known as “reduced sulphur compounds”. Many thiols have strong and repulsive odours. In their pure forms, some thiols are flammable. Thiols are commonly added to natural gas so that people can smell the gas in case of a leak.

Thiols are a family of organic chemicals that contain sulphur.

It is difficult to talk about thiols without making mention of other reduced sulphur compounds. Hydrogen sulphide (H₂S) is a close relative of the thiol family and is commonly found with thiols. Other reduced sulphur compounds commonly found with thiols include dimethyl sulphide and dimethyl disulphide.

Occurrence of thiols

Thiols are often encountered in the petroleum and pulp and paper industries. Thiols also occur naturally: propanethiol is found in onions, butanethiol is associated with skunks and allyl disulphide, a related substance, is found in garlic oil.

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Government of Alberta ■
Employment and Immigration

Petroleum industry

Thiols are usually present together with hydrogen sulphide but often in smaller quantities:

- Oil and gas fields containing hydrogen sulphide usually contain thiols as impurities in raw natural gas. They are most often found in light oil and gas fields and rarely found with heavy oils. Scrubbing processes that remove hydrogen sulphide from gas streams may not remove thiols.
- The type and concentration of thiols present varies from one gas field to another. These sulphur compounds are primarily found in the gas, with lesser amounts in the liquids. Thiols usually end up in gas condensates.
- High pressure steam injected into bitumen reacts with organosulphur compounds to create hydrogen sulphide and thiols in the produced gas.
- Methanethiol is sometimes found as an impurity in dimethyl disulphide, a substance used to remove sulphur from wells and activate certain catalysts.
- Thiols may be present at locations where they are added to natural gas and propane to give these gases their characteristic odour.
- When the “Merox” sweetening process is used to remove sulphur from gasoline, thiols, sulphides and disulphides end up in the spent caustic.

Accepted practice in the petroleum industry is to address the safety concerns of thiols and H₂S together. Measurement techniques used for H₂S often detect thiols, although sometimes with less sensitivity. Engineering controls, administrative controls and personal protective equipment (PPE) used to control H₂S exposures also protect workers from thiol exposures. Thiols may be present at concentrations that exceed their Occupational Exposure Limits (OELs), even when the concentration of hydrogen sulphide is below its OEL.

Controls used to control H₂S exposures also protect workers from thiol exposures.

Pulp and paper industry

Sulphur is a major ingredient used in the Kraft pulping process. It is this sulphur that eventually leads to the production of thiols. Non-Kraft processes are less common and are not likely to produce thiols.

The most commonly encountered thiol in the Kraft pulping process is methanethiol. Hydrogen sulphide, dimethyl sulphide and dimethyl disulphide are also produced.

Pulping is a closed-loop process and it is therefore unusual for any substantial quantity of sulphur compounds to be released. Workers are most likely to be exposed to these substances during plant shutdown activities when normally closed systems are opened for maintenance. Thiols are found in the “black liquor” and in the “foul condensate”, sometimes referred to as “red oil”. On-site wastewater treatment plants can also generate hydrogen sulphide and thiols during the treatment process.

As with the petroleum industry, standard practice in the pulp and paper industry is to address the safety concerns of thiols and H₂S together. This is done through exposure monitoring and the use of engineering, administrative and the PPE controls.

Effects on the body

The effects of thiols on the body are often compared with those of hydrogen sulphide. Most experts believe that thiols have properties similar to hydrogen sulphide but may be less dangerous.

Thiols have excellent warning properties — they can be smelled at concentrations well below levels that may be harmful. For example, methanethiol can be smelled at levels below 0.002 parts per million (ppm), 250 times lower than the level where harmful effects may begin to be noticed. The most commonly encountered complaint associated with thiols is their bad smell. When present at high concentrations, some thiols may have the ability to temporarily reduce a person’s ability to smell odours.

Thiols have excellent warning properties.

Thiols are strong irritants and can be toxic at high concentrations. Persons exposed to high concentrations have reported headaches, nausea, vomiting, coughing, lung irritation, and inflammation of the eyes nose and throat. Exposure to very high concentrations of thiols can lead to breathing problems, unconsciousness, and muscle spasms. The irritant effects of thiols generally disappear quickly after an exposed person is moved to clean air.

The exact thiol concentrations that may trigger these adverse health effects are not known. However, experts believe that exposure to thiols is less harmful than exposure to equal concentrations of hydrogen sulphide. Thiols are also very fat-soluble. This means that they are readily absorbed through the skin when direct contact is made with their liquid form.

Little is known about the long-term health effects of thiol exposure. Workers usually remove themselves from high exposure areas to get away from the irritating effects of the exposure. However, workers who continue to work while exposed to thiols may adapt and not notice the smell or irritating effects as much as they originally did.

The related substances, dimethyl sulphide and dimethyl disulphide, can be easily smelled at levels as low as 0.0001 to 0.002 ppm, but their odours are not nearly as strong or repulsive as the odours of thiols. Dimethyl disulphide's toxicity is believed to be similar to that of thiols whereas dimethyl sulphide, is far less toxic by comparison. At high enough concentrations, dimethyl sulphide and dimethyl disulphide may cause eye, nose and throat irritation and can lead to muscle paralysis.

Occupational Exposure Limits (OELs)

Workers in Alberta must not be exposed to airborne concentrations of a chemical contaminant that exceed the Occupational Exposure Limit (OEL) for that chemical. If no OEL has been established, exposures must be kept as low as reasonably practicable. OELs represent minimum standards for worker protection. All reasonable and practical efforts should be taken to keep exposure levels as low as possible.

Health and safety requirements for thiols are the same as those for any hazardous substance found at a workplace. OELs must not be exceeded and workers must not be exposed to levels that cause harmful effects. The fact that some substances do not have an OEL does not mean that they are safe under all circumstances. At a high enough concentration, any substance can pose a danger to persons exposed to it.

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Commonly encountered thiols that have established OELs include methanethiol and ethanethiol. Thiols that might be encountered, but do not have established OELs include propanethiol, pentanethiol, hexanethiol and heptanethiol.

Where a worker is exposed to two or more similarly toxic substances at the same time, employers are required to keep the combined exposure low enough that the worker is not harmed. OELs are reviewed and revised periodically. The most current occupational exposure limits can be found in Alberta's occupational health and safety legislation.

It may be necessary to monitor workplace air to ensure that airborne levels of thiols and other reduced sulphur compounds do not exceed their OELs. The recognized method of testing for thiols is the National Institute of Occupational Safety and Health (NIOSH) method number 2542, "Mercaptans". The NIOSH test method is posted at the NIOSH web site at the following address:

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 www.cdc.gov/niosh/nmam/pdfs/2542.pdf

Detector tubes, electronic gold film analyzers and electrochemical sensors may be acceptable testing alternatives. Some of these alternatives have successfully been used to measure concentrations of thiols and other reduced sulphur compounds in the field.

Controls and emerging situations

Engineering and administrative controls can protect workers. The control(s) used depend on conditions at the work site. Respirators and other personal protective equipment must be supplied if engineering or administrative measures inadequately protect workers from exposure to thiols and other substances, or in the event of an emergency. If personal protective equipment is used or relied upon, it must be properly selected and cared for. Workers must also be trained in the proper use of personal protective equipment.

If thiols or other reduced sulphur compounds are, or may be present at a work site, the employer must inform workers of the hazards of these substances, how to protect themselves from excessive exposure, and what to do in an emergency.

Employers and workers both have responsibilities in emergency situations. The employer must

- develop emergency procedures before any potential emergency involving the release of thiols happens at a work site,
- ensure that workers are aware of the emergency procedures, are trained, and adequately supervised in an emergency, and
- provide workers with full facepiece positive pressure self-contained breathing apparatus (SCBA) or other suitable equipment.

Employers and workers have responsibilities in emergency situations.

The worker must

- quickly leave the area for fresh air (if available, quickly put on the nearest suitable respirator),
- seek medical attention right away if large amounts of thiols or other harmful substances are inhaled,
- not re-enter a contaminated area of unknown concentration unless equipped with an SCBA, and
- be prepared to assist co-workers while making sure that correct emergency procedures are followed. It is important for workers to ensure their own safety when rescuing or assisting a co-worker.

For additional information

 *Technical Bulletin No. 691: Health Effects of Reduced Sulfur Gases*, National Council of the Paper Industry for Air and Stream Improvement, New York, February 1995.

Web site: www.ncasi.org

 Tatum, Vickie L., *Health Effects of TRS Compounds*, 1995 International Environmental Conference Proceedings, Technical Association of the Pulp and Paper Industry, Atlanta, pp. 969-972. Web site: www.tappi.org

 *DMS/DMDS: Review of Health Effects*, Forest Industry Health Research Program, December 1995.

Web site: www.paperforum.com

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