OCCUPATIONAL SAFETY AND HEALTH GUIDELINE
FOR ACROLEIN

INTRODUCTION
This guideline summarizes pertinent information about acrolein for workers and employers as well as for physicians, industrial hygienists, and other occupational safety and health professionals who may need such information to conduct effective occupational safety and health programs. Recommendations may be superseded by new developments in these fields; readers are therefore advised to regard these recommendations as general guidelines and to determine periodically whether new information is available.

SUBSTANCE IDENTIFICATION

- Formula
  \[ C_3H_4O \]

- Structure
  \[ CH_2==CHCHO \]

- Synonyms
  Acraldehyde, acrylic aldehyde, acrylaldehyde, trans-acrolein, allyl aldehyde, propenal, 2-propenal, propylene aldehyde, ethylene aldehyde, Aqualine, Biocide, Crolein, Magnacide

- Identifiers
  1. CAS No.: 107-02-8
  2. RTECS No.: AS1050000
  3. DOT UN: 1092 30 (inhibited form)
  4. DOT labels: Flammable Liquid, Poison (for the inhibited form)

- Appearance and odor
  Acrolein is a clear, colorless to yellow, flammable liquid with a disagreeable, choking odor. The odor threshold is reported to be between 0.02 and 0.4 part per million (ppm) parts per air.

CHEMICAL AND PHYSICAL PROPERTIES

- Physical data
  1. Molecular weight: 56.1
  2. Boiling point (760 mm Hg): 52.5°C (126.5°F)
  3. Specific gravity (water = 1): 0.84 at 20°C (68°F)
  4. Vapor density (air = 1 at boiling point of acrolein): 1.94
  5. Melting point: -87.7°C (-159.9°F)
  6. Vapor pressure at 20°C (68°F): 210 mm Hg
  7. Solubility: Soluble in water, alcohol, ether, and acetone
  8. Evaporation rate: Data not available

- Reactivity
  1. Conditions contributing to instability: Heat, sparks, or open flame. The vapors of acrolein form explosive mixtures with air.
  2. Incompatibilities: Acrolein is very reactive and polymerizes rapidly and violently in the presence of strong acid or basic catalysts, light, heat, and volatile amines. Upon storage, it forms shock-sensitive and heat-sensitive explosive compounds. Fire and explosions may result from contact of acrolein with oxidizers, acids, alkalis, or ammonia.
  3. Hazardous decomposition products: Toxic gases and vapors, including peroxides and oxides of carbon, may be released in a fire involving acrolein.
  4. Special precautions: An inhibitor, usually hydroquinone, should be added to this highly unstable material to prevent self-polymerization.

- Flammability
  The National Fire Protection Association has assigned a flammability rating of 3 (severe fire hazard) to acrolein.
  1. Flash point: -26°C (-15°F) (closed cup)
  2. Autoignition temperature: 220°C (428°F)
  3. Flammable limits in air (% by volume): Lower, 2.8; upper, 31

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service  Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Standards Development and Technology Transfer

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

1992  Acrolein 1
4. Extinguishment: Use carbon dioxide, dry chemical, or alcohol foam to extinguish fires involving acrolein. Water may be ineffective, but it may be used to keep fire-exposed containers cool or to protect persons attempting to stop a leak involving this substance.

Fires involving acrolein should be fought upwind and from the maximum distance possible. Isolate the hazard area and deny access to unnecessary personnel. Emergency personnel should stay out of low areas and ventilate closed spaces before entering. Containers of acrolein may explode in the heat of the fire and should be moved from the fire area if it is possible to do so safely. If this is not possible, cool containers from the sides with water until well after the fire is out. Stay away from the ends of containers. Personnel should withdraw immediately if they hear a rising sound from a venting safety device or if a container becomes discolored as a result of fire. Dikes should be used to contain fire-control water for later disposal. Firefighters should wear a full set of protective clothing (including a self-contained breathing apparatus) when fighting fires involving acrolein. Chemical protective clothing specifically recommended for acrolein may not provide thermal protection unless so stated by the clothing manufacturer. Firefighters’ protective clothing may not provide protection against permeation by acrolein.

**EXPOSURE LIMITS**

- **OSHA PEL**
  
The current Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for acrolein is 0.1 ppm (0.25 mg/m³) as an 8-hr time-weighted average (TWA) concentration and 0.3 ppm (0.8 mg/m³) as a short-term exposure limit (STEL). A STEL is a 15-min TWA exposure that should not be exceeded at any time during a workday [29 CFR 1910.1000, Table Z-1-A].

- **NIOSH REL**
  
The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) of 0.1 ppm (0.25 mg/m³) as an 8-hr TWA and 0.3 ppm (0.8 mg/m³) as a STEL [NIOSH 1992].

- **ACGIH TLV**
  
The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned acrolein a threshold limit value (TLV) of 0.1 ppm (0.23 mg/m³) as a TWA for a normal 8-hr workday and a 40-hr workweek and a STEL of 0.3 ppm (0.69 mg/m³) for periods not to exceed 15 min [ACGIH 1991b].

- **Rationale for limits**
  
The limits are based on the risk of severe eye, nose, and respiratory irritation associated with exposure to acrolein.

**HEALTH HAZARD INFORMATION**

- **Routes of exposure**
  
Exposure to acrolein can occur through inhalation, ingestion, and eye or skin contact.

- **Summary of toxicology**
  
1. **Effects on Animals:** Acrolein is a severe irritant and corrosive to the eyes, skin, mucous membranes, and respiratory tract in animals. Eye contact with liquid acrolein has caused severe burns, corrosion, and corneal injury [Grant 1986; Proctor et al. 1988]. The dermal LD₅₀ in rabbits is 562 mg/kg [NIOSH 1991]. Skin contact can cause erythema, edema, severe irritation, corrosion, and burns [NIOSH 1991]. The mouse RD₅₀ (concentration that decreases respiratory rate by 50% in exposed animals) is 1.7 ppm [NLM 1992]. The 10-min, 30-min, and 8-hr LC₅₀ in rats are 375, 131, and 8 ppm, respectively [AIHA 1989]. Cats exposed for 3.5 hr to 10 ppm showed signs of respiratory irritation, mild narcosis, lacrimation, and salivation [ACGIH 1991a]. The oral LD₅₀ is 42 to 46 mg/kg in rats and 28 mg/kg in mice [AIHA 1989]. When swallowed, acrolein induces gastrointestinal distress, pulmonary congestion, and edema [NLM 1992]. Rats, guinea pigs, dogs, and monkeys were repeatedly exposed to 0.7 or 3.7 ppm for 8 hr/day, 5 days/week for 6 weeks. All animals exposed to 0.7 ppm developed inflammatory lung changes. Empysema was infrequently but more predominantly observed in dogs and monkeys than in rats or guinea pigs. Animals exposed to 3.7 ppm salivated and had ocular and respiratory irritation. Histopathology of survivors revealed nonspecific inflammatory changes in the lungs, liver, and kidneys. Squamous metaplasia of dog and monkey trachea and necrotizing bronchitis with squamous metaplasia of monkey lungs was also observed. In addition, these four species were continuously exposed to 0.21, 0.23, 1.0, or 1.8 ppm acrolein 24 hr/day for 90 days. Findings similar to those cited for the repeated exposure experiment were likewise observed, with the inflammatory changes also being noted in the brains of all acrolein-exposed animals [Lyon et al. 1970]. Male rats died (32 of 57) following exposures to 4 ppm for 6 hr/day, 5 days/week for 62 exposure days. Terminal histopathology revealed bronchiolar necrosis and pulmonary edema in treated animals [Proctor et al. 1988]. Intra-amniotic or intravenous administration of acrolein to pregnant rats induced malformations or embryolethality, respectively [NIOSH 1991]. Acrolein is mutagenic in bacterial test systems [NIOSH 1991]. Mice that were derrmally injected with acrolein for 24 weeks did not develop injection-site sarcomas during the ensuing 70-week observation period [NLM 1992]. Syrian golden hamsters inhaled 4 ppm for 7 hr/day, 5 days/week for 52 weeks. Additional groups were also administered benzo(a)pyrene or
N-nitrosodiethylamine. Following 29 weeks without exposure, terminal sacrifice in week 81 demonstrated that no increased tumor incidence had been induced by acrolein [NLM 1992].

2. Effects on Humans: Acrolein is a powerful lacrimating agent and severe tissue irritant. Eye contact with liquid acrolein can cause pain, intense lacrimation, blepharoconjunctivitis, swelling of the lids, purulent discharge, photophobia, and corneal injury [Grant 1986; Gosselin et al. 1984; NLM 1992]. Contact of the skin with liquid acrolein causes redness, edema, swelling, vesiculation, and burns. In addition, acrolein can be absorbed through the skin in sufficient amounts to cause systemic effects [Gosselin et al. 1984]. This chemical is a weak skin sensitizer in some exposed individuals [Proctor et al. 1988]. Exposure to 0.25 ppm for 5 min causes moderate irritation of the eyes, mucous membranes, and upper respiratory tract [Clayton and Clayton 1981; Grant 1986]. Exposure to a 1-ppm (2.3-mg/m³) concentration of acrolein vapor for the same interval is described as intolerable and causes intense lacrimation and severe eye, nose, and throat irritation [Clayton and Clayton 1981; Grant 1986]. Acrolein is a severe lung irritant and tear-inducer at 3 ppm (7 mg/m³) [IARC 1985]. At higher exposure levels, it can induce significant delayed-onset lung injury, including dyspnea, asthma, congestion, edema, and persistent respiratory insufficiency with decreased pulmonary function [NLM 1992]. Prolonged exposure to 21 ppm causes pulmonary edema, and fatalities have been reported at concentrations as low as 10 ppm; exposure to 150 ppm for 10 min is lethal to humans [Proctor et al. 1988].

- Signs and symptoms of exposure

1. Acute exposure: Acrolein can cause severe irritation or corrosion of the eyes, nose, throat, and lungs, with tearing, pain in the chest, and delayed-onset pulmonary injury with depressed pulmonary function. Contact of liquid acrolein with the eyes may cause corneal burns, corrosion, and blindness; skin contact may result in redness, swelling, chemical burns with blisters, and corrosion.

2. Chronic exposure: The signs and symptoms of chronic exposure to acrolein include skin sensitization and contact dermatitis.

- Emergency procedures

Keep unconscious victims warm and on their sides to avoid choking if vomiting occurs. Immediately initiate the following emergency procedures, continuing them as appropriate en route to the emergency medical facility:

1. Eye exposure: Tissue destruction and blindness may result from exposure to concentrated solutions, vapors, mists, or aerosols of acrolein! Immediately but gently flush the eyes with large amounts of water for at least 15 min, occasionally lifting the upper and lower eyelids.

2. Skin exposure: Severe burns, skin corrosion, and absorption of lethal amounts may result! Immediately remove all contaminated clothing! Immediately and gently wash skin for at least 15 min. Use soap and water if skin is intact; use only water if skin is not intact.

3. Inhalation exposure: If vapors, mists, or aerosols of acrolein are inhaled, move the victim to fresh air immediately.

If the victim is not breathing, clean any chemical contamination from victim's lips and perform cardiopulmonary resuscitation (CPR); if breathing is difficult, give oxygen.

4. Ingestion exposure: Take the following steps if acrolein or a solution containing it is ingested:

—Do not induce vomiting.

—Have the victim rinse the contaminated mouth cavity several times with a fluid such as water. Immediately after rinsing, have the victim drink one cup (8 oz) of fluid and no more.

—Do not permit the victim to drink milk or carbonated beverages!

—Do not permit the victim to drink any fluid if more than 60 min have passed since initial ingestion.

NOTE: These instructions must be followed exactly. Drinking a carbonated beverage or more than one cup of fluid could create enough pressure to perforate already damaged stomach tissue. The tissue-coating action of milk can sometimes impede medical assessment of tissue damage. Ingestion of any fluid more than 60 min after initial exposure could further weaken damaged tissue and result in perforation.

5. Rescue: Remove an incapacitated worker from further exposure and implement appropriate emergency procedures (e.g., those listed on the material safety data sheet required by OSHA’s hazard communication standard [29 CFR 1910.1200]). All workers should be familiar with emergency procedures and the location and proper use of emergency equipment.
EXPOSURE SOURCES AND CONTROL METHODS

The following operations may involve acrolein and may result in worker exposures to this substance:

—Use of acrolein as an intermediate in the production of glycerine and methionine analogs (poultry feed protein supplements)

—Manufacture of colloidal forms of metals, artificial resins, synthetic fibers, and polyurethane foams

—Chemical synthesis of 1,3,6-hexanetriol, glutaraldehydes, and acrylates

—Use of acrolein as a slimicide in the manufacture of paper

—Use of acrolein in biomedical applications to fix tissue and, with its polymers, to immobilize enzymes

—Subsurface injection of wastewaters to control the growth of microbes in feed lines and to control the growth of algae, aquatic weeds, and mollusks in recirculating process water systems

—Manufacture of pharmaceuticals, perfumes, and food supplements

—Use of acrolein as an alcohol denaturant

—Heating of oils and fats containing glycerol

—Use of acrolein as a liquid fuel

The following methods are effective in controlling worker exposures to acrolein, depending on the feasibility of implementation:

—Process enclosure

—Local exhaust ventilation

—General dilution ventilation

—Personal protective equipment

Good sources of information about control methods are as follows:


MEDICAL MONITORING

Workers who may be exposed to chemical hazards should be monitored in a systematic program of medical surveillance that is intended to prevent occupational injury and disease. The program should include education of employers and workers about work-related hazards, placement of workers in jobs that do not jeopardize their safety or health, early detection of adverse health effects, and referral of workers for diagnosis and treatment. The occurrence of disease or other work-related adverse health effects should prompt immediate evaluation of primary preventive measures (e.g., industrial hygiene monitoring, engineering controls, and personal protective equipment). A medical monitoring program is intended to supplement, not replace, such measures. To place workers effectively and to detect and control work-related health effects, medical evaluations should be performed (1) before job placement, (2) periodically during the term of employment, and (3) at the time of job transfer or termination.

• Preplacement medical evaluation

Before a worker is placed in a job with a potential for exposure to acrolein, a licensed health care professional should evaluate and document the worker's baseline health status with thorough medical, environmental, and occupational histories, a physical examination, and physiologic and laboratory tests appropriate for the anticipated occupational risks. These should concentrate on the function and integrity of the eyes, skin, and respiratory system. Medical monitoring for respiratory disease should be conducted using the principles and methods recommended by the American Thoracic Society [ATS 1987].

A preplacement medical evaluation is recommended to assess an individual’s suitability for employment at a specific job and to detect and assess medical conditions that may be aggravated or may result in increased risk when a worker is exposed to acrolein at or below the prescribed exposure limit. The health care professional should consider the probable frequency, intensity, and duration of exposure as well as the nature and degree of any applicable medical condition. Such conditions (which should not be regarded as absolute contraindications to job placement) include a history and
other findings consistent with eye, skin, or respiratory disease.

- **Periodic medical examinations and biological monitoring**

Occupational health interviews and physical examinations should be performed at regular intervals during the employment period, as mandated by any applicable Federal, State, or local standard. Where no standard exists and the hazard is minimal, evaluations should be conducted every 3 to 5 years or as frequently as recommended by an experienced occupational health physician. Additional examinations may be necessary if a worker develops symptoms attributable to acrolein exposure. The interviews, examinations, and medical screening tests should focus on identifying the adverse effects of acrolein on the eyes, skin, and respiratory system. Current health status should be compared with the baseline health status of the individual worker or with expected values for a suitable reference population.

Biological monitoring involves sampling and analyzing body tissues or fluids to provide an index of exposure to a toxic substance or metabolite. No biological monitoring test acceptable for routine use has yet been developed for acrolein.

- **Medical examinations recommended at the time of job transfer or termination**

The medical, environmental, and occupational history interviews, the physical examination, and selected physiologic or laboratory tests that were conducted at the time of job placement should be repeated at the time of job transfer or termination. Any changes in the worker’s health status should be compared with those expected for a suitable reference population.

**WORKPLACE MONITORING AND MEASUREMENT**

A worker’s exposure to airborne acrolein is determined by using a solid sorbent sampling tube containing 2-(hydroxymethyl)piperidine on XAD-2 adsorbent. Samples are collected at a maximum flow rate of 0.1 liter/min until a maximum air volume of 48 liters is collected. The sample is then treated with toluene to extract the acrolein. Analysis is conducted by gas chromatography using a nitrogen-phosphorus detector. This method has a sampling and analytical error of 0.12 and is sufficiently sensitive for full-shift personal monitoring below the PEL of 0.1 ppm. For STEL measurements, the limit of the method is 0.8 ppm for a 15-min sample. This method is included in the OSHA Computerized Information System [OSHA 1989] and in Method 52 of the OSHA Analytical Methods Manual [OSHA 1985]. A similar method (Method 2501) can be found in the NIOSH Manual of Analytical Methods [NIOSH 1984].

**PERSONAL HYGIENE**

If acrolein contacts the skin, workers should immediately wash the affected areas with soap and water.

Clothing contaminated with acrolein should be removed immediately, and provisions should be made for safely removing this chemical from these articles. Persons laundering contaminated clothing should be informed about the hazardous properties of acrolein, particularly its potential to cause severe irritation of the eyes and skin.

A worker who handles acrolein should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, or using toilet facilities.

Workers should not eat, drink, or use tobacco products in areas where acrolein or a solution containing acrolein is handled, processed, or stored.

**STORAGE**

Acrolein should be stored in a cool, dry, well-ventilated area in tightly sealed containers that are labeled in accordance with OSHA’s hazard communication standard [29 CFR 1910.1200]. Outside or detached storage is preferred. Acrolein must be stored under a nitrogen blanket. Uninhibited acrolein may not be stored, and the level of the inhibitor must be checked regularly during prolonged storage. The storage area should be equipped with an automatic sprinkler or other extinguishing system. All electrical service in the storage area must be of explosionproof design. Containers of acrolein should be protected from physical damage and should be stored separately from alkaline materials (such as caustics, ammonia, or amines), oxidizers, heat, sparks, and open flame. To prevent static sparks, containers and equipment should be grounded and bonded when transferring liquid acrolein. Because empty containers formerly containing acrolein may still hold product residues, they should be handled appropriately.

**SPILLS AND LEAKS**

In the event of a spill or leak involving acrolein, persons not wearing protective equipment and clothing should be restricted from contaminated areas until cleanup is complete. The following steps should be undertaken following a spill or leak:

1. Do not touch the spilled material; stop the leak if it is possible to do so without risk.
2. Notify safety personnel.
3. Remove all sources of heat and ignition.
4. Provide maximum explosionproof ventilation.
5. If feasible, remove leaking containers to a safe place.
6. Absorb small liquid spills with sand, vermiculite, or other noncombustible absorbent material and place the material in a covered container for later disposal.
7. For large liquid spills, build dikes far ahead of the spill to contain the acrolein for later reclamation or disposal, or absorb with vermiculite or sand.
8. After cleanup, the spill area should be washed thoroughly with soap and water.

SPECIAL REQUIREMENTS

U.S. Environmental Protection Agency (EPA) requirements for emergency planning, reportable quantities of hazardous releases, community right-to-know, and hazardous waste management may change over time. Users are therefore advised to determine periodically whether new information is available.

- Emergency planning requirements

If 500 lb or more of acrolein is present at a facility, the owner or operator must comply with EPA's emergency planning requirements [40 CFR 355.30].

- Reportable quantity requirements for hazardous releases

A hazardous substance release is defined by EPA as any spilling, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, or disposing of hazardous substances into the environment (including the abandonment or discarding of contaminated containers). In the event of a release that is equal to or greater than the reportable quantity for that chemical, employers are required by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [40 CFR 355.40] to notify the proper Federal, State, and local authorities.

The reportable quantity for acrolein is 1 lb. If an amount equal to or greater than this quantity is released within a 24-hr period in a manner that will expose persons outside the facility, employers are required to do the following:

—Notify the National Response Center immediately at (800) 424–8802 or at (202) 426–2675 in Washington, D.C. [40 CFR 302.6].

—Notify the emergency response commission of the State likely to be affected by the release [40 CFR 355.40].

—Notify the community emergency coordinator of the local emergency planning committee (or relevant local emergency response personnel) of any area likely to be affected by the release [40 CFR 355.40].

- Community right-to-know requirements

Employers who own or operate facilities in SIC codes 20 to 39, who employ 10 or more workers, and who manufacture 25,000 lb or more or otherwise use 10,000 lb or more of acrolein per calendar year are required by EPA [49 CFR 372.30] to submit a Toxic Chemical Release Inventory Form (Form R) to EPA reporting the amount of acrolein emitted or released from their facility annually.

- Hazardous waste management requirements

EPA considers a waste to be hazardous if it exhibits any of the following characteristics: ignitability, corrosivity, reactivity, or toxicity as defined in 40 CFR 261.21–261.24. Acrolein is listed as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) [40 USC 6901 et seq.] and has been assigned EPA Hazardous Waste No. P003. This substance has been banned from land disposal and may be treated by fuel substitution or incineration. Acrolein also may be disposed of in an organometallic or organic lab pack that meets the requirements of 40 CFR 264.316 or 265.316.

Providing detailed information about the removal and disposal of specific chemicals is beyond the scope of this guideline. The U.S. Department of Transportation, EPA, and State and local regulations should be followed to ensure that removal, transport, and disposal of this substance are conducted in accordance with existing regulations. To be certain that chemical waste disposal meets EPA regulatory requirements, employers should address any questions to the RCRA hotline at (800) 424–9346 or at (202) 382–3000 in Washington, D.C. In addition, relevant State and local authorities should be contacted for information about their requirements for waste removal and disposal.

RESPIRATORY PROTECTION

- Conditions for respirator use

Good industrial hygiene practice requires that engineering controls be used where feasible to reduce workplace concentrations of hazardous materials to the prescribed exposure limit. However, some situations may require the use of respirators to control exposure. Respirators must be worn if the ambient concentration of acrolein exceeds prescribed exposure limits. Respirators may be used (1) before engineering controls have been installed, (2) during work operations such as maintenance or repair activities that
involve unknown exposures, (3) during operations that require entry into tanks or closed vessels, and (4) during emergencies. Workers should use only respirators that have been approved by NIOSH and the Mine Safety and Health Administration (MSHA).

- Respiratory protection program

Employers should institute a complete respiratory protection program that, at a minimum, complies with the requirements of OSHA’s respiratory protection standard [29 CFR 1910.134]. Such a program must include respirator selection, an evaluation of the worker’s ability to perform the work while wearing a respirator, the regular training of personnel, fit testing, periodic workplace monitoring, and regular respirator maintenance, inspection, and cleaning. The implementation of an adequate respiratory protection program (including selection of the correct respirator) requires that a knowledgeable person be in charge of the program and that the program be evaluated regularly. For additional information on the selection and use of respirators and on the medical screening of respirator users, consult the NIOSH Respirator Decision Logic [NIOSH 1987b] and the NIOSH Guide to Industrial Respiratory Protection [NIOSH 1987a].

PERSONAL PROTECTIVE EQUIPMENT

Protective clothing should be worn to prevent skin contact with acrolein. Impervious clothing, gloves, boots, and other protective clothing are recommended when handling this substance. Chemical protective clothing should be selected on the basis of available performance data, manufacturers’ recommendations, and evaluation of the clothing under actual conditions of use. The only material that has been tested against permeation by acrolein and has demonstrated good-to-excellent resistance for longer than 8 hr is butyl rubber. Natural rubber, neoprene, nitrile, polyvinyl alcohol, polyvinyl chloride, Teflon®, and Viton® have demonstrated poor resistance to permeation by acrolein.

If acrolein is dissolved in water or an organic solvent, the permeation properties of both the solvent and the mixture must be considered when selecting personal protective equipment and clothing.

Safety glasses, goggles, or face shields should be worn during operations in which acrolein might contact the eyes (e.g., through splashes of solution). Eyewash fountains and emergency showers should be available within the immediate work area whenever the potential exists for eye or skin contact with acrolein. Contact lenses should not be worn if the potential exists for acrolein exposure.

REFERENCES CITED


