Spotlight on Nitric Acid

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Several thousand different chemicals are used in chemical laboratories and process operations throughout the DOE complex. One used in large quantities is nitric acid. This article spotlights nitric acid as a hazardous chemical whose storage and use must be carefully controlled in order to protect worker safety.

Nitric acid is a transparent colorless, or yellowish to light brown liquid. It is both corrosive and toxic. It can cause severe eye and skin burns, and may be harmful if inhaled. Upon exposure to light or elevated temperatures, nitric acid decomposes, and may become yellow to reddish in color due to the release of nitrogen dioxide.

Nitrogen dioxide is itself a hazardous substance. At temperatures above 21◦C (70◦F) it is a reddish brown gas with a pungent odor whose inhalation, in even moderate exposures, can lead to burning nose and throat, and pulmonary edema.

The American Conference of Governmental Industrial Hygienists recommends that worker exposures to airborne concentrations of nitric acid and nitrogen dioxide not exceed 2ppm and 3ppm, respectively, during the workday.

Neither nitric acid nor nitrogen dioxide is combustible. However, nitric acid is a strong oxidizer that reacts vigorously with combustibles and readily oxidizable materials, organic solvents, metal powders, carbides, cyanides, sulfides, and alkalies. Contact of concentrated nitric acid with combustible materials may increase the hazard from fire or may lead to an explosion. Nitrogen dioxide is also incompatible with combustible materials because it accelerates burning.

Nitric acid is usually shipped in glass bottles and carboys or special metal drums. It may be transported in tanks on trucks, rail cars, or barges. It should be stored in cool, dry, well-ventilated locations separate from alkalies, metals, organics, and other oxidizing materials.

At DOE facilities, nitric acid is usually used as an aqueous liquid solution, often at concentrations of about 50%. Such aqueous solutions have saturated vapor pressures significantly lower than that of their anhydrous counterpart. Spills of aqueous nitric acid form slowly evaporating pools and present a significant hazard only if either large quantities are present or a spray or an aerosol is present in the air.

Hazard Profiles for Nitric Acid and Nitrogen Dioxide

Chemical	Description	Hazards	OSHA PSM/ EPA RMP Threshold Quantities (lbs)	Exposure Limits ACGIH/ NIOSH/OSHA (ppm, mg/m^3)	ERPG-1/ ERPG-2/ ERPG-3	Properties	Incompatibilities and Reactivities	NFPA Rating N_H, N_F, N_R
Nitric acid (HNO_3) Synonyms*: aqua fortis, engraver's acid, azoic acid (CAS 7697-37-2)	Transparent colorless, yellowish, or light brown fuming, hygroscopic, liquid with an acrid, suffocating odor. Fuming nitric acid is concentrated nitric acid in which nitrogen dioxide is dissolved. It is reddish in color.	Toxic by inhalation. Affects eyes, skin, teeth, respiratory system. Corrosive to skin and mucous membranes. Causes severe eye and skin burns. Corrosive. Attacks almost all metals. Noncombustible, but increases the flammability of combustible materials. Fire risk in contact with organic materials.	OSHA: 500 lbs (≥ 94.5% by weight) EPA: 15,000 lbs (conc ≥ 80%)	ACGIH: TWA 2 ppm 5.2 mg/m^3 ACGIH: STEL 4 ppm 10 mg/m^3 NIOSH: TWA 2 ppm 5 mg/m^3 NIOSH: STEL 4 ppm 10 mg/m^3 OSHA: TWA 2 ppm 5 mg/m^3	not available	Boiling point = 78◦C (172◦F). Freezing/melting point = -42◦C (-44◦F). Strong oxidizing agent. Soluble in water. Decomposes in alcohol. Decomposes at boiling.	Incompatible with combustible materials, metal powders, hydrogen sulfide, carbides, alcohols. Reacts vigorously with organic solvents, cyanides, sulfides, and alkalies. Reacts with water to produce heat. Attacks almost all metals.	3, 0, 0 3, 0, 1 fuming
Nitrogen Dioxide (NO_2) (CAS 10102-44-0)	**Gas:** Reddish brown with a pungent odor. **Liquid:** Yellowish-brown below 21◦C (70◦F).	Toxic by inhalation. May be fatal if inhaled. Affects nose, throat, respiratory system. Corrosive to mucous membranes. Moderate exposure may cause	OSHA: 250 lbs EPA: none	ACGIH: TWA 3 ppm 5.6 mg/m^3 ACGIH: STEL 5 ppm 9.4 mg/m^3 NIOSH: STEL 1 ppm 1.8 mg/m^3	not available	Boiling point = 21◦C (70◦F). Freezing/melting point = -9◦C (15◦F).	Incompatible with combustible materials, chlorinated hydrocarbons, carbon disulfide, and ammonia. Reacts strongly with reducing materials/agents.	3, 0, 0

		pulmonary edema. Noncombustible, but accelerates the burning of combustible materials.					Reacts with water to form nitric acid.	

White fuming nitric acid contains > 97.5% nitric acid, < 2% water, and < 0.5% NO_x. Red fuming nitric acid contains > 85% acid, < 5% water, and 6-15% NO_x.

References

Fire Protection Guide to Hazardous Materials, 10th Edition, National Fire Protection Association, Quincy, MA, 1991.

Brethrick, L., *Brethrick's Handbook of Reactive Chemicals*, 4th Edition, Butterworth & Co., Ltd., London, 1990.

NIOSH Pocket Guide to Chemical Hazards, National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, Public Health Service, U.S. Department of Health and Human Services, 1994.

1996 TLVs® and BEIs®: Threshold Limit Values for Chemical Substances and Physical Agents; Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, 1996.

Lewis, Richard J., Jr., *Hawley's Condensed Chemical Dictionary*, 12th Edition, Van Nostrand Reinhold Company, New York, 1993.

The AIHA 1998 Emergency Response Planning Guidelines and Workplace Environmental Exposure Level Guidelines Handbook, American Industrial Hygiene Association, Fairfax, Virginia, 1998.

Acronyms and Abbreviations

ACGIH - American Conference of Governmental Industrial Hygienists
AIHA - American Industrial Hygiene Association
◦C - degrees centigrade (Celsius)
Ceiling - The maximum allowable human exposure limit for an airborne substance (NIOSH/OSHA). The ceiling value should/must not be exceeded during any part of the workday.
CAS - Chemical Abstracts Service (registry number)
CFR - Code of Federal Regulations
conc - concentration
EPA - Environmental Protection Agency
ERPG - Emergency Response Planning Guideline (AIHA), chemical concentration in air designed to assist in the development of emergency response strategies
ERPG-1 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly defined objectionable odor.
ERPG-2 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to take protective action.
ERPG-3 - The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.
◦F - degrees Fahrenheit
lbs - pounds
mg - milligram
mg/m^3 - milligrams per cubic meter
NFPA - National Fire Protection Association
N_H - NFPA 704, hazard rating for health
N_F - NFPA 704, hazard rating for fire
N_R - NFPA 704, hazard rating for reactivity
NIOSH - National Institute of Occupational Safety and Health
OSHA - Occupational Safety and Health Administration
PEL - Permissible exposure limit (OSHA), a time-weighted average (TWA) chemical concentration in air that must not be exceeded during any 8-hour work shift of a 40-hour workweek
ppm - parts per million
PSM - Process safety management (OSHA), regulation that contains requirements for management of hazards

associated with processes using highly hazardous chemicals to prevent or minimize the consequences of chemical accidents, promulgated as 29 CFR 1910.119, "Process Safety Management of Highly Hazardous Chemicals"

REL - Recommended exposure limit (NIOSH), a time-weighted average (TWA) chemical concentration in air for up to a 10-hour workday during a 40-hour workweek

RMP - Risk management program, (EPA), regulation to prevent accidental releases of regulated substances and reduce the severity of releases that occur, promulgated as 40 CFR Part 68, "Accidental Release Prevention Requirements: Risk Management Programs Under the Clean Air Act, Section 112(r)(7)"

STEL - Short-term exposure limit (NIOSH/OSHA), a 15-minute TWA chemical exposure concentration in air that should not be exceeded at any time during a workday

TQ - Threshold quantity, (OSHA/EPA), the amount of a listed substance necessary to be covered by either PSM (29 CFR 1910.119) or RMP (40 CFR Part 68)

TLV - Threshold limit value (ACGIH), occupational exposure limit recommended by the ACGIH

TWA - Time-weighted average, the most frequently used exposure guideline term, representing the average concentration over a workday