

IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Environmental Data

Thiols constitute a class of organic sulfur compounds whose chemistry has been well studied [9,17]. Only limited quantitative data are found on air concentrations of thiols in occupational environments, probably since they are easily detectable by their odor at the ppb or ppm levels [16,45,48,50,79-81]. Indeed, odors of sulfur-containing components are readily discernible near plants that manufacture and use thiols [82].

Sampling and Analytical Methods

(a) Sampling

A variety of techniques has been used to collect airborne thiols. Collection systems are required to be more effective for lower molecular weight thiols than for those with higher molecular weights in order to sample with optimal collection efficiency because of the greater volatility of the first group [83].

Methanethiol has been collected in an aqueous solution of mercuric acetate-acetic acid [84,85], in an aqueous solution of mercuric cyanide [86], with the use of refrigerated solvents at -78 C [87,88], or in a Porasil D trap at -80 C [89]. With direct gas-chromatographic analysis, the air sample was either first collected into a gas sampling bottle [90] or picked up with an inert sampling line connected to the chromatograph [91,92]. Aqueous collection is essentially complete [84], but some losses can be expected if the thiol is to be freed for the analytical step. The refrigerated solvent systems do provide at least 94% collection [87]. However, no information is found on the sampling efficiency with the Porasil D trap. Direct injection into a gas chromatograph will collect 100% of the methanethiol present in air, if transient reactions are blocked.

Similarly, ethanethiol has been collected in an aqueous solution of mercuric acetate-acetic acid [84], in an aqueous solution of mercuric cyanide [86], or in a sorbent tube containing Chromosorb 104 [93]. Complete absorption was obtained in six tests with the mercuric acetate, but results with the mercuric cyanide were not reported. The Chromosorb 104 sorbent did not provide satisfactory recoveries, even after ethyl acetate was substituted as a desorbing solvent. Only 80% recovery was obtained after 3 days and less than 10% after 8 days.

With propanethiol, only two reports indicate methods of collection: absorption in mercuric cyanide solution [86] and direct gas chromatography from a gas sampling bottle [90]. Neither report has information concerning the efficiency of these methods.

Collection of butanethiol in an aqueous mercuric acetate-acetic acid solution has been described, with 97% collection efficiency and a coefficient of variation of 0.6% on the basis of six tests [84]. Absorption in mercuric cyanide solution also has been used, but the collection efficiency was not reported [86]. Butanethiol is the only thiol for which a NIOSH-validated method has been approved [94]. This method uses a sorbent tube containing Chromosorb 104 and achieves effective adsorption and desorption in the range required. The Chromosorb 104 method offers convenience and reliability. This recommended method for lower molecular weight thiols is described in Appendix I.

No mention of a specific method for pentanethiol collection was found in the literature, but the mercuric acetate-acetic acid method should be applicable. Hexanethiol collection has had about a 94% efficiency with this absorbing system and a coefficient of variation of 0.6% on the basis of six tests [84]. Specific methods for higher molecular weight thiols were not reported in the literature.

In conclusion, the use of sorbent tubes containing the proper type of adsorbent, such as Chromosorb 104 for butanethiol, is the most efficient and convenient method of collection for thiols and is the method recommended in Appendix I. The use of refrigerated solvents, particularly ethylbenzene, which provides good separation in the gas chromatographic analytical stage, should be considered as a second choice. The lower molecular weight thiols (C_1 - C_3) can be collected in ethylbenzene at $-78\text{ }^\circ\text{C}$, and the higher molecular weight thiols (C_6 - C_{18}) are retained in the same solvent at $0\text{ }^\circ\text{C}$ [87,88].

(b) Analysis

Ryland and Tamele [95] published an extensive review on the application of titrimetric, polarographic, spectrophotometric, gas-liquid chromatographic, mass spectrometric, and radiometric methods to thiol determinations.

One report [96] described potentiometric titration, with a silver wire coated with silver sulfide as the indicating electrode, in an alkaline medium with silver nitrate solution for the determination of thiols and hydrogen sulfide. This method applies directly to lower molecular weight thiols (C_1 - C_3) and also to hexanethiol and heptanethiol, provided any hydrogen sulfide present is first removed. The method is useful for rapid analysis of a large number of samples.

Spectrophotometric methods for the determination of lower molecular weight alkane thiols in industrial air also have been described [84,85]. Collected in mercuric acetate solution, thiols reacted with N,N-dimethyl-p-phenylenediamine to form a red complex, with an absorption maximum at 500 nm. Hydrogen sulfide, sulfur dioxide, and nitrogen dioxide did not interfere with the reaction. The method applied to the determination of total thiols only and did not differentiate among individual thiols. Methanethiol at concentrations ranging from 0.5 to 25 ppm was readily detected.

A titrimetric method for determination of thiol sulfur in gases or distillates containing more than 0.001% (wt) of thiol sulfur has been reported [97]. Thiols are converted to silver mercaptides by reaction with silver nitrate, the excess of which is determined by titration with ammonium thiocyanate with ferric alum as the indicator. When hydrogen sulfide is present in the test sample, it is precipitated with cadmium sulfate, and the clear aqueous layer is titrated as above. Acetylenes interfere with this method, and this limitation should be considered when this method is used in monitoring thiols.

A simple and accurate colorimetric method for measurement of odorant levels and isopropylthiol and tert-butylthiol mixtures in natural gas was developed by Knight and Verma [98]. The test was based on the reaction of alkane thiol with N-ethylmaleimide; the color developed immediately and was stable for 10 minutes. Under field conditions, when a spectrophotometer was not available, a visual comparison with a standard color chart was used. A linear response was obtained with 1-9 μmol of thiols.

Analytical methods aimed at measuring methanethiol in the atmosphere of kraft paper mills take into account the presence of other sulfur compounds such as dimethyl sulfide, dimethyl disulfide, hydrogen sulfide, and sulfur dioxide; these compounds usually occur at concentrations higher than that of methanethiol. Analysis of kraft mill gases containing sulfur by titrimetric [99-102], polarographic [103], and gas chromatographic methods, which include flame-ionization detection [104,105] and flame-photometric detection [106,107], has been extensively studied.

The alkane thiols, especially those with lower molecular weights (C_1 - C_5), have high vapor pressures; at concentrations detectable by their odor, in the ppb range, gas chromatographic methods have been the most effective because such methods are highly sensitive and allow clear separation and precise measurement of thiols. Feldstein et al [86] reported on the gas chromatographic determination of a number of organic sulfur compounds, including methanethiol, ethanethiol, and propanethiol, using a variety of partitioning agents.

Stevens et al [108] described an automated gas chromatographic system for measuring ambient air concentrations as low as 2 ppb for sulfur

dioxide, hydrogen sulfide, methanethiol, and dimethyl sulfide. They found fluorinated ethylene-propylene (Teflon) tubing to be better than stainless steel, soft glass, or borosilicate glass, in that no undesirable retention of sulfur dioxide at levels below 10 ppm occurred. Powdered Teflon coated with polyphenyl ether (5-ring variety) and orthophosphoric acid was the best column packing. A flame-photometric detection system was used. Following essentially the same procedure, Bremner and Banwart [109] identified and separated methane-, ethane-, propane-, and butanethiol as well as hydrogen sulfide, dimethyl sulfide, carbon disulfide, diethyl sulfide, and diethyl disulfide from soils. Many of these compounds may occur in the atmosphere surrounding manufacturing processes or industrial operations.

Additional experimental modifications include graphitized carbon black, treated with phosphoric acid and Dexsil-300, as packing material, and, for calibration, an exponential dilution flask constructed entirely of Teflon [110]; cyanosilicone coating material (XE-60) instead of Dexsil and a double detection system with a combination of flame-ionization and flame-photometric detectors [111]; a stainless steel column packed with Triton X-305 on Chromosorb G for the separation of ethanethiol and dimethyl sulfide [112]; an all stainless steel column and connections and Porapak QS treated with 5% QF-1 Chromosorb G treated with polyphenyl ether to overcome problems associated with low concentrations of individual thiols in natural gas that have a tendency to absorb on column walls and are readily oxidized in the presence of traces of oxygen and Porapak QS column treated with acetone [113,114].

Recently, Vitenberg et al [115] described another possible gas chromatographic method (combining gas chromatographic head space analysis and microcoulometric detection) for the determination of trace sulfur compounds in industrial effluents. In addition to the gain in sensitivity, this method improves the quality of the separation and the accuracy of the quantitative values obtained. Water solutions of methanethiol and ethanethiol can be measured at the ppm level with less than 10% analytical error.

Although a variety of techniques can be applied to the analysis of thiols in occupational environments, most of them are nonspecific and rely upon the reactions of the thiol group. Gas chromatographic and mass spectroscopic methods allow the separation, detection, and quantitative determination of individual thiols in the presence of other sulfur-containing substances encountered in industrial environments. In summary, gas chromatographic techniques using flame-photometric detection are available and provide a specific quantitative analytic method for thiols [106,107,109,111,112,114]. Resolution of interferences from various compounds, such as H₂S, sulfides, or alkanes, has been accomplished by selection of the appropriate stationary phases [86]. Other columns that have been used successfully to quantitatively analyze thiols are reported in a number of publications [108,110-114].

A gas chromatographic method with flame-photometric detection [94] is recommended for analysis of samples of thiols collected from the workplace environment. It has the ability to separate and quantitatively determine thiols from mixtures containing structurally similar compounds. This method is precise, accurate, and sensitive and is described in detail in Appendix I. It has been tested and validated by NIOSH.

Engineering and Administrative Controls

Industrial methods for the production of thiols are described in the literature [116-124]. These methods indicate the nature of raw materials, waste products, physical characteristics of the various processes, and products that may be encountered in occupational environments where thiols are manufactured and used.

Raw materials, products, and sulfur-containing byproducts from the production of thiols are potentially hazardous in the occupational environment. In general, thiols, carbon disulfide, hydrogen sulfide, and related materials should be contained in closed systems and vented to flare or scrubber systems to prevent inadvertent discharge of these odorous compounds into occupational and community environments [82].

All systems should be designed, operated, and maintained to prevent spills or release of thiols, particularly during the transfer of products (shipping and receiving) or in the collection of samples. An example of good design was observed in a plant where the drum and tank car transfer stations had return lines vented to flares. When the thiol was pumped into drum or tank, the displaced atmosphere (diluted with nitrogen or another inert gas) was not released into the environment [82]. For fast and safe intervention in routine (and emergency) operations, systems handling thiols should have adequate instrumentation, such as levels indicators, pressure gauges and thermometers, volumetric flow recorders, etc. In addition, remote controls are recommended so that operators are sheltered from accidental spills and overflows, since they can work at a safe distance from systems they are controlling. The two techniques, instrumentation and remote controls, are found in the most recent plant installations. A closed system to prevent the release of materials is recommended. An engineering control program, providing for frequent inspections, preventive maintenance, and prompt repair of any faulty equipment, is essential. In tank-car or drum-filling operations, submerged transfer lines and return vent lines, or vent lines connected to flares, with provision for line flushing before disconnection, should be used [82].

Because hydrogen sulfide is a raw material generated, or used, in thiol manufacturing plants, special precautions are necessary to avoid its release in hazardous concentrations. As specified in the NIOSH criteria document on hydrogen sulfide, remote sensors at fixed locations to detect

hydrogen sulfide [125] or other sulfur-containing gases should be integrated into plant warning systems [82]. The design and operation of the plant should provide for rapid evacuation of employees, preferably by sufficient egress routes to allow employees to take advantage of the wind direction by moving away from the buildings either upwind or crosswind as indicated by the location of the release site. Wind direction indicators, such as wind socks, should be installed so as to be clearly visible from all the plant work areas [82].

Where closed systems are not practical or when leaks develop, occupational exposure to thiols becomes possible, and the likelihood of exposure increases for operations that require handling, transferring, or sampling of thiols. In addition, an employee can become exposed during routine maintenance and repair of equipment by entering tanks, vessels, or other confined spaces or when an emergency or nonroutine situation develops. Ventilation systems, such as hood, glove box, or local exhaust systems, are necessary when thiols are handled in an open system. In addition, a ventilation system is desirable as a standby, should a closed system fail. Guidance for the selection of ventilation systems is provided in NIOSH's Recommended Industrial Ventilation Guidelines [126] and Industrial Ventilation--A Manual of Recommended Practice [127] and in Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971 [128]. Proper control of atmospheric concentrations and capture of released thiols during those operations when exposure is possible should be based on the principles set forth in those publications.

Ventilation systems require regular inspection and maintenance to ensure effective operation. Routine inspections should include face velocity measurements of the hood and examination of the air mover and the collection or dispersion system. Any changes in the process or equipment that may affect the ventilation system must be promptly evaluated to ensure that control measures provide adequate protection for employees. Measurements of atmospheric concentrations of thiols in the work environment are needed to evaluate the efficiency of the ventilation system.

Because hydrogen sulfide, which may be present, is extremely corrosive in the presence of moisture, all facilities require frequent inspection and preventive maintenance to ensure that leaks are readily detected and repaired. Thiols in general are corrosive, and systems must be composed of corrosion-resistant materials, such as stainless steel or passivated metal. All exhaust gases from ventilation systems should pass through a sulfur recovery system or be exhausted to a scrubber or flare for oxidation. Alternatively, UV light, which can destroy ethanethiol in a scrubber application, may be considered [129].

Contingency planning for emergencies, the inadvertent release of materials, and equipment breakdown is vital; planned procedures should be

supported by the availability of appropriate equipment at strategic locations and by trained personnel. In addition to overall contingency planning for the entire plant site, written departmental plans, updated as necessary, and well understood by the department's personnel, are required. They should include:

- (a) Reporting requirements--how and whom to notify for help; how to document the incident later.
- (b) Steps to prevent spilled chemical from reaching a waterway, overloading a waste-water treatment system, or creating an airborne cloud.
- (c) Toxicity, solubility, flammability, and reactivity data on materials being handled.
- (d) Inventory and location of spill contingency equipment.
- (e) Procedures for handling water-soluble, insoluble, and other chemicals requiring special consideration.

In addition to having knowledge of internal reporting procedures, plant management personnel should understand the need for keeping good records to fulfill the reporting obligations established by various regulatory agencies. With such organized logging of every aspect of their operations, plant operators should also be able to answer any legitimate questions that may be raised by other interested groups. Information on the proper way to satisfy these requirements should be readily accessible to plant supervisors, along with lists of other company officials to help them with the necessary data.

As a general approach, the employer should review material handling operations, maintenance and repair procedures, and process operations in order to identify areas and job locations where employees may come in contact with thiols. Where the process is continuous, an analysis of the hazardous operations should be performed once a year at a minimum; where production is intermittent, a similar analysis should be performed at the start of each separate campaign. Factors to be considered include, but are not limited to, the following:

- (a) Transfer, loading, and unloading facilities, including procedures for moving chemicals to and from drums, storage tanks, trucks, railcars, and marine equipment; procedures to secure equipment during loading or unloading; equipment design; instrumentation; and employee monitoring of operations.

- (b) Sources of process upsets (startup, shutdown, and cleanup procedures).
- (c) Equipment and storage tank diking, surface drainage routing, and sewer system layout.
- (d) History of individual departments--spills, current operating procedures, and contingency plans.
- (e) Mooring practices, together with booming, dock design, hose systems, catch or drip pans, collection systems, curbing, spill contingency equipment, preferred valve types, equipment blanking practices, barge design, loading logs, and communication systems for marine facilities.
- (f) Operating procedures in piping--valve identification, capping or plugging of drain valves, vent valves, hose connection design, and winterizing practices for in-plant process and transfer equipment.

Administrative control through selective assignment of employees may be necessary to protect hypersensitive or sensitized individuals. Sensitive individuals may experience adverse reactions to thiols and related materials at lower concentrations than those tolerated by most other employees.

V. WORK PRACTICES

Work practices appropriate to the manufacture, handling, storage, and use of thiols are primarily concerned with preventing inhalation of, and skin and eye contact with, liquids, aerosols, and vapors of thiols. There is limited evidence from animal studies that thiols may be absorbed through the intact skin (WW Wannamaker III, written communication, December 1977). Inhaled methane- and ethanethiol are exhaled unchanged to some extent, but most thiols appear to be detoxified by metabolic oxidation [70]. Early recognition that an exposure has occurred, together with immediate countermeasures, should prevent adverse effects.

Good industrial hygiene practice requires that all reasonable effort be made to prevent contact of thiols with the skin or eyes and to prevent the inhalation of thiols. Areas of potential exposure by inhalation or skin or eye contact should be posted as restricted areas, and access should be limited to designated employees. If skin contact with a thiol occurs, the affected area should be washed immediately with soap and water. Evaporation of low molecular weight thiols can cause rapid cooling and frostbite. Organic solvents should not be applied to the affected area because defatting of the skin or absorption of the solvent may result. Organic solvents may also enhance absorption of the thiols. Emergency showers and soap should be available where exposures may occur. Where contact of thiols with the eyes is possible, emergency eyewash stations should be provided.

Washrooms and showers should be located conveniently, and employees should be urged to wash or shower after each workshift. To minimize exposure time, whenever employees are exposed through skin contact, they should be required to clean up immediately and change their work clothes.

Work practices and procedures for the use of personal protective devices to minimize contact with thiols should be developed. Personal protective equipment is necessary for additional positive protection in situations where exposures occur in spite of other precautions.

Training

In all areas where thiols are handled, written instructions informing employees of the particular hazards of the compounds, methods for handling the material, procedures for cleaning up spills, personal protective equipment requirements, and procedures for emergencies should be on file and readily available to employees. Employers should establish programs of instruction to familiarize all potentially exposed employees with these procedures. A Material Safety Data Sheet described in Appendix III should

be used as a guide by employers in providing the necessary information; but this should be supplemented with specific instruction and training in work operations involving potential contact with, or inhalation exposure to, hydrogen sulfide, carbon disulfide, other raw materials, and waste products, as well as thiols.

In addition, a continuing education program should be established. Such a program could include, but not be limited to, the following:

(a) Adoption of standardized written procedures, with appropriate personnel training and periodic review, for all routine phases of plant operations.

(b) Job procedures analysis for identification of spill potential.

(c) Encouragement of employees to report unsafe conditions.

(d) Development of a reporting form for all leaks and spills, whether or not they reach a waterway; investigation and review of all significant leaks and spills with the objective of preventing recurrence.

(e) Periodic inspections of dikes and transfer station valves, and review of work practices.

(f) Drills in containing spills.

(g) Bulletins to publicize "near miss" incidents or unsafe conditions.

(h) Communication of new ideas on health and safety aspects of the job.

(i) Use of slogans, posters, etc, to maintain employee interest.

(j) Publicizing of plant and department health and safety performances.

(k) Use of editorials by the plant manager in plant newspaper or bulletins, and regular emphasis on importance at employees' and supervisors' meetings.

Only individuals properly trained in the use of respirators and other protective equipment (including selection, fitting and checking, use, and care) should be permitted access to areas in which exposures to thiols as a result of spills or other accidents are likely. This is particularly important in areas, or during operations, where hydrogen sulfide, carbon disulfide, or low molecular weight thiols (C_1 through C_6) may be released. All such areas and operations should be clearly identified by appropriate posted warnings.

The effective use of recommended work practices to prevent exposures depends on the knowledge and cooperation of employers and employees. Employees must be thoroughly trained in all work operations and emergency procedures and in the use of required equipment and protective devices. They should be provided with the proper tools, equipment, and personal protective clothing or devices and receive adequate, responsible supervision to ensure that all safety requirements and practices are followed. Periodically, at least annually, refresher sessions and drills should be conducted to maintain a high level of competence in safe work practices and emergency procedures.

Protective Clothing and Equipment

Gloves, boots, aprons, goggles, face shields, and other personal protective devices should be made available for employee use. This equipment must be correctly fitted and kept in good condition. Respiratory protective devices must be kept clean and in good working order (29 CFR 1910.134) and must be cleaned and inspected after each use. Respirator canister/cartridges must be changed periodically and at least when the odors of thiols are detected within the mask. Adequate supervision must be exercised to ensure that respirators are worn regularly and properly. Cleanliness of respirators is important because of the hazard associated with skin exposure to thiols, particularly the low molecular weight compounds. Respirators will often restrict the wearer's field of vision and perhaps mobility. This may pose additional safety hazards, so that safety procedures appropriate to the job must be developed also. All personal protective equipment should be cleaned frequently, inspected regularly, and repaired or replaced as necessary. This equipment must be stored in appropriately designated containers or locations when not in use.

Each employee potentially exposed to thiol vapor, or likely to come in contact with solutions of these compounds, must be provided with, and required to wear, adequate protective clothing, such as cotton coveralls, splash-resistant aprons, etc, and equipment appropriate to the tasks and area of work. Adequate supervision must be exercised to ensure that the protective clothing and equipment are regularly and properly worn. All personal protective devices must be cleaned thoroughly after each wearing and before being reused. If any such item becomes contaminated with a thiol, raw material, or waste product during the workshift, it should be flushed with large amounts of water; when such flushing makes the item unsuitable for continued wear, it must be removed and replaced by a clean one.

Eye protection is of particular importance because of the irritant effects of thiols [59], raw materials, and waste products [125,130]. Well-fitted chemical safety goggles must be worn in posted areas as protection from irritating concentrations of thiol mists and splashes.

When using a respirator, employees also should have a full facepiece to provide the necessary eye protection. Full-length, plastic face shields may be worn to protect the face from splashes and spills, but chemical safety goggles are still necessary to protect the eyes from vapor, mists, and splashes that can enter behind the edge of the shield.

Emergency and First-Aid Practices

Each employer should establish a program to meet any emergency that can reasonably be anticipated. Employees assigned to emergency teams should be thoroughly informed of and trained in their responsibilities. First-aid supplies and oxygen resuscitation equipment, approved respiratory protective devices, protective garments, and other equipment that may be needed should be maintained in readiness at emergency stations close to areas of likely emergencies.

Respiratory protective devices approved for escape or evacuation from areas of excessive exposure to a thiol should either be provided to every employee in areas of potential emergency or be readily available at prominently and clearly identified locations throughout such areas.

In emergencies or other operations where airborne concentrations are unknown, respiratory protection must be provided to employees. The type of respirator required is described in Tables I-1 and I-2.

When employees are required to enter any confined space suspected of, or possibly subject to, contamination by a thiol, tests should be made to determine the safety of the atmosphere before entering. The odor of thiols and other sulfur-containing materials may warn of the presence of these compounds but does not necessarily indicate the extent of respiratory protection required.

Eye-flushing stations and safety showers should be available in plant areas where splashes or spills of thiols are possible. If contact with any thiol occurs, the affected skin areas and eyes should be flushed immediately with a copious flow of water. In case of eye contact with benzenethiol or with a mixture including benzenethiol, the affected eye shall be treated with not more than two drops of a 0.5% solution of silver nitrate (AgNO_3), applied from a bougie or other previously sealed container, and then flushed with copious quantities of water. When eye contact with any thiol has taken place, the affected person should be referred to a physician after eyewashing has been completed.

Material Handling

Employers must establish material-handling procedures to ensure that employees are not exposed at hazardous concentrations or amounts of thiols.

The following practices and procedures should be observed by all employees who handle thiols, raw materials, and wastes:

- (a) Containers of thiols, raw materials, and wastes should be properly labeled and securely closed during transport.
- (b) Thiols should be transported or stored in sealed, intact containers. A sealed container is one that has been closed and kept closed so that there is no release of thiols. An intact container is one that has not deteriorated or been damaged to the extent that the contained thiol is released. Because sealed, intact containers would pose no threat of exposure to employers, it should not be necessary to comply with required monitoring and medical surveillance requirements in operations involving only such containers. If, however, containers are opened or broken so that the contained thiols are released, then all provisions of the recommended standard should apply.
- (c) Large containers (carboys, drums, and others) should be moved and handled by mechanical equipment of appropriate design and construction.
- (d) The transfer of thiols from bulk containers should be done by pumping through a hermetically sealed system of lines. These lines must be vented to a scrubber, flare, or other recovery or destructive process to prevent release of material to both the occupational and community environment.
- (e) The transfer of thiols, raw materials, and wastes or solutions from tank cars or tank trucks should be done only by specially trained employees under responsible supervision.
- (f) Enclosed process machinery and containers of thiols or solutions thereof should be kept closed or covered, except when operations require otherwise.
- (g) Tanks, machines, pumps, valves, and lines should be drained and residual thiols removed by steam followed by an oxidizing solution and before maintenance or repair work. Care must be exercised to avoid contact with the drained or flushed fluids. Containers and lines must be purged of thiols, raw materials for their production, and wastes before performance of any external welding, grinding, or other operation that might offer a source of ignition for flammable vapor.

- (h) No individual should enter any tank or equipment until it has been flushed free of thiols, raw materials, and wastes, the atmosphere therein has been determined to be safe, and a permit has been issued by a responsible supervisor.
- (i) No individual should be permitted to enter any tank or confined space whose entrance is not large enough to admit an individual fitted with safety harness, lifeline, and an emergency respiratory protective device.
- (j) An individual may work in a tank or confined space only with another person outside in constant contact and with rescue equipment and assistance available.
- (k) Pipelines and hoses should be blanked off or disconnected to prevent inadvertent entry of thiols, raw materials, and wastes into a confined space in which an individual is working.
- (l) Spills and leaks of thiols should be immediately contained, absorbed, or neutralized with household bleach solution and flushed with an abundant flow of water. Employees should wear appropriate respiratory protective equipment and clothing during cleanup of spills.
- (m) Eyes and skin surfaces coming into contact with thiols should be immediately flushed with large amounts of water. In the case of contact with the eyes, a physician should be consulted as soon as possible.
- (n) Respirators and protective clothing and equipment should be worn in accordance with recommendations and requirements. Employees should exercise care not to transfer thiols, raw materials used in the production of thiols, and waste products from contaminated gloves or other protective garments to unprotected eye or skin surfaces.
- (o) Employees should comply with occupational safety and health provisions and all rules and regulations applicable to their own actions and conduct.

Sanitation

Appropriate locker rooms should be provided for changing into required protective clothing in accordance with 29 CFR 1910.141(e). To prevent and limit contact dermatitis from, and skin absorption of, thiols, employees should practice good personal hygiene. Employers should encourage employees to shower at the end of the workshift.

Food should not be stored, prepared, dispensed (including vending machines), or eaten in areas where thiols are manufactured, stored, or used. Lunchroom or lounge areas, if provided, should be separated from work areas and protected from contamination by thiols, raw materials, or wastes.

Wastes containing thiols, raw materials for the production of thiols, or byproducts should not be flushed into a community sewer system unless such action will not interfere with sewage treatment. Organic components of waste water may be treated by either chemical or biologic oxidation processes. The latter processes usually involve impounding the waste liquor, in which case precautions must be taken to ensure that seepage of effluent from the impoundment does not contaminate ground water or adjacent watercourses. Recycling spilled material back into the process should be considered.