Occupational Health Guideline for Nitric Acid

INTRODUCTION
This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION
• Formula: HNO₃
• Synonyms: Aqua fortis; white fuming nitric acid (WFNA); red fuming nitric acid (RFNA); hydrogen nitrate
• Appearance and odor: Colorless, yellow, or red fuming liquid with a suffocating, acrid odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)
The current OSHA standard for nitric acid is 2 parts of nitric acid per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 5 milligrams of nitric acid per cubic meter of air (mg/m³). NIOSH has recommended a permissible exposure limit of 2 ppm averaged over a work shift of up to ten hours per day, forty hours per week. The NIOSH Criteria Document for Nitric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION
• Routes of exposure
Nitric acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.
• Effects of overexposure
  1. Short-term Exposure: Nitric acid vapor or mist is an irritant of the eyes, nose, throat, and skin. Liquid nitric acid or high concentrations of nitric acid vapor may cause severe burns of the eyes with permanent damage. Liquid nitric acid or high concentrations of nitric acid vapor may produce skin burns and ulcers. Nitric acid may stain the skin a bright yellow. Exposure to high concentrations of nitric acid vapor may cause severe breathing difficulties which may be delayed in onset and may also cause pneumonia. Swallowing nitric acid may cause burns of the mouth, throat, and stomach.
  2. Long-term Exposure: Repeated or prolonged exposure to nitric acid mists or strong concentrations of nitric acid vapors may cause erosion of the exposed teeth.
  3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nitric acid.
• Recommended medical surveillance
The following medical procedures should be made available to each employee who is exposed to nitric acid at potentially hazardous levels:
  1. Initial Medical Examination:
     — A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes, respiratory tract, skin, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.
     — 14" x 17" chest roentgenogram: Nitric acid causes human lung damage. Surveillance of the lungs is indicated.
     — FVC and FEV (1 sec): Nitric acid is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.
     — Eye disease: Nitric acid is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.
     — Skin disease: Weak nitric acid is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.
2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis or at some other frequency to be determined by the responsible physician.

• Summary of Toxicology

Nitric acid vapor or mist is an irritant of the eyes, mucous membranes, and skin. When nitric acid is exposed to air or comes in contact with organic matter, it decomposes to yield a mixture of toxic oxides of nitrogen, including nitric oxide and nitrogen dioxide. Exposure to high concentrations of nitric acid vapor or mist causes pneumonitis and pulmonary edema which may be fatal; onset of symptoms may be delayed for 4 to 30 hours. In contact with the eyes, the liquid produces severe burns which may result in permanent damage and visual impairment. On the skin, the liquid or concentrated vapor produces immediate, severe and penetrating burns; concentrated solutions cause deep ulcers and stain the skin a bright yellow or yellowish-brown color. The vapor and mist may erode the exposed teeth. Ingestion of the liquid will cause immediate pain and burns of the mouth, esophagus, and gastrointestinal tract.

CHEMICAL AND PHYSICAL PROPERTIES

• Physical data
  1. Molecular weight: 63 (solute)
  2. Boiling point (760 mm Hg): 121.6 C (251 F) (for “constant boiling,” 68%); 84 C (183 F) (white fuming nitric acid); 60 C (140 F) (red fuming nitric acid)
  3. Specific gravity (water = 1): 1.41 (constant boiling); 1.5 (white fuming); 1.55 (red fuming)
  4. Vapor density (air = 1 at boiling point of nitric acid): 2 – 3 approximately
  5. Melting point: -41 C (-42 F) (for “constant boiling,” 68%); -41.6 C (-43 F) (white fuming); -52 C (-61 F) (red fuming)
  6. Vapor pressure at 20 C (68 F): 2.9 mm Hg (HNO3) (constant boiling); 2.6 mm Hg (H2O) (constant boiling); 62 mm Hg (white fuming); 103 mm Hg (red fuming)
  7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
  8. Evaporation rate (butyl acetate = 1): Data not available

• Reactivity
  1. Conditions contributing to instability: Elevated temperatures may cause containers to burst and liberate toxic oxides of nitrogen.
  2. Incompatibilities: Reacts explosively with combustible organic or readily oxidizable materials such as wood, turpentine, metal powders, hydrogen sulfide, etc. Contact with strong bases may cause violent spattering.
  3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of nitrogen) may be released when nitric acid decomposes.
  4. Special precautions: Nitric acid will attack some forms of plastics, rubber, and coatings.

• Flammability
  1. Not combustible, but is a strong oxidizer.

• Warning properties
  1. Odor Threshold: No quantitative information is available concerning the odor threshold of nitric acid.
  2. Eye Irritation Level: The AIHA Hygienic Guide, concerning eye contact with nitric acid, states that “nitric acid produces very severe immediate damage which may result in permanent damage and visual impairment.”
  3. Other Information: The AIHA Hygienic Guide notes that “nitrous fumes,” expressed in terms of nitrogen dioxide, may cause immediate irritation of the throat at concentrations as low as 62 ppm.”

4. Evaluation of Warning Properties: Patty points out that “nitric acid manufacture is more hazardous than hydrochloric acid manufacture in that . . . the oxides of nitrogen have inadequate warning properties in low, toxic concentrations.” For the purposes of this guideline, nitric acid is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• General

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee’s breathing zone (air that would most nearly represent that inhaled by the employee).

• Method

Nitric acid may be measured by collection of nitric acid in a midget impinger, followed by ultraviolet spectrophotometric analysis. An analytical method for nitric acid is in the NIOSH Manual of Analytical Methods. 2nd

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

**PERSONAL PROTECTIVE EQUIPMENT**

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nitric acid or liquids containing nitric acids having a pH equal to or less than 2.5.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing nitric acid having a pH greater than 2.5.

• Clothing contaminated with nitric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of nitric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nitric acid, the person performing the operation should be informed of nitric acid’s hazardous properties.

• Where there is any possibility of exposure of an employee’s body to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with nitric acid should be removed immediately and not reworn until the nitric acid is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nitric acid or solutions containing nitric acid contacting the eyes.

• Where there is any possibility that employees’ eyes may be exposed to liquid nitric acid or solutions containing nitric acid having a pH equal to or less than 2.5, an eye-wash fountain should be provided within the immediate work area for emergency use.

**SANITATION**

• Skin that becomes contaminated with nitric acid should be immediately washed or showered to remove any nitric acid.

**COMMON OPERATIONS AND CONTROLS**

The following list includes some common operations in which exposure to nitric acid may occur and control methods which may be effective in each case:

<table>
<thead>
<tr>
<th>Operation</th>
<th>Controls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use in metallurgy as a pickling agent; in metal refining, ore recovery,</td>
<td>Local exhaust ventilation; general dilution ventilation;</td>
</tr>
<tr>
<td>metal etching, and photoengraving</td>
<td>personal protective equipment</td>
</tr>
<tr>
<td>Use in acidulation of phosphate rock and manufacture of nitrogen solutions</td>
<td>Local exhaust ventilation; general dilution ventilation;</td>
</tr>
<tr>
<td>for use in fertilizer industry</td>
<td>personal protective equipment</td>
</tr>
<tr>
<td>Use as a laboratory reagent; in wood pulping industry</td>
<td>Process enclosure;</td>
</tr>
<tr>
<td></td>
<td>local exhaust ventilation;</td>
</tr>
<tr>
<td></td>
<td>general dilution ventilation;</td>
</tr>
<tr>
<td></td>
<td>personal protective equipment</td>
</tr>
<tr>
<td>Use during inorganic synthesis in manufacture of fertilizers, explosives,</td>
<td>Process enclosure;</td>
</tr>
<tr>
<td>herbicides, antibiotics, meat-curing, pickling, ceramics, and</td>
<td>local exhaust ventilation;</td>
</tr>
<tr>
<td>pharmaceuticals</td>
<td>general dilution ventilation;</td>
</tr>
<tr>
<td></td>
<td>personal protective equipment</td>
</tr>
<tr>
<td>Use during organic synthesis in manufacture of nitrating and oxidizing</td>
<td>Process enclosure;</td>
</tr>
<tr>
<td>agents, nylons, foams, lubricants, insecticides, dyes, explosives,</td>
<td>local exhaust ventilation;</td>
</tr>
<tr>
<td>photographic films, lacquers, and celluloids</td>
<td>general dilution ventilation;</td>
</tr>
<tr>
<td></td>
<td>personal protective equipment</td>
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</tbody>
</table>

**EMERGENCY FIRST AID PROCEDURES**

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**
  If nitric acid or strong concentrations of nitric acid vapors get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**
  If nitric acid or strong concentrations of nitric acid vapors get on the skin, immediately flush the contaminated skin with water. If nitric acid soaks through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**
  If a person breathes in large amounts of nitric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration.
Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Swallowing
When nitric acid has been swallowed and the person is conscious, give the person large quantities of water immediately to dilute the nitric acid. Do not attempt to make the exposed person vomit. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue
Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If nitric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Flush with copious quantities of water and neutralize with alkaline material (such as soda ash, lime, etc.).

• Waste disposal method:
Nitric acid may be disposed of by neutralizing with water and alkaline material (such as soda ash, lime, etc.) and disposing in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Nitric Acid," Documentation of the Threshold Limit Values for Substances in Workroom Air (3rd ed., 2nd printing), Cincinnati, 1974.


# Respiratory Protection for Nitric Acid

<table>
<thead>
<tr>
<th>Condition</th>
<th>Minimum Respiratory Protection* Required Above 5 mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particulate or Vapor Concentration</strong></td>
<td></td>
</tr>
<tr>
<td>250 mg/m³ or less</td>
<td>A chemical cartridge respirator with a full facepiece providing protection against nitric acid.**</td>
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<tr>
<td></td>
<td>A gas mask with a chin-style or a front- or back-mounted organic vapor canister providing protection against nitric acid.</td>
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<tr>
<td></td>
<td>Any supplied-air respirator with a full facepiece, helmet, or hood.</td>
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<tr>
<td></td>
<td>Any self-contained breathing apparatus with a full facepiece.</td>
</tr>
<tr>
<td></td>
<td>A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.</td>
</tr>
<tr>
<td>Greater than 250 mg/m³*** or entry and escape from unknown concentrations</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
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<tr>
<td></td>
<td>A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.</td>
</tr>
<tr>
<td>Fire Fighting</td>
<td>Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.</td>
</tr>
<tr>
<td>Escape</td>
<td>Any gas mask containing non-oxidizable sorbents and providing protection against nitric acid.</td>
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<tr>
<td></td>
<td>Any escape self-contained breathing apparatus.</td>
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</tbody>
</table>

*Only NIOSH-approved or MSHA-approved equipment should be used.

**Nitric acid is an oxidizer and should not come in contact with oxidizable materials. Some cartridges and canisters may contain oxidizable materials, such as activated charcoal, and therefore and should not be used to provide protection against nitric acid. Only non-oxidizable sorbents are allowed.

***Use of supplied-air suits may be necessary to prevent skin contact while providing respiratory protection from airborne concentrations of nitric acid; however, this equipment should be selected, used, and maintained under the immediate supervision of trained personnel. Where supplied-air suits are used above a concentration of 250 mg/m³, an auxiliary self-contained breathing apparatus operated in positive pressure mode should also be worn.