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HANDLING MERCAPTANS IN THE LABORATORY

Mercaptans are a class of organosulfur compounds characterized by the presence of one or more sulfhydryl (-SH) groups. The terms thiol, mercapto, and sulfhydryl are used interchangeably, with thiol being the preferred term for formal scientific communications, referring to the sulfur analog of the hydroxyl group characterizing alcohols. The term mercaptan will be used exclusively in the following discussion.

Odor

Mercaptans are characterized by their disagreeable odors at parts per million (ppm) and parts per billion (ppb) concentrations in air. Some odor threshold values are given in Table 1. Methyl mercaptan is a gas at room temperature and the other mercaptans are liquids. The C_1-C_6 alkyl mercaptans are characterized by high vapor pressure at ambient temperatures. Their boiling points range between 5.9EC and 152EC at 760 mm Hg. Some physical constants of mercaptans available from Atochem in commercial quantities are listed in Table 2. The C_1-C_6 alkyl mercaptans display a disagreeable odor at much lower concentrations than the higher mercaptans. Continuous exposure to mercaptans results in a progressive inability to detect their odors, thus the odor threshold will increase.

Solubility

Mercaptans, with the exception of methyl and ethyl, are quite insoluble in water, but soluble in bases to form alkali metal mercaptides (see Table 3). C_1-C_4 alkyl mercaptans can be readily extracted from water-immiscible solvents with aqueous alkali metal hydroxides. The solubility of higher molecular weight mercaptans drops off rapidly in aqueous alkali metal hydroxides.

Toxicity

Mercaptans exhibit a moderate level of toxicity. The acute toxicological properties of selected mercaptans are listed in Table 1. For detailed information, consult the appropriate Material Safety Data Sheets.

Odor-Control Techniques

During the past 30 years, Elf Atochem personnel have developed a number of odor-control techniques for handling mercaptans in the laboratory. Many of these techniques are no more difficult to apply than those required for handling a number of other chemicals frequently used in the laboratory.

The careful design and assembly of equipment is paramount to the control of mercaptan odors. Although careful planning reduces the chances for leaks developing in the system, it is important to be prepared to locate and stop small leaks promptly. It is recommended that a leak check be made prior to every run carried out under pressure in metal equipment with a mercaptan or hydrogen sulfide present.

A very effective method to obtain a leak-free system involves two steps:

1. Charge the system with nitrogen gas or other inert, nontoxic gas to a pressure at least as high as will be used in practice, and check for a drop in pressure with time on a suitable gauge. In some cases, it is advantageous to block off sections of the system to facilitate finding the leak. If any leaks are detected by using a foaming detergent solution, correct them and recheck.

2. Recharge the system with hydrogen sulfide gas. Since hydrogen sulfide is very toxic, it is good practice to charge the system in steps of increasing pressure, until it is certain that no large leaks are present. Any remaining small leaks can be located quickly by examining the system with lead acetate paper. Dilution of the hydrogen sulfide with nitrogen can also be considered.

The following discussion summarizes the techniques used to control odors in mercaptan reactions in the laboratory. All reactions must be carried out in a hood or, in the case of pressure reactions, in a closed-in area equipped with an efficient exhaust fan. In the laboratory, the two basic types of reactions used are batch and continuous. Batch-type reactions at atmospheric pressure are generally conducted in glass equipment. If no significant quantity of a volatile mercaptan is present, the reaction can be carried out in a hood equipped with a charcoal bed in the exhaust line to absorb the mercaptan. In reactions where appreciable quantities of a volatile mercaptan are present, a vent gas line can be connected to two caustic scrubbers in series, with an empty trap inserted between the reaction and scrubbers to avoid reverse flow of caustic into the reaction. Continuous-type reactions often include a continuous flow of volatile C_1 to C_4 mercaptans. In this case, the vented gases can be fed to an outside gas burner and stack for destruction of the odor by combustion.

RECOMMENDED EQUIPMENT AND MATERIALS

A listing and explanation of the equipment and materials found useful in the handling of mercaptans is as follows:

General Hints:

Always work in a hood. Use stoppered Erlenmeyer flasks, not beakers, for weighing. Measure by volume when possible to minimize escape of vapor. Cool the mercaptan to reduce vapor pressure before transferring. Wash spillage and used glassware immediately with Clorox**7** (5.25% sodium hypochlorite).

Hood:

A hood, equipped with a charcoal filter in the exhaust line, and a high linear air velocity (100 ft./min., minimum) is a must for mercaptan reactions carried out in glass and certain small-scale reactions with stainless-steel. In reactions where relatively small amounts of mercaptans can escape, the charcoal bed can absorb the mercaptans and prevent the escape of odor to the outside atmosphere. However, in reactions with hydrogen sulfide or lower molecular weight mercaptans, e.g., C_1-C_4 mercaptans, the quantity of effluent gases is directed to an outside gas burner to convert the odorous compounds to acceptable combustion products, including CO_2 and SO_2.

Caustic Scrubber:

A very familiar and successful method for containing the odors of mercaptan (primarily C_1 and C_6) in laboratory reactions and distillations is to connect the condenser vent to two caustic scrubbers in series with an empty trap between the system and the scrubbers to catch the caustic in the event of reverse flow. Gas bubblers fitted with sintered-glass dip tubes and charged with aqueous sodium hydroxide (5 to 20%) are commonly used. Frequently, a low flow of inert gas, e.g., nitrogen, is used to maintain a steady flow through the bubbler. Solubilities of mercaptans in NaOH are given in Table 3.

Clorox7:

Clorox does an excellent job of destroying the odor by converting the mercaptan predominantly to the corresponding sulfonic acid (sodium salt). A wash bottle with Clorox is very convenient for quickly eliminating or controlling the odor from small spills or when cleaning up glass equipment. A Clorox bath is also very useful. WARNING! Do not add Clorox to a large quantity of concentrated mercaptan, since a violent reaction may occur. Never use dry, powdered hypochlorite or other strong oxidizer for mercaptan spills, as autoignition can occur.

Lead Acetate:

A 30-40% aqueous solution of lead acetate trihydrate serves as an excellent leak detector for methyl and ethyl mercaptan as well as hydrogen sulfide. A wash bottle of lead acetate solution is used to moisten a piece of filter paper or paper towel which is then held close to (no contact) the suspected leak. With hydrogen sulfide the paper turns black and with the two mercaptans a yellow color is obtained (high sensitivity).

Plastic Bag:

A large plastic bag should be kept in the hood, to store any odorous waste materials. The plastic bags can then be sealed in fiber drums for disposal. Glass bottles containing mercaptans and other odorous compounds can also be packed in fiber drums for odor-containment and properly marked for disposal.

Disposal Gloves:

A box of disposable gloves should be available, and the gloves should be discarded (in plastic bag in hood) after each use. Disposable aprons or lab coats are recommended, since clothing contacted with mercaptan is often difficult to deodorize.

Special Tubing:

Types of tubing found useful with mercaptans include: Teflon**7**, TFE, FEP, and PFA, Bev-a-line (IV or V), and 316 stainless steel. Bev-a-line tubing has a polyethylene liner cross-linked to an ethylene vinyl acetate shell, a useful temperature range of -60E to +250EF, and is heat bondable. It is less expensive than TFE tubing and is convenient for flexible connections between glass and metal tubing lines. It is available from most laboratory supply houses. Copper and brass are unacceptable materials for handling mercaptans, because mercaptans are H_2S are highly corrosive to copper and brass. Care should be taken not to use valves and gauges with brass components.

Charcoal Filter Bed:

Activated charcoal adsorption units are made by installing a housing into the duct of the hood that will hold the filter assembly containing the carbon. Spare filter trays should be available to replace the charcoal when it is spent. The housing is, essentially, a metal box, with an access panel, through which the filter tray can be installed, and may either precede or follow the exhaust motor of the fume hood. The tray must allow free passage of air, and should be able to hold approximately 40 pounds or more of the adsorbent. This type of assembly is sufficient to handle the brief occasional discharge of odorous chemicals in low concentrations. For those laboratories needing to handle a continuous mercaptan discharge of high concentrations, a larger more effective type of filter unit must be installed. These filter assemblies consist of multiple trays packed with the activated carbon; in the form of a wall, and installed in a cabinet mounted out of the laboratory, through which the exhaust duct of the fume hood passes.

Gas Burner:

A typical flare would be installed outside at some distance from the process site, with the waste gases being conveyed to the flare in pipes, by the forces developed in the reactors. The waste-gas piping should have a sight-glass and a drip-leg in the lower portion of each riser to observe and collect condensed waste, with suitable valving for removal of said condensables when the level has reached the sight glass. The piping may be black iron rather than stainless steel, but then must be periodically inspected for leaks due to corrosion, and pressure-tested for blockages in the lines. The pipe size must be sufficient to prevent back-pressure in the waste-gas piping under normal operating conditions.

From the reactor site to the burner, no in-line valves are used. A flame-arrestor must be installed in the piping at the burner to prevent flashbacks to the reactor or laboratory. The flame-arrestor should be easily accessible for maintenance and periodic replacement of the arrestor element.

A natural-gas burner is installed in the base of the stack, just below the outlet the waste gas pipe. The natural-gas burner must be kept continuously burning while the reactors are in use. The waste gases will be forced into the flames as they are generated by the pressures in the reactor. To keep the burner in operation and supervise it, a flame detector, such as a Minneapolis-Honeywell "Protectoglo" electronic flame monitor, should be installed. This unit monitors ultra-violet emissions of the flame and, upon detecting a flame-out condition, shuts off the flow of natural gas to the burner and sounds an audible alarm, alerting the operating personnel. A remote start-device can be incorporated into this unit, so that when initiated, it will open the natural-gas solenoid valve, permitting flow of gas to the burner head, and energizing the ignition transformer and the spark-igniter, which then lights the burner head.

The stack of the burner should be at a site away from any air intakes and high enough to vent the combustion products away from air intakes. A stack turbine can be installed to permit sufficient air to enter the base of the stack and restrict air currents and water from entering the top of the stack.

With a little extra care and good housekeeping, mercaptans can be handled without creating odor problems. Make them part of your research plans. There's still a lot of good mercaptan chemistry to be discovered!

TABLE 1

ACUTE TOXICOLOGICAL PROPERTIES OF MERCAPTANS

Mercaptan	Odor Threshold ppm	IHL (a) LC_{50} ppm	ORL(b) LD_{50} (mg/kg)	DER (d) LD_{50} (mg/kg)
Methyl	0.011	675	--	--
Ethyl	0.00026	4420	682	> 2000
n-Propyl	0.0016	7300	1790	> 2000*
t-Butyl	0.0005	22,200	4729	>2000*
n-Butyl	0.001	4020	1500	> 2000
n-Hexyl	--	1080	1254	> 2000
n-Octyl	--	--	2000	> 2000
n-Dodecyl	--	--	5000	> 2000

(a) Inhalation - Rats exposed for four hours.
(b) Oral - Rats
(d) Dermal - Rats except where noted (*) when Rabbits were evaluated-occluded contact period: 24 hours.

TABLE 2

PHYSICAL CONSTANTS OF MERCAPTANS AVAILABLE IN COMMERCIAL QUANTITIES

Mercaptan	CAS Registry Number	Boiling Point EC (mm Hg)	Freezing Point EC	Density d^{20}_{4}
Methyl	74-93-1	5.9	-123.8	0.8665
Ethyl	75-08-1	35.0	-147.9	0.8391
n-Propyl	107-03-9	67.8	-113.1	0.8415
Iso Propyl	75-33-2	52.6	-130.5	0.8143
n-Butyl	109-79-5	98.4	-115.7	0.8416
t-Butyl	75-66-1	64.2	+1.1	0.8002
n-Hexyl	111-31-9	152.6	-80.5	0.8424
Cyclohexyl	1569-69-3	158.0	--	0.9782
n-Octyl	111-86-6	199.1	-49.2	0.8433
t-Nonyl	--	188-201 (a)	--	0.85 (b)
n-Dodecyl	112-55-0	142.5 (15)	-9.2	0.8450
t-Dodecyl	--	227-248 (a)	--	0.86 (b)

(a) Range - Initial boiling point to 95% distilled.

(b) Specific gravity - 15.5/15.5EC.

TABLE 3

SOLUBILITIES OF SOME MERCAPTANS IN WATER AND IN NaOH SOLUTION

(grams per liter)

Mercaptans	In Water	1N NaOH
Methyl	23.30	Very Soluble
Ethyl	6.76	Very Soluble
Propyl	1.96	Very Soluble
Butyl	0.56	Very Soluble
Amyl	0.164	328.0
Hexyl	0.047	94.0
Heptyl	0.0138	27.6
Octyl	0.0040	8.0
Nonyl	0.00115	2.3

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