VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1954, the American Conference of Governmental Industrial Hygenists (ACGIH) proposed tentative threshold limit values (TLV's) of 50 ppm for methyl mercaptan (methanethiol), 250 ppm for ethyl mercaptan (ethanethiol), and 10 ppm for butyl mercaptan (butanethiol) [128], expressed as time-weighted average (TWA) concentrations for an 8-hour day. All three of these values were adopted in 1962. In 1963, the TLV's, defined as TWA concentrations except when designated as ceiling concentrations, for both ethyl mercaptan and methyl mercaptan were changed to ceiling concentrations of 20 ppm.

In 1964, the ACGIH proposed a reduced TLV of 10 ppm for methyl mercaptan, which was adopted in 1966. In 1965, the ACGIH proposed a ceiling value of 10 ppm for ethyl mercaptan. This was adopted in 1967. The ACGIH established the TLV's by analogy with the toxicity of hydrogen sulfide [131]. Methyl mercaptan was regarded as having an acute toxicity similar to, but less than, that of hydrogen sulfide, according to studies by de Rekowski [132] and Frankel [133]. This analogy was supported by citing the Ljunggren and Norberg report [53], and a TLV of 10 ppm was recommended. By a similar analogy, ethyl mercaptan was regarded as being only one-tenth as toxic as hydrogen sulfide. The inhalation studies by Fairchild and Stokinger [59] on mice and rats were cited, with 4-hour LC_{50}'s for ethyl mercaptan of 2,770 and 4,420 ppm, respectively. These values were considered to be similar to values obtained for butyl mercaptan. Reports of headache, nausea, and irritation experienced by humans at levels approaching 10 ppm led the ACGIH to propose and adopt a ceiling concentration of 10 ppm for ethyl mercaptan. In contrast, butyl mercaptan at 10 ppm was considered to be odorous, but not sufficiently so to be seriously objectionable. In addition, the odor of butyl mercaptan was considered to be similar to that of hydrogen sulfide, and a TLV of 10 ppm was recommended. In the notice of intended changes for the 1968 TLV list, the ACGIH stated values of 0.5 ppm as the proposed TLV's for butyl, ethyl, and methyl mercaptans. These TLV's were adopted as TWA limits in 1970, and no further changes have been made in the recommended values for these thiols through the 1977 TLV listing. In 1977, the ACGIH [134] proposed a TLV for phenyl mercaptan (benzenethiol) of 0.5 ppm (2 mg/cu m), expressed as a TWA concentration.

The justification for the change respecting methanethiol was presented in the 1976 edition of Documentation of the Threshold Limit Values for Substances in Workroom Air [131]. Methanethiol was cited as being similar to hydrogen sulfide in toxicity but with a stronger, more disagreeable odor; the latter statement was not supported. The 0.5 ppm TLV is the

equivalent (approximately) of 0.98 mg methanethiol/cu m. For ethanethiol, the TLV of 0.5 ppm (approximately 1.3 mg/cu m) was based on the effects in humans--headache, nausea, and irritation--of exposure to the chemical at 4 ppm for 3 hours/day [48]. For butanethiol, the TLV of 0.5 ppm (approximately 2 mg/cu m) just noted and from its readily noticeable odor at 0.1-1.0 ppm (approximately 0.4-4.0 mg/cu m of air).

In 1968, Mississippi had TWA limits of 50 ppm for methyl mercaptan and 10 ppm for butyl mercaptan [135], and Massachusetts listed a TWA limit of 250 ppm for ethyl mercaptan. Pennsylvania listed a TWA limit of 5 ppm for methyl mercaptan in 1968; earlier TWA limits were 20 ppm for ethyl mercaptan and 10 ppm for butyl mercaptan.

The current Occupational Safety and Health Administration limits, stated in 29 CFR 1910.1000, based on the ACGIH-adopted values for 1968, are 10 ppm for butyl mercaptan, expressed as a TWA concentration, and a ceiling value of 10 ppm for methyl and ethyl mercaptans.

Austria, Belgium, Finland, Switzerland, and Yugoslavia have established limits for methyl, ethyl, and butyl mercaptans at 0.5 ppm. The Netherlands has limits for only methyl and butyl mercaptans at 0.5 ppm, and the Federal Republic of Germany lists a limit for ethyl mercaptan at 0.5 ppm. The USSR limit is 0.8 ppm for ethyl mercaptan. Rumania has limits of 30, 50, and 30 ppm for methyl, ethyl, and butyl mercaptans, respectively [135].

Basis for the Recommended Standard

(a) Environmental Concentration Limits

There is no definitive study that allows derivation of a dose-effect relationship for thiols in humans or in animals. Human studies are available for methane-, ethane-, and butanethiol, but these are essentially acute exposures designed to measure odor thresholds. The human exposure data presented in Chapter III indicated that exposure to thiols can produce CNS depression [12-14], and one death has been reported [12] following overwhelming exposure. In an experimental study [15], human exposure to ethanethiol at 4 ppm (1 mg/cu m) for 3 hours/day for 5 days caused olfactory fatigue and mucosal irritation. These effects returned to normal after cessation of exposure. Furthermore, exposure at 0.4 ppm under the same conditions did not cause the effects mentioned above. In another controlled experiment with volunteers [45], no significant adverse effects were noted after exposure to ethanethiol at 50 ppm (120 mg/cu m) or 112 ppm (270 mg/cu m) for 20 minutes, except for increases in breathing rate, which returned to normal after cessation of exposure. Signs and symptoms of CNS toxicity occurred in workers exposed for 1 hour to butanethiol at concentrations guessed to lie within the range of 50-500 ppm (180-1,800 mg/cu m) [15]. The workers exhibited asthenia, muscular weakness, and malaise.

Based on the animal toxicity data presented in Chapter III, the thiols can be categorized into two classes according to the degree of toxicity: (1) C_1-C_{12}, C_{16}, and C_{18} alkane thiols and cyclohexanethiol; and (2) benzenethiol. The inhalation toxicity data presented suggest that ethanethiol and butanethiol were equitoxic in rats and mice. Propanethiol was slightly less toxic than ethanethiol when inhaled or when administered orally and ip. Hexanethiol was four to five times as toxic as ethanethiol by inhalation but was only slightly more toxic than ethanethiol to rats and mice when given orally or ip [59]. Other acute inhalation studies in animals [54,60] indicated that methanethiol and pentanethiol are of approximately the same order of toxicity as ethanethiol. Therefore, the C_1-C_6 thiols can be grouped together as approximately equitoxic.

Several studies demonstrate subchronic toxicity of thiols in animal species [54,62]. Twenty-five exposures to methanethiol at 300 ppm (591 mg/cu m) killed all the mice [54]. Inhalation exposures of monkeys, rats, and mice to methanethiol at 50 ppm (98.5 mg/cu m) continuously for 90 days caused morbidity and mortality [62] in all three species.

Although the LD_{50} values for a mixture of C_7-C_{11} thiols and for dodecanethiol suggest a lower order of acute toxicity [61], subchronic inhalation exposure to these thiols does produce some organ changes suggestive of those seen in animals intoxicated with the lower molecular weight thiols. Therefore, these thiols are grouped with the C_1-C_6 thiols on the basis of their subchronic effects. Single exposure of mice by iv route for thiols C_3, C_4, C_6-C_{12}, C_{16}, C_{18}, and cyclohexanethiol resulted in similar LD_{50}'s (WW Wannamaker III, written communication, December 1977). Thus, available toxicity data presented in Chapter III for cyclohexanethiol as well as the information available on skin sensitization in guinea pigs and rats for higher molecular weight thiols indicate that this compound and the C_{16} and C_{18} thiols should all be grouped with the C_1-C_{12} thiols [59,61,66,67].

Both the human and animal toxicity data show adverse effects resulting from relatively short-term inhalation exposure to thiols at 50 ppm. These findings indicate that workplace concentrations of thiols should be kept well below this concentration. The minimal effects of olfactory fatigue and mucosal irritation [15] observed when individuals were exposed to 4 ppm ethanethiol ceased when the inhalation exposure was stopped, and no effects were observed at 0.4 ppm exposure. Because there is no evidence that adherence to the TLV of 0.5 ppm has resulted in any cases of toxicity, NIOSH recommends that the concentration of C_1-C_{12}, C_{16}, C_{18} alkane thiols, or cyclohexanethiol, or any combination of these thiols, in the workplace air should not exceed 0.5 ppm as a ceiling concentration for any 15-minute period. Since the toxic action of thiols, on short term-exposure, is expressed largely by reversible mucosal irritation [12,13,15,16], a ceiling

concentration limit is deemed more appropriate than a TWA concentration limit. The use of a ceiling concentration instead of a TWA has the effect of increasing the protection provided to the worker about twofold. NIOSH believes that adherence to the proposed ceiling concentration would prevent both irritative and systemic effects arising from occupational exposure to the aliphatic thiols.

Because C_1-C_{12}, C_{16}, C_{18} alkane thiols, or cyclohexanethiol can cause respiratory changes leading to respiratory failure, muscular weakness leading to paralysis, mild to severe cyanosis, and coma leading to death [12,15,53], exposure to several of them, even at or below the recommended workplace environmental concentration, may produce additive effects. These possibly additive effects should be considered when simultaneous exposure to several thiols occurs. The formula stated in 29 CFR 1910.1000(d)(2)(i) can be used to calculate the equivalent exposure limit (E_m) for the mixture when such plural exposures may occur:

$$E_m = \frac{C_1}{L_1} + \frac{C_2}{L_2} + \ldots\ldots \frac{C_n}{L_n}$$

where:

C = the concentration of a thiol
L = the permissible exposure limit of the thiol

Table VI-1 gives the mg/cu m equivalent to 0.5 ppm for each of these thiols.

Because benzenethiol is not only more toxic than the other thiols [59] but also has a comparatively marked potential for causing eye and organ damage, eg, at 0.72 ppm, at one-third the concentration of ethanethiol (2.1 ppm), as indicated by Katz and Talbert [16] (Table VI-2), NIOSH recommends that the concentration of benzenethiol in the workplace air should not exceed 0.1 ppm (0.45 mg/cu m) as a ceiling concentration for any 15-minute period.

(b) Sampling and Analysis

The technology is currently available to sample and analyze thiols at the recommended environmental limits and to allow institution of the required engineering controls. As discussed in Chapter IV and presented in greater detail in Appendix I, use of a sampling kit containing freeze-out traps and ethyl benzene at -78 C is recommended for collection of lower molecular weight thiols (C_1-C_3), and adsorption on Chromosorb 104 is recommended for personal breathing zone air sampling of higher molecular weight thiols (C_4-C_{18}). A possible solution to the problem would be the application of thermal desorption techniques. With the use of such methods, the entire sample adsorbed on a solid sorbent can be delivered to

TABLE VI-1

NIOSH RECOMMENDED EXPOSURE LIMITS FOR THIOLS

Thiol	Ceiling Concentration Limits*	
	mg/cu m	Approximate ppm Equivalents
Methanethiol	1.0	0.5
Ethanethiol	1.3	0.5
1-Propanethiol	1.6	0.5
1-Butanethiol	1.8	0.5
1-Pentanethiol	2.1	0.5
1-Hexanethiol	2.4	0.5
1-Heptanethiol	2.7	0.5
1-Octanethiol	3.0	0.5
1-Nonanethiol	3.3	0.5
1-Decanethiol	3.6	0.5
1-Undecanethiol	3.9	0.5
1-Dodecanethiol	4.1	0.5
1-Hexadecanethiol	5.3	0.5
1-Octadecanethiol	5.9	0.5
Cyclohexanethiol	2.4	0.5
Benzenethiol	0.5	0.1

*Limit not to exceed 0.5 ppm when more than one thiol is present except for benzenethiol

TABLE VI-2

ODOR INTENSITY OF THIOLS IN HUMANS

Thiol	Degrees of Odor Intensity Vs Thiol Concentration in ppm*											
	0		1		2		3		4		5	
Methanethiol	0.003000	(0.0059)	0.04100	(0.081)	0.570	(1.1)	7.90	(16)	110	(220)	1,500	(3,000)
Ethanethiol**	0.000021	(0.000053)	0.00097	(0.0025)	0.045	(0.11)	2.10	(5.3)	97	(250)	4,500	(11,000)
	0.000006	(0.000015)	0.00026	(0.00066)	0.011	(0.028)	0.49	(1.2)	21	(53)	920	(2,300)
1-Propanethiol	0.000110	(0.00034)	0.00160	(0.005)	0.024	(0.075)	0.36	(1.1)	05.4	(17)	81	(250)
1-Butanethiol**	0.002700	(0.0099)	0.04800	(0.19)	0.840	(3.1)	15.00	(55)	260	(960)	4,600	(17,000)
	0.000045	(0.00017)	0.00100	(0.0037)	0.022	(0.081)	0.50	(1.8)	11	(40)	250	(920)
Benzenethiol	0.000005	(0.000023)	0.00025	(0.0012)	0.014	(0.063)	0.72	(3.2)	38	(170)	2,000	(9,000)

*0 = no odor, 1 = detectable, 2 = faint, 3 = quite noticeable, 4 = strong, 5 = very strong;
numbers in parentheses = concentration in mg/cu m
**Results of two tests are presented for ethanethiol and butanethiol.

Adapted from reference 16

the gas chromatograph for analysis, reducing the amount of sample that must be collected. Before such methods can be used with confidence, however, it must be established that these smaller samples can be desorbed efficiently. Gas-liquid chromatography is recommended for analyzing the desorbed thiols; the proposed method allows the separation, detection, and quantitative determination of alkane thiols, aliphatic cyclic thiols, and aromatic thiols in mixtures and in the presence of other sulfur-containing derivatives.

(c) Medical Surveillance and Recordkeeping

Medical surveillance, including preplacement and periodic medical examinations, should be made available to all workers who are occupationally exposed to thiols. Because percutaneous absorption, inhalation, and ingestion of thiols have resulted in CNS depression, lesions in the liver, kidneys, spleen, and lungs, and irritation of skin, eye, or respiratory tract [12,59,62,66], special attention should be given to identifying by history and physical examination individuals with any preexisting disorders of these organs and systems. Newly hired, existing, or transferred employees should be informed about possible increased risk of health impairment as a result of workplace exposure to thiols. Blood tests, urinalyses, and other tests considered necessary by the attending physician should also be included. Periodic medical examinations should be made annually.

In an emergency involving eye contact with benzenethiol or mixtures of thiols that contain benzenethiol, the affected personnel shall be provided with immediate first aid, followed by prompt medical evaluation and care. 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 (see Appendix II).

Medical and other pertinent records for all employees exposed to thiols should be retained for at least 30 years after employment ends.

(d) Personal Protective Equipment and Clothing

Percutaneous absorption experiments [66,67] using butanethiol, octanethiol, dodecanethiol, or octadecanethiol have indicated no remarkable effects in mice, rabbits, rats, and guinea pigs. Instillation of propanethiol (0.1 ml in the conjunctival sac) in the eyes of rabbits caused severe irritation, heavy discharge, redness, and chemosis [59]. A similar experiment with benzenethiol (0.1 ml instilled in the conjunctival sac) caused severe irritation, corneal injury lasting 3-4 months, and depilation of skin around the eye socket by the resultant solution when the exposed eye was washed with water [59]. Therefore, care must be exercised to ensure adequate protection against eye contact with thiols, raw materials for their production, and sulfur-containing wastes. Personal protective

equipment, including eye protectors should be available and worn where exposure to liquid thiols is likely. Leather is not recommended for use in protective equipment and clothing against thiols. Splash-resistant clothing is preferred in most operations; however, ordinary clothing can be more easily cleaned and the odors of thiols removed by household bleach [82]. Work practices that prevent skin and eye contact must be followed. Showers and eyewash fountains must be available for immediate use if accidental contact occurs.

All employees assigned to areas where there may be occupational exposure to thiols should wear clean long-sleeved shirts, splash-resistant shoe and head coverings, and penetration-resistant gloves. Respirators may be needed by employees engaged in nonroutine maintenance or repair operations that require opening of usually closed systems. Employees working in posted areas should wear goggles with side guards to protect the eyes. Contaminated shoes and clothing should be removed immediately to prevent skin absorption. Clothing that cannot be decontaminated and contaminated leather should be discarded or destroyed to prevent reuse.

(e) Informing Employees of Hazards

At the beginning of employment where possible exposure to thiols exists, all employees must be informed of the hazards from such exposure and those to raw materials for their synthesis and sulfur-containing wastes. Brochures and pamphlets may be effective as aids in informing employees of hazards. In addition, signs warning of the danger of exposure must be posted in any work area where there is a likelihood of occupational exposure to these compounds.

A continuing education program is an important part of an industrial hygiene program for employees potentially exposed to hazardous materials such as thiols and related sulfur-containing materials. Such a continuing education program, which includes training in the use of protective equipment, emergency procedures, first aid, and information about the advantages of participation in the medical surveillance program, should be available to the employees. Qualified persons should periodically inform employees of possible sources of exposure to thiols, the adverse health effects possibly associated with such exposure, the engineering controls and work practices in use to limit exposure and those being planned, and the environmental monitoring and medical surveillance procedures used to check control procedures and to evaluate the health status of employees. Personnel potentially exposed to any of these thiols, raw materials, and sulfur-containing wastes associated with manufacturing, material handling, or uses must be warned of the adverse effects of accidental exposure and must be informed of the signs and symptoms that may occur. Employees should be warned that the onset of these symptoms may be delayed, particularly with exposures to higher molecular weight thiols [59]. Although thiols have a characteristic odor, employees should be informed that odor alone does not indicate the degree of protection required.

(f) Work Practices

The likelihood of exposure to thiols can best be reduced by implementing appropriate work practices. Since toxic effects from exposure to thiols have been produced by skin and eye contact [59,65,82] and inhalation [59], work practices must protect against exposure by these routes. The effects produced by exposure to thiols by inhalation, skin, and eye contact have been discussed in Sections (a) and (d) of this chapter.

Operations should be performed so as to minimize and prevent leaks of hazardous substances and to prevent spills during material handling, transfer, storage, and sampling. If thiols are handled or stored in intact, sealed containers, compliance with the recommended requirements contained in this chapter, except for Sections (e) and (f), should not be necessary. However, if intact, sealed containers are opened or damaged, then all requirements of the recommended standard should apply. For operations that may increase the concentration of airborne thiols in the work environment, adequate ventilation must be used at all times. In case of an accidental leak or spill, anyone entering the area should be protectively clothed to prevent accidental contacts with the skin or eyes and must wear appropriate respiratory protective devices if needed.

(g) Engineering Controls

Engineering controls must be used whenever possible to maintain concentrations of airborne thiols within the recommended environmental concentration limits. A closed system or local scrubber system should be used when any of the thiols is present. During the time required to install adequate controls and equipment, to make process changes, to perform routine maintenance operations, or to make emergency repairs, exposure to the thiols described can be minimized by the use of respirators and protective clothing. However, respirators should not be used as a substitute for engineering controls during routine operations. The employer should prepare contingency plans for nonroutine and cold-weather operations, process upset, and emergencies. Facilities for emergencies should be evaluated on a regular basis. Appropriate equipment and supplies should be available at proper locations to meet any unusual operating conditions and emergencies. All contingency plans should be prepared in writing, understood by operating personnel and managers, and updated as required.

(h) Monitoring and Recordkeeping Requirements

To ensure that workers are not exposed to thiols at concentrations that exceed the recommended environmental limit, concentrations in the workplace should be monitored at least annually and, if found to be necessary by an industrial hygiene survey, quarterly. If changes in production or

processes are likely to increase air concentrations, the workplace should be monitored within 10 days after these changes. If the concentration exceeds the recommended workplace environmental limit, personal monitoring should be performed at least weekly. Such monitoring should continue until two consecutive determinations, at least 1 week apart, show that workplace air levels no longer exceed the recommended ceiling limits. Quarterly monitoring should then be resumed. Records of environmental measurements should be retained for at least 30 years after employment ends.

VII. RESEARCH NEEDS

Sampling and analytical methods specific for individual thiols are needed to provide accurate and routine measurement of thiols in occupational environments. For protection of the workers, the areas of engineering controls and monitoring need to be developed. Definitive toxicologic investigations and epidemiologic studies are required for the evaluation of the potential occupational hazard of thiols.

Sampling and Analytical Studies

A perusal of the available literature and an assessment of the discussions held and observations made during plant visits have clearly shown a need for a continuous monitoring of the concentration of thiols in the workplace and on the personal sampling of air for thiols in the occupational environment. Area sampling for methanethiol has been extensively studied because of the prevalence of this thiol as a byproduct in the kraft paper industry, and several sampling kits [86-88,98,106] have been suggested. However, a suitable, uncomplicated sampling kit still needs to be developed for sampling other thiols. Additionally, a personal sampling device based on polymeric absorbents such as Chromosorb and cooling devices for such absorbent systems to increase collecting efficiency should also be developed. Analytical methods for the estimation of thiols, based on a number of physicochemical principles, have been described adequately in the scientific literature [84,95,97,103,136,137]. The separation, identification, and estimation of parts per billion quantities of thiols, by a number of gas chromatography procedures, also have been described [86,87,94,104-114]. With this available technical information, suitable analytical methods should be developed with the capability for adaptation to the routine analysis of samples obtained for occupational environment studies.

Epidemiologic Studies

A retrospective cohort or cross-sectional morbidity study of a population with occupational exposure to monofunctional organic thiols would provide valuable information. The former type of study would be possible if suitable medical and personnel records were available for workers employed either in thiol manufacturing plants or in the industrial plants using thiols for the production of synthetic rubber, plastics, agricultural chemicals, or other products. Such studies should be accompanied by industrial hygiene surveys and by appropriately timed analysis of the air in the workplace.

Long-Term Animal Exposure Studies

There is considerable information on the effects of short-term exposure to C_1-C_6 alkane thiols and benzenethiol in humans as well as in experimental animals [12-16,45,48,51,53,54,58-60, and WW Wannamaker III, written communication, December 1977]. Although there are similar data [53-55,58-60] for C_7-C_{18} alkane thiols, information on the long-term effects of these thiols is inadequate [51,58,59,61,62,64-67]. Studies on the effects of long-term exposure of experimental animals to thiols under occupational exposure conditions are needed. The inclusion of higher mammalian species and a greater emphasis on inhalation, dermal, and ocular routes of exposure would be most meaningful to human occupational exposure.

Carcinogenicity Studies

Microscopic examination of the epidermis and determinations of the levels of epidermal cholesterol and epidermal delta-7-cholestenol has shown, according to one report [67], that octadecanethiol when applied to mouse skin had effects similar to those of methylcholanthrene, a known carcinogen. However, similar effects were not found for octanethiol or dodecanethiol. A more elaborate and in-depth study of the carcinogenic potentials of monofunctional organic thiols, and especially of octadecanethiol, is indicated. Studies using two or more mammalian species for both the inhalation and the dermal routes of exposure should be conducted. The duration of exposure and the dosage of thiols should simulate as far as possible the conditions of occupational exposure.

Mutagenicity Studies

The results of a few studies [46,68,69] have indicated some mutagenic potential for methanethiol and dodecanethiol. Although the mutagenic effects have not been established unequivocally, these studies nevertheless point out the need to examine critically the mutagenic potential of n-alkane mono thiols. Such studies should include lower organisms and mammalian species and should consider the occupational environment when designing experimental conditions such as route, dose, and duration of exposure. The studies should also include specific locus tests, heritable translocations, multigeneration tests, and characterization of chromosomal lesions.

Teratogenic and Related Reproductive Effects

Information indicating teratogenic and related reproductive effects on any of the monofunctional organic thiols included in the recommended standard has not been found. Thus, a research effort is needed to evaluate this potential in different species.

Electroencephalographic Studies

Electroencephalographic (EEG) studies in volunteers should be conducted to determine whether significant stress may result from exposure to thiols. Concentrations of thiols required to significantly change the EEG pattern should be determined and compared with the odor threshold concentrations [16,45,48,50].

Skin Effects

The skin-sensitizing effects of butane-, octane-, dodecane-, hexadecane-, and octadecanethiols have been studied in guinea pigs and mice [66,67]. The data suggest correlation between the skin effect and the chain length of the higher molecular weight thiols (C_8-C_{18}). Although no skin effect was observed following exposure to butanethiol, dodecanethiol and octadecanethiol caused intense and moderate dermatitis, respectively, and caused definite delayed effects. These studies emphasize the need for a more thorough evaluation of the skin effects for all the thiols. Experiments using two or more mammalian species with a skin structure similar to that of humans would be valuable, and experimental conditions such as duration of exposure and dose should simulate occupational exposures.

Metabolic Studies

Studies on the influence of alkyl, cycloalkyl, and aryl groups on the rate and character of metabolic degradation of thiols may lead to the identification of unique products that might serve as marker metabolites for occupational and environmental monitoring of thiols.

Although enzymatic sulfhydryl-disulfide interchange is possible between SH-group-containing substances within the cell [74,77] leading to the formation of mixed sulfides, no information is available in this regard for monofunctional thiols. The effect of glutathione transferases on thiols and the effect of such reactions on the activities of proteins such as insulin [138,139] should be investigated.

Personal Protective Equipment

Thiols have obnoxious odors and are absorbed tenaciously into wearing apparel, especially apparel made of synthetic materials. Some of the thiols may cause skin sensitization. It is essential therefore to identify materials impervious to thiols for use in protective clothing, boots, gloves, and air-supplied hoods. Finally, better respirator sorbent materials must be identified for removing thiols from respirable air.

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