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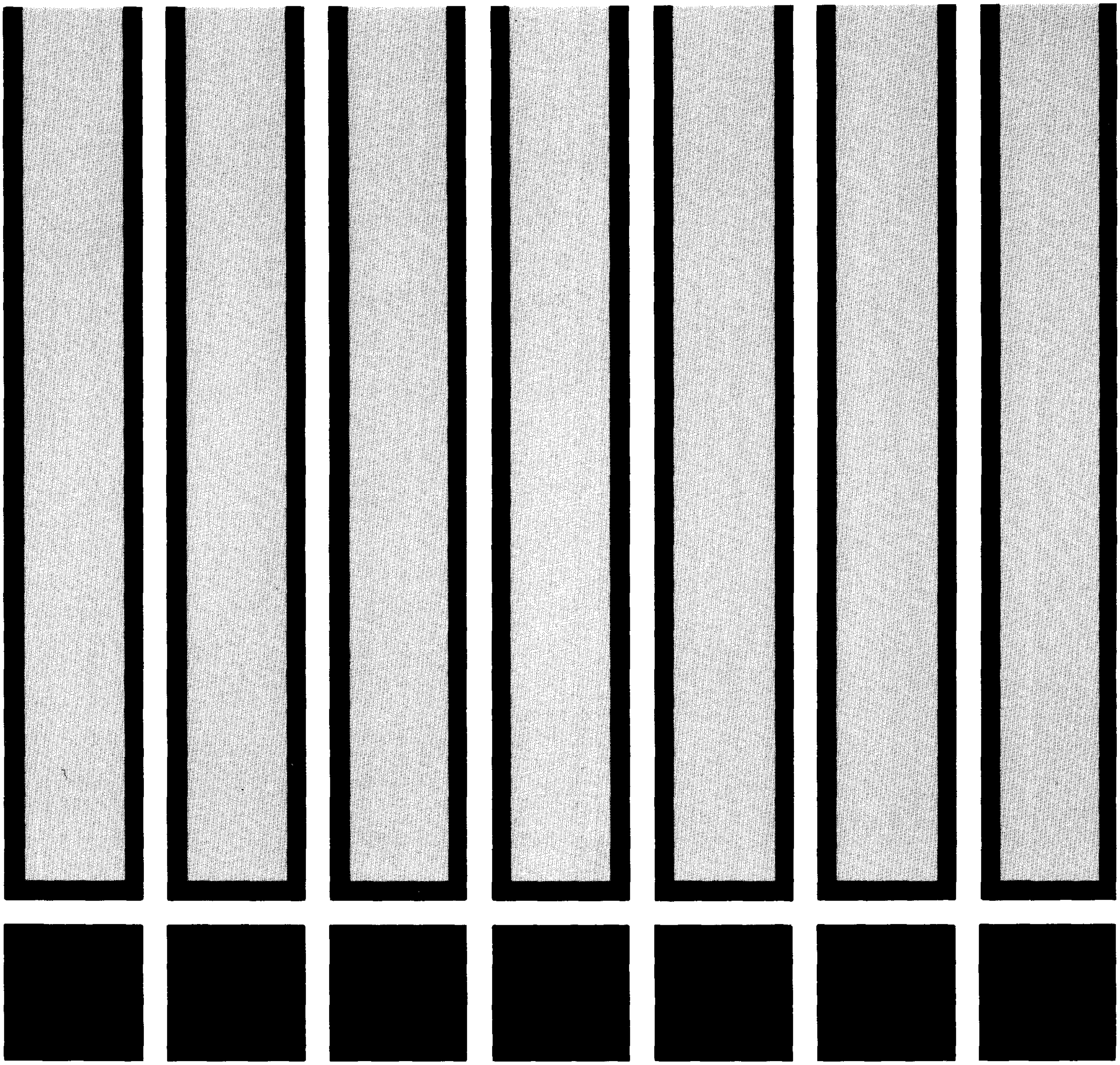

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service Center for Disease Control
National Institute for Occupational Safety and Health

criteria for a recommended standard....

OCCUPATIONAL EXPOSURE
TO
NITRIC ACID

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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National Institute for Occupational Safety and Health

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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on nitric acid by members of my staff and the valuable constructive comments by the Review Consultants on Nitric Acid, ad hoc committees of the American Industrial Hygiene Association and the American Occupational Medical Association, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by Mary O. Amdur, Ph.D., NIOSH consultant in toxicology. The

NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on nitric acid. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

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The Office of Research and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and the recommended standard for nitric acid. Tabershaw-Cooper Associates, Inc. developed the basic information for consideration by NIOSH staff and consultants under contract No. HSM 99-73-26. B. Thomas Scheib served as criteria manager and Douglas L. Smith, Ph.D., had NIOSH program responsibility for development of the document.

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CRITERIA DOCUMENT: RECOMMENDATIONS FOR OCCUPATIONAL EXPOSURE STANDARD FOR NITRIC ACID

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I. RECOMMENDATIONS FOR A NITRIC ACID STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that exposure to nitric acid in the workplace be controlled by compliance with the following sections. The standard is designed to protect the health and safety of workers for up to a 10-hour workday, 40-hour workweek over a working lifetime. Compliance with the standard should prevent adverse effects of occupational exposure to nitric acid. The standard is measurable by techniques that are valid, reproducible, and available. Sufficient technology exists to permit compliance with the recommended standard. The standard will be subject to review and revision as necessary.

"Nitric acid" is defined as the aqueous solutions of nitric acid and the vapor and mist thereof. "Occupational exposure to nitric acid" is defined as exposure to airborne concentrations of nitric acid equal to or exceeding one-half the recommended workroom environmental limit. Adherence only to sections 3, 4(a), 4(b), 4(c) (1) (C), 5, and 6 is required when workplace environmental concentrations of nitric acid are not greater than one-half of the recommended workplace environmental limit. It must be recognized that a potential exposure to oxides of nitrogen exists whenever airborne nitric acid is present in the workplace environment. Therefore, sampling for oxides of nitrogen, as specified in Criteria for a Recommended Standard....Occupational Exposure to Oxides of Nitrogen, must accompany measurements for airborne nitric acid.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Occupational exposure to nitric acid shall be controlled so that no worker is exposed to a concentration of nitric acid vapor in excess of 2 ppm of air (5 mg/cu m air) determined as a time-weighted average (TWA) exposure for up to a 10-hour workday, 40-hour workweek.

(b) Sampling and Analysis

Procedures for sampling, calibration of equipment, and analysis shall be as provided in Appendices I and II, or by any method shown to be equivalent in precision, accuracy, and sensitivity to the methods specified.

Section 2 - Medical

Medical surveillance shall be made available as specified below for all workers occupationally exposed to nitric acid.

(a) Preplacement and periodic medical examinations shall include:

(1) Comprehensive or interim work and medical histories.

(2) 14" x 17" posterior-anterior chest X-ray.

(3) Pulmonary function tests including, as a minimum, a measurement of Forced Vital Capacity (FVC) and Forced Expiratory Volume in the first second (FEV 1).

(4) Visual examination of the teeth for evidence of dental erosion.

(5) A judgment of the worker's physical ability to use negative or positive pressure respirators as specified in 29 CFR 1910.134.

(b) Periodic examinations shall be at 1-year intervals or at some other frequency to be determined by the responsible physician.

(c) Proper medical management shall be provided for workers exposed to nitric acid.

(d) Initial annual examinations for presently employed workers shall be offered within six months of the promulgation of a standard incorporating these recommendations.

(e) The medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, and of the employer shall have access to all pertinent medical records. Physicians designated and authorized by any employee or former employee shall have access to that worker's medical records.

(f) Medical records shall be maintained for persons employed one or more years in work involving exposure to nitric acid. X-rays for the 5 years preceding termination of employment and all medical records with pertinent supporting documents shall be maintained at least 20 years after the individual's employment is terminated.

Section 3 - Labeling (Posting)

(a) Containers of nitric acid shall carry a label, and areas where exposure to nitric acid is likely to occur shall be posted with a sign, on which the following is stated:

NITRIC ACID

DANGER! CAUSES SEVERE BURNS

VAPOR EXTREMELY HAZARDOUS

SPILLAGE MAY CAUSE FIRE OR LIBERATE DANGEROUS GASES

Do not breathe vapor.

Do not get in eyes, on skin, on clothing.

In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. Get medical attention.

(b) The above label shall be in addition to, or in combination with, labels required by other statutes, regulations, or ordinances.

(c) The warning sign shall also be printed in the predominant language of non-English-speaking workers. All employees shall be trained and informed of the hazardous areas, with special instruction given to illiterate workers.

Section 4 - Personal Protective Equipment

Engineering controls shall be used to maintain nitric acid concentrations below the prescribed limit. Requirements for personal protective equipment shall be as approved under provisions of 29 CFR 1910 (Federal Register 37:22102, October 18, 1972, as amended).

(a) Skin Protection

(1) Skin contact with concentrated nitric acid will produce burns at the site of contact. Impervious protective clothing, such as rubber gloves, aprons, suits, and boots shall be provided by the employer and used by the employee when there is a likelihood of body contact with liquid acid.

(2) Nitric acid-wetted clothing shall be flooded with water and then removed promptly.

(3) All protective clothing and equipment shall be maintained in a clean, sanitary, and workable condition.

(b) Eye Protection

Eye protective equipment shall be provided by the employer and used by the employee where potential for eye contact with liquid nitric acid exists.

(1) Selection, use, and maintenance of eye protective equipment shall be in accordance with provisions of the American National Standard Institute Practice for Occupational and Educational Eye and Face Protection, ANSI Z87.1-1968.

(2) Chemical safety goggles -- Cup-type, cover-cup-type, or rubber-framed goggles, equipped with approved impact-resistant glass or plastic lenses, shall be worn whenever using or handling concentrated nitric acid.

(3) Face shields -- If there is danger of nitric acid striking the eyes or around the sides of the face, a full length, 8-inch minimum plastic shield with forehead protection shall be worn in addition to chemical safety goggles.

(c) Respiratory Protection (1) Engineering controls shall be used wherever feasible to maintain airborne nitric acid concentrations below the prescribed limit. Compliance with the permissible exposure limit may not be achieved by the use of respirators except:

(A) During the time period necessary to install or test the required engineering controls.

(B) For nonroutine operations such as a brief exposure to concentrations in excess of the permissible exposure limit as a result of maintenance or repair activities.

(C) During emergencies when air concentrations of nitric acid may exceed the permissible limit.

(2) When a respirator is permitted by paragraph (c) (1) of this Section, it shall be selected and used pursuant to the following requirements. For the purpose of determining the type of respirator to be used, the employer shall measure the atmospheric concentration of nitric acid in the workplace initially and thereafter whenever process, worksite, climate, or control changes occur which are likely to increase the airborne nitric acid concentrations; this requirement shall not apply when only atmosphere-supplying positive pressure respirators will be used. The employer shall ensure through proper respirator selection fit, use, and maintenence that no worker is being exposed to airborne nitric acid in excess of the standard.

(3) A respiratory protective program meeting the general requirements outlined in Section 3.5 of American National Standard Institute Practices for Respiratory Protection Z88.2-1969 shall be established and enforced by the employer. In addition, Sections 3.6 (Program Administration), 3.7 (Medical Limitations), and 3.8 (Approval) shall be adopted and enforced.

(4) The employer shall provide respirators in accordance with Table I-1 and shall ensure that the employee uses the respirator provided.

(5) Respiratory protective devices described in Table I-1 shall be those approved under provisions of 30 CFR 11.

(6) Respirators specified for use in higher concentrations of nitric acid are permitted in atmospheres of lower concentrations.

(7) Employees shall be given instructions on the use of

respirators assigned to them, day-to-day maintenance and cleaning of the respirators, and how to test for leakage.

(8) Emergency and escape-type respirators shall be made immediately available at the work stations for each worker.

TABLE I-1

REQUIREMENTS FOR RESPIRATOR USAGE

Maximum Use Concentration (Multiples of Limit for Airborne Nitric Acid)	Respirator Type
Less than or equal to 125 mg/cu m	(1) A chemical cartridge respirator with a full facepiece and cartridge(s) providing protection against airborne nitric acid and oxides of nitrogen
	(2) A gas mask with a chin-style or front- or back-mounted canister providing protection against airborne nitric acid and oxides of nitrogen
	(3) Any supplied-air respirator with a full facepiece, helmet, or hood
	(4) Any self-contained breathing apparatus with a full facepiece
Less than or equal to 250 mg/cu m	(1) Type C supplied-air respirator operated in demand mode (negative pressure) with full facepiece
	(2) Self-contained breathing apparatus operated in demand mode (negative pressure) with full facepiece

TABLE I-1 (CONTINUED)

REQUIREMENTS FOR RESPIRATOR USAGE

Maximum Use Concentration (Multiples of Limit for Airborne Nitric Acid)	Respirator Type
Less than or equal to 500 mg/cu m	(1) Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, hood, or helmet operated in continuous flow mode
Greater than 100 X or entry and escape from unknown concentrations	(1) Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode
	(2) 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
Firefighting	(1) Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode
Emergency, Escape	(1) Self-contained breathing apparatus operated in pressure-demand mode (positive pressure) with full facepiece

Section 5 - Informing Employees of Hazards from Nitric Acid

At the beginning of employment in a nitric acid area, employees exposed to nitric acid shall be informed of all hazards, relevant symptoms of overexposure, appropriate emergency procedures, and proper conditions and precautions for safe use or exposure. Instruction shall include, as a minimum, all information in Appendix III which is applicable to nitric acid. The information shall be posted in the work area and kept on file and readily accessible to the worker at all places of employment where nitric acid is used.

A continuing educational program shall be instituted to ensure that all workers have current knowledge of job hazards, proper maintenance procedures and cleanup methods, and correct use of respiratory protective equipment and protective clothing.

Information as specified in Appendix III shall be recorded on US Department of Labor Form OSHA-20 "Material Safety Data Sheet" or a similar form approved by the Occupational Safety and Health Administration, US Department of Labor.

Section 6 - Work Practices

Protection against hazards from nitric acid requires the development and employment of sound work practices for use during routine operations as well as in emergencies. Procedures designed to prevent nitric acid contact with tissues must be used in the manufacturing, handling, transfer, and storage of the acid, in the cleaning, maintenance, and repair of tanks, other vessels, piping, and other appurtenances with which the acid may come in contact, as well as in the prevention, minimization, cleanup, and disposal of acid spills. Appropriate personal protective equipment must be provided and used. There must also be equipment and procedures to ensure immediate flushing off of any acid coming in contact with the eyes or skin. In addition, suitable plans must be developed and personnel trained in the procedures to be followed in the event of major emergencies, such as large spills of nitric acid, massive release of airborne nitric acid or nitrogen oxides, fire, explosion, or other hazardous occurrences.

The mechanics of handling, transfer, and storage of nitric acid will be related to the quantities involved, depending upon whether it is received in bottle, carboy, drum, tank truck, or tank car lots. The US Department of Transportation regulations governing the packaging and other requirements for shipment of nitric acid are found in 49 CFR 100-199 for highway and rail, in 14 CFR 103 for air, and in 46 CFR 146-149 for water.

(a) Emergency Procedures

For all work areas in which there is a reasonable potential for emergencies, procedures as specified below, as well as any other procedures appropriate for a specific operation or process where large spills of nitric acid or massive release of nitrogen oxides may occur, shall be formulated in advance and employees shall be instructed in their implementation.

(1) Procedures shall include prearranged plans for obtaining first aid, emergency medical care, and necessary transportation of injured workers.

(2) All employees shall be evacuated from exposure areas during emergencies. Authorized personnel shall reenter only after donning proper eye, skin, and respiratory protection equipment and clothing.

(3) All injured personnel shall be removed upwind to a fresh air environment and a physician shall be called immediately. If the

injured person is not breathing, give artificial respiration. If breathing is difficult, give oxygen. Remove any contaminated clothing and shoes. In case of contact with material, immediately flush skin or eyes with running water (low pressure) for 15 minutes. Keep the patient warm and quiet.

(4) For the purpose of flushing any acid coming in contact with body tissues, safety showers and eyewash fountains shall be readily available in areas where nitric acid is being handled. The safety showers should have quick-acting valves and deluge-type heads. Eyewash fountains and safety showers should be inspected every 7 days. Also, each safety item shall have a tag to be dated and initialed at each inspection.

(5) Approved eye, skin, and respiratory protection as specified in Section 4 shall be used by personnel in emergency operations.

(b) Handling and Storage

(1) Carboys and drums of nitric acid shall be inspected, when received, for signs of leakage or damage. Any of the latter in damaged condition shall be set aside for special handling. Any tanks (rail, truck, etc) containing nitric acid shall be inspected for leaks before they are allowed to enter the plant. Necessary precautions shall be taken for prompt and safe unloading of leaking vehicles. The regulations of the US Department of Transportation (49 CFR, Chapters I and III) for the loading and unloading of tank cars, tank trucks, and portable tanks shall be adhered to.

(2) Only capable, trained employees shall be permitted to make connections from tank trucks or tank cars to receiving tanks. Moreover, the receiving tank must be properly vented. Wherever practicable, unloading should be done by pumping. If compressed air must be used, the pressure must never exceed the safe working pressure of the tank, and the

pressure must never exceed 30 pounds per square inch gauge (psi) under any circumstances.

(3) Storage shall be in noncorrosive containers fabricated of materials suitable for the concentration of the acid. Storage shall be out of the direct rays of the sun, preferably under cover. The storage area shall be isolated from materials such as turpentine, carbides, metallic powders, and combustible materials. Storage tanks shall not be used for purposes of bleaching the acid. Stored containers shall be inspected at least once a week for signs of leakage.

(4) Areas where nitric acid is stored, transferred, or used shall be posted with warning signs containing the same information specified in Section 3(a). Posted areas shall delineate locations where eating and food storage are prohibited.

(5) Carboys and drums of nitric acid shall be emptied by gravity or siphon, never by pressure. Faucets or siphons shall be made of material resistant to nitric acid, and siphons must not be started orally. Employees opening such containers shall wear goggles, face shields, and rubber gloves. Where the potential exists for exposure to either airborne nitric acid or oxides of nitrogen when opening drums or carboys, respiratory protective equipment shall be worn.

(6) Transfer of nitric acid from one container to another, or into any process, shall be performed in such a manner as to minimize the potential for leaks and spills. The safe practices described in Chemical Safety Data Sheet SD-5, "Properties and Essential Information for Safe Handling and Use of Nitric Acid," issued by the Manufacturing Chemists Association, are recommended.

(c) Spills, Leaks, and Waste Disposal

(1) In the event of spills or leaks of nitric acid, the contaminated area shall be immediately zoned off and flushed with copious amounts of water in order to dilute the acid as rapidly as possible. The water should be supplied through low pressure systems in order to avoid conveyance of the acid to uncontaminated areas. Water spray should also be used to absorb oxides of nitrogen. Contact with combustibles or organic materials such as sawdust, excelsior, wood scraps and shavings, paper, cotton waste, and burlap bags shall be prevented. Contact of nitric acid with such materials can result in spontaneous combustion. In the absence of water, clean sand or other noncombustible material may be employed to prevent the spread of the acid.

(2) Waste (including tank washings) or spilled nitric acid shall be diluted or neutralized before disposal. Soda ash, lime, slaked lime, or other alkali or alkaline earth metal carbonates and bicarbonates may be used for neutralization.

(3) All local, state, and federal regulations concerning waste disposal to streams, waste treatment plants, or impounding basins shall be followed.

(4) All employees handling nitric acid, or who might be involved in cleanup operations in the event of a leak or spill, shall be instructed in the safe practices involved in such work, including not only the prevention of skin contact with the acid, but also the prevention of inhalation of either the acid vapor or the oxides of nitrogen. Instruction shall be given before the employee commences such work. A continuing educational program on these instructions (or improvised ones) should be instituted to ensure responsible and efficient handling of emergency situations.

(d) Cleaning and Repair

(1) Cleaning, inspecting, and repairing tanks which contain or have contained nitric acid shall be under the direction of thoroughly trained personnel who are aware of the potential health, safety, fire, and explosion hazards. Tanks and equipment, pumps, lines, and valves should be drained and thoroughly flushed with water before being repaired. Personal contact with liquid from such equipment should be avoided. Pipe lines leading from tanks shall be sealed with blanks during maintenance of pumps, lines, valves, or ancillary equipment. After tanks to be entered have been flushed, soda ash, lime, or slaked lime shall be used to neutralize any residual acid. The tank shall then be purged with air and tested for oxides of nitrogen before personnel are permitted to enter. Testing shall be done by using nitrogen dioxide detector tubes certified by the National Institute for Occupational Safety and Health or portable, direct reading nitrogen dioxide meters of at least equivalent sensitivity and reliability. The tank atmosphere shall not be considered safe for use without respiratory protection until no discoloration is observed in the detector tube.

(2) No one shall enter a tank or confined space until a work permit has been signed by an authorized employer representative certifying that the area has been tested and found safe, or that preparation of the confined space, precautionary measures, including personal protective equipment, and procedures to be followed are all adequate.

(3) Personnel entering confined spaces shall be furnished with appropriate personal protective equipment and protected by a lifeline

tended outside the space by another worker who shall also be equipped for entry with approved respiratory, eye and skin protection, and a lifeline, and who shall have contact with a third party.

(4) Mechanical ventilation of the tank is required where the levels of airborne nitric acid, oxides of nitrogen, and oxygen are unknown.

(e) Ventilation

(1) Where operations or processes result in the evolution of nitric acid vapor or mist, or oxides of nitrogen, ventilation shall be provided which will protect employees from airborne concentrations in excess of the standard specified in <u>Criteria for a Recommended Standard</u>....<u>Occupational Exposure to Oxides of Nitrogen</u>. Ventilation systems shall be designed to prevent the accumulation or recirculation of nitric acid vapor or the oxides of nitrogen in the workroom and to effectively remove such vapors and gases from the breathing zones of workers.

(2) Ventilation systems shall be inspected quarterly and shall be subject to regular preventive maintenance and cleaning. Ventilation efficiency shall be assessed at the time of inspection by airflow measurements in accordance with procedures recommended by the American Conference of Governmental Industrial Hygienists. [1]

(3) Exhaust ventilation systems discharging to outside air must conform with applicable local, state, and federal air pollution regulations.

Section 7 - Monitoring and Recordkeeping

(a) Workers are considered "occupationally exposed" to nitric acid if environmental levels, as determined on the basis of an industrial hygiene survey conducted within 6 months of the promulgation of this standard, equal or exceed one-half of the TWA limit. Records of these surveys, including the basis for concluding that airborne levels are below the level defining "occupational exposure," shall be maintained. Surveys shall be repeated within 30 days of installing new equipment or processes, process modifications, or worksite changes which are likely to result in an increase of airborne nitric acid. If it has been decided that nitric acid levels equal or exceed the level defining "occupational exposure," then the following requirements apply.

(1) A program of personal monitoring shall be instituted to identify and measure or permit calculation of the exposure of all employees occupationally exposed to nitric acid.

(2) Routine monitoring of employee exposure shall be conducted at least semiannually.

(3) If an employee monitoring program measurement reveals that an employee is exposed in excess of the recommended limit as prescribed in Section 1(a), the exposure of that employee shall be monitored at 15-day intervals. Measures designed to control employee exposure to nitric acid shall be implemented, and the employee shall be notified of his or her exposure as well as the control measures being implemented. Monitoring shall continue until 2 consecutive determinations indicate that employee exposure no longer exceeds the recommended environmental limit. Semiannual monitoring may then be resumed.

(4) In all personal monitoring, samples representative of the exposure in the breathing zone of the employee shall be collected. Procedures for sampling, calibration of equipment, and analysis of airborne

nitric acid samples shall be as provided in Section 1(b).

(5) For each TWA determination, a sufficient number of samples shall be taken to characterize the employee's exposure during each workshift. The accuracy of the sampling and analytical methods as well as the variation of employee exposure shall be considered in determining whether full-period consecutive sampling, partial-period consecutive sampling, or partial-period nonconsecutive sampling is used. A determination of compliance with the recommended environmental limit shall be made based upon the accuracy of the sampling and analytic methods, the frequency and type of sampling, and the recommended environmental limit as prescribed in Appendix I.

(6) The number of representative TWA determinations for an operation or process shall be based upon the mobility of the workers and the variation in work procedures in that operation or process.

(b) The employer shall keep records on all industrial hygiene surveys and all breathing zone TWA determinations. Records of the latter shall include the determined concentration of exposure and a description of the monitoring, sampling, and analytic methods. In addition, records shall be maintained on the types of respirators and personal protective equipment, if any, worn by employees. The monitoring records shall identify the employees for whom breathing zone air samples were collected, and the employer shall make such records available to representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, and to the employee or former employee.

(c) The employer shall keep the records of all environmental monitoring on the levels of airborne nitric acid for each employee for whom breathing zone air samples were collected for at least 20 years after the employee's employment is terminated.

II. INTRODUCTION

This report presents the criteria and the recommended standards based thereon which were prepared to meet the need for preventing occupational diseases resulting from exposure to nitric acid. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare, under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "... develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health of functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health of workers from exposure to hazardous chemical and physical agents. It should be pointed out that any criteria and recommended standard should enable management and labor to develop better engineering controls resulting in more healthful work practices and should not be used as a final goal.

These criteria for a standard for nitric acid are in a continuing series of criteria developed by NIOSH. The proposed standard applies to the processing, manufacture, and use of nitric acid as applicable under the Occupational Safety and Health Act of 1970.

One of the more important chemicals in use in American industry, nitric acid presents a dual problem of skin and eye contact hazard from the liquid acid as well as one from inhalation of the acid vapor or mist.

Since the vapor, if present in the work environment, usually occurs in varying mixtures with oxides of nitrogen, reference is frequently made to the provisions and information contained in *Criteria for a Recommended Standard....Occupational Exposure to Oxides of Nitrogen*.

The development of the recommended standard for occupational exposure to nitric acid has revealed deficiencies or limitations in the available data in the following areas:

(1) epidemiologic data which focus on changes in the pulmonary system or the incidence of chronic obstructive pulmonary diseases in workers exposed to nitric acid vapor and mist in the occupational environment;

(2) acute changes in pulmonary function in both humans and experimental animals exposed to low concentrations of airborne nitric acid;

(3) chronic effects of long-term low-level exposure in experimental animals exposed 8-10 hours/day for 12-18 months;

(4) mutagenic, carcinogenic, or teratogenic effects of exposure to nitric acid; and

(5) additive, synergistic, or inhibitory effects of nitric acid in combination with hydrocarbons, fibrous dusts, and other pulmonary irritants on neoplastic dose-response relationships.

III. BIOLOGIC EFFECTS OF EXPOSURE

Definitions

An examination of the technical literature on nitric acid shows a lack of consistency in the interpretation and use of such terms as fumes, gases, vapors, and mists. For clarification, the following definitions, as published by the American National Standards Institute, [2] are offered:

"Fumes: Solid particles generated by condensation from the gaseous state, generally after volatilization from molten metals, etc, and often accompanied by a chemical reaction such as oxidation. Fumes flocculate and sometimes coalesce.

"Mists: Suspended liquid droplets generated by condensation from the gaseous to liquid state or by breaking up a liquid into a dispersed state, as by splashing, foaming, and atomizing.

"Vapors: The gaseous form of substances which are normally in the solid or liquid state and which can be changed to these states either by increasing the pressure or decreasing the temperature alone. Vapors diffuse.

"Gases: Normally formless fluids which occupy the space of enclosure and which can be changed to the liquid or solid state only by the combined effect of increased pressure and decreased temperature. Gases diffuse."

The term "aerosol", frequently used in the experimental literature, refers to "any system of liquid droplets or solid particles dispersed in air, of fine enough particle size, and consequent low settling velocity, to possess considerable stability as an aerial suspension." [3] As such, "fumes" and "mists" must be considered subsets of this category.

Extent of Exposure

Although the earliest mention of nitric acid dates back to the 8th century, from at least the 18th century until World War I manufacture of nitric acid was primarily accomplished by distillation of potassium or sodium nitrate with sulfuric acid. [4] In the last several decades, the distillation process has been essentially replaced by the ammonia oxidation process. With the aid of a platinum catalyst, ammonia is oxidized with air to yield nitric oxide. This is further oxidized with excess air to produce nitrogen dioxide, which is absorbed in water to form an aqueous solution of nitric acid and additional nitric oxide. [4,5]

Nitric acid is produced in a variety of strengths ranging from approximately 50 to 99%. The pure acid is a rarity. [4] Reagent grade nitric acid is, according to specifications of the American Chemical Society, approximately 70% by weight. Stronger grades are produced by dehydration with sulfuric acid. [5] According to military specifications the terms "white fuming" and "red fuming" are applied to differentiate two concentrations of fuming nitric acid. White fuming nitric acid contains about 97.5% nitric acid by weight while red fuming nitric acid contains 82.4-85.4%. [6] The percentages of nitrogen dioxide content in white fuming and red fuming nitric acid are 0.5 and 14 ± 1.0, respectively. Some physical and chemical properties of various strengths of nitric acid are given in Tables XI-1 and XI-2. [7] Data showing the comparative vapor pressures of nitric acid and nitrogen dioxide at different temperatures are presented in Table XI-3. [8]

Production of nitric acid in the United States steadily increased during the 1950-1967 era. [5,9] Between 1960 [5] and the end of 1967, [9] production almost doubled so that by the end of 1967 total production exceeded 6 million tons. [9] According to a 1970 report, [5] nitric acid was the second most important industrial acid and its production represented the sixth largest chemical industry in the United States.

The largest use of nitric acid is in the production of fertilizers, in the form of ammonium nitrate. This accounts for about 75% of all the nitric acid produced in the United States. Almost 15% of the production goes into the manufacture of explosives, with the remaining 10% distributed among a wide variety of uses. [5,10] Most of the ammonium nitrate obtained from nitric acid is produced at the site where the acid is made. [11] Table XI-4 lists some of the potential occupational exposures to nitric acid. [12]

Exposures to nitric acid may be divided into two basic types - those involving topical contact with the liquid acid, [13,14,15] and those where the hazard is from inhalation. [17,18,19,20,21,22,23,24] In practice, the inhalation exposures invariably include exposures to such nitrogen oxides as nitrogen dioxide and nitric oxide, and these may well constitute the principal hazard involved. [8,17,20,21,22,23,25,26] NIOSH's review of the literature showed that reports of environmental measurements of occupational exposures involving nitric acid have been limited to measurements of nitrogen oxides. No published reports of airborne concentrations of nitric acid in workroom air were found. Such emphasis on measurements of exposures to nitrogen oxides is not surprising in view of the fact that in the numerous uses involving nitric acid with metals or with oxidizable substances, as well as when nitric acid is exposed to air, nitrogen oxides are released. [27] Wade et al, [25] reporting in 1950 on the composition of nitrogen oxides evolved from various industrial processes, indicated that the probable average composition of such gases from acid dipping would be 78% nitrogen dioxide and 22% nitric oxide.

NIOSH estimates that 27,000 persons in the national work force could have potential exposure to nitric acid.

Historical Reports

One of the earliest accounts of the toxic effects of inhalation of vapors and gases from spilled nitric acid, and from the ensuing reaction between the nitric acid and organic material, is that of Desgranges [19] in 1804. Two canisters of concentrated nitric acid broke in a storeroom and reacted with a quantity of wood with the evolution of what has been translated as suffocating fumes. The merchant entered the room for two periods of approximately 5 minutes each, in close succession. He experienced an immediate suffocating sensation and his hair turned yellowish red in color. He improved for the first 4 hours following exposure, but after this time he was weak, dyspneic, and complained of a painful sensation of constriction around the epigastrium. Although the merchant felt better several hours after his exposure, he survived only for 25-26 hours. The medical report indicated that the cause of death was apparently due to the toxic effects of the "nitrous gas" on the pulmonary organs and digestive tract.

Since that early report, there have been numerous descriptions in the literature of incidents similar to the one above in which individuals or groups were exposed to the gaseous products of the reaction between spilled nitric acid and materials such as wood, woodshavings, sawdust, [19,20,21,22] or metals, [20] or from the dipping of metals in nitric acid. [23]

Effects on Humans

(a) Skin and Eye Effects

Concentrated nitric acid, including fuming nitric acid, destroys tissues because of its corrosive chemical properties. Skin contact with concentrated nitric acid produces burns, and a change in skin color from yellow to brown will occur from contact with the acid at lower concentrations. [14,28] The actions of concentrated nitric acid on the skin have been reviewed by White [13] who states that the staining process is from the formation of xanthoproteic acid due to the action of nitric acid on skin proteins. Dilute solutions of nitric acid produce a mild irritation of the skin and tend to harden the epithelium without destroying it. [28] Leymann [as cited in 29] reported that the annual incidence of nitric acid burns to the skin of workers engaged in its manufacture early in this century was almost 12%.

In contact with the eye, concentrated nitric acid causes immediate opacification of the corneal and conjunctival epithelia. [15] In severe cases, this may result in permanent corneal opacification with attendant blindness, symblepharon (fusion of the eyelids), and shrinkage of the eyeball. [30] In a clinical description of the case of a chemist who was "showered" with hot nitric acid in a laboratory mishap, McAdams and Krop [14] reported that the right cornea was "semiopaque" by the second day after the accident, while the left appeared similar but less severely burned. However, by the 28th day the right cornea had cleared, but the left became opaque. In milder cases involving a very small quantity of acid, greater dilution, or very prompt first aid irrigation, the opacified epithelium may slough after a day or two, revealing a clear underlying cornea, and complete recovery may take place with epithelial regeneration.

[16 as cited in 15]

(b) Inhalation Effects

As already discussed, reports of inhalation exposures to the vapor or mist of nitric acid, as distinct from the gases liberated from the reaction of nitric acid with certain metals or with organic material, have not been found. The term "nitric acid fumes" [20,22,23] has been used to describe what may be considered as a mixture of nitric acid vapor and oxides of nitrogen (predominantly nitrogen dioxide and nitric oxide). In addition, the less exact term "nitrous fumes" has also been used. [31]

The acute effects of inhalation of such mixtures of nitric acid and of nitrogen oxides are characterized by a variable degree of upper respiratory irritation, which may [20,21] or may not be manifested immediately. [22] The signs exhibited minutes after inhalation can include dryness of the throat and nose, cough, chest pain, and dyspnea. [20] In some individuals, similar or more severe signs may be observed after a latent period of several hours following inhalation. [20,21,22,23] Within 24 hours after inhalation, patients may exhibit moderate to severe dyspnea and cyanosis. [21,22,23] Signs of pulmonary edema may also become apparent upon medical examination. [21,23] It is noteworthy that similar adverse respiratory effects have been observed following exposures to most of the oxides of nitrogen from sources other than nitric acid. [32,33,34]

The recovery of patients exposed to mixtures of nitric acid and oxides of nitrogen appears to be unpredictable. [20,21,22,23] Apparently, the prognosis depends upon the airborne concentration of nitric acid or oxides of nitrogen as well as the duration of exposure. [23] In some cases, recovery was essentially complete within two weeks, [20,22] but in others, it took place after a much prolonged period of bronchopneumonia.

[20] In several cases, however, the patients did not recover and died after suffering from bronchopneumonia and various other illnesses. [20,21,23] In one instance, death was said to be caused by pulmonary fibrosis. [23]

Two cases have been reported [31] with yet another clinical picture, that of only minor respiratory symptoms during and after exposure, followed by severe cyanosis, dyspnea, chest pain, cough, and general malaise, and death in one patient after a delay of a week or more. One case resulted from the inhalation of the gases and vapors evolved by the reaction of nitric acid with metals, and the second from the inhalation of gases and vapors evolved by the reaction of both nitric and sulfuric acid with metals. [31] The first patient died 1 week after the onset of the severe symptoms (2 weeks after the exposure) which had been intense, although very short in duration (allegedly 30 seconds). In the second case, the patient recovered following 2 weeks' hospitalization with intensive therapy. It was clinically evident that both patients suffered from bronchiolitis. The cause of death in the first case was attributed to a generalized obliterative bronchiolitis. The term "bronchiolitis fibrosa obliterans" was coined in 1902 by Fraenkel [35] to describe the respiratory syndrome of a brassfounder who was exposed while dipping castings in a mixture of nitric and sulfuric acids.

More recently, [36] the syndrome of bronchiolitis fibrosa obliterans was described in 2 of 4 agricultural workers exposed to gases produced in farm silos. The primary contaminant was thought to be nitrogen dioxide. [36] There was no progression of pulmonary disease in two patients; however, the other two died within a few weeks after their inhalation exposure. The descriptive term "silo-filler's disease" was used by the authors [36] to designate "any bronchial or pulmonary condition produced by the inhalation of oxides of nitrogen derived from fresh silage."

According to Fairhall, [28] continued exposure to the vapor of nitric acid may cause a chronic bronchitis and more severe exposure may cause a chemical pneumonitis. These effects are not well established because exposures to nitric acid vapor per se, as opposed to vapor and gases generated by the decomposition of nitric acid, have not been found in the literature. However, it seems very plausible that nitric acid, being highly ionized and having strong corrosive properties, would be a potent respiratory irritant.

(c) Ingestion Effects

Accidental or suicidal ingestion of liquid nitric acid, though rare in industry, has occasionally been described from nonoccupational incidents. The following reports serve to illustrate the severely corrosive and tissue-destructive effects of concentrated nitric acid when it comes into contact with mucous membranes.

In 1921, Gray [24] reported a case in which an unknown quantity of nitric acid was ingested by a young Naval fireman, who died in shock within 12 hours. At autopsy, gross pathologic changes were limited to the skin, mouth, esophagus, stomach, duodenum, and kidneys. It was evident that the acid burned, lacerated, or inflamed numerous portions of these tissues and organs. In a case of suicidal ingestion reported by Ide [37] in 1925, the patient survived for several months despite total destruction of the esophagus, and finally died apparently from lobar pneumonia. Another case of suicidal ingestion in which the patient survived was reported by Alsted [38] in 1937. The amount ingested was stated to be a "half a cup" of nitric acid. After a period of years, the patient developed classical pernicious anemia, presumably due to the destruction of the gastric mucosa with its vital intrinsic factor secreting function. Eight years after the ingestion of the acid, X-ray examination revealed that the stomach was converted into a small sausage-shaped organ with the diameter of a normal colon. Finally, a patient studied by Holinger et al [39] in 1953 developed "corrosive esophagitis" after the inadvertent gargling with 30-40 ml of nitric acid and the swallowing of a much smaller amount, most of it having been immediately expectorated. This victim died 14 days later of gastric hemorrhage following loss of the inner lining of the esophagus on the eighth day.

(d) Dental Erosion

In 1968, tenBruggen Cate [40] published the results of an extensive survey concerned with dental erosion in workers exposed to mineral acid aerosols and mist. Out of 783 workers examined, only 32 were exposed to nitric acid alone. Of these 32, 3 (9%) were reported to have "active dental erosion," the teeth of the remaining 29 being reported as "uneffected." None of the 293 workers comprising the control group showed signs of active dental erosion. Although no environmental data were reported in this study, results indicated that nitric acid vapor and mists were not as potent a factor in causing dental erosion as sulfuric and hydrochloric acids. Two other reports on dental erosion attributed to nitric acid vapors are described under <u>Epidemiologic Studies</u>. [41,42]

Epidemiologic Studies

A search of the literature has revealed no epidemiologic studies of the effects of exposure to nitric acid vapor or mist on general health or on the pulmonary system.

Dettling [41] in 1935 described the occurrence of dental erosion phenomenon in male workers engaged in the manufacture of nitrocellulose where a mixture of nitric and sulfuric acids was used in what was translated as a nitriding process. Twenty-six of 31 workers examined showed traces of dental erosion. Of the 5 workers who had no dental erosion, 4 had been employed for less than 1 year. No environmental data were given. The author speculated that the dental erosion was caused by exposure to nitrous and nitric acid fumes. The formation of nitrous and nitric acids was believed to be due to the development of nitric oxide during the nitriding process which, in turn, combined with the water present in the atmosphere to form the acids.

In 1947, Lynch and Bell [42] reported the prevalence of dental erosion in female workers involved in the manufacture of guncotton and nitrocellulose. At one stage, raw materials were dipped in earthenware baths. The baths contained a solution of 70% sulfuric acid, 22% nitric acid, and 8% water. Although no environmental analysis was made, acid "fumes" were implicated in contamination of the workplace air, despite the fact that a local exhaust ventilation system was in operation. A "localized fire" would sometimes break out resulting in the liberation of "nitrous fumes" which, in turn, contaminated the working environment. Of 26 women employed in this work for 1-3 months, 6 (23%) showed evidence of dental erosion. Of 29 women employed 3-12 months, 11 (38%) showed dental erosion, and of 42 women employed from 1 - 3 1/2 years, 26 (62%) showed dental erosion. The implication in the preceding 2 reports that dental erosion was caused by the nitric acid in the nitration mixture must be viewed with reservation since sulfuric acid alone is known to be a potent cause of dental erosion. [43]

Animal Toxicity

There are few reports on animal toxicologic studies of nitric acid. Diggle and Gage, [44] in 1954, made the simple statement that "a single exposure to 63 mg/cu m of nitric acid (approximately 25 ppm) has no apparent effect on rats." The duration of the exposure or supporting evidence was not given.

In 1966, Pham-Huu-Chanh et al [45] reported a series of experiments using isolated guinea pig lungs. The isolated lungs were kept alive by placing and maintaining them in an artificial thoracic cage. Aerosols of several acids, including fuming nitric acid (100%), were individually administered to the isolated lungs. The aerosol sprays consisted of submicronic particles, 0.2-0.5 μm in size. Under the experimental conditions, the investigators were able to determine the changes in the ventilatory capacity of the isolated preparation resulting from the action of the aerosol spray. The effect of the aerosol sprays on the lungs was presumed by the authors to take place in the alveolar region. Nitric acid caused bronchoconstriction only after several consecutive administrations, each of which was of considerable duration. Moreover, administration of a bronchodilator aerosol spray (Aerolone R--0.25% isoproterenol, 0.5% cyclopentamine, 80% propylene glycol, and 20% water) to the lungs prior to the administration of the nitric acid aerosol spray prevented bronchoconstriction. No report was given of epithelial destruction.

The toxic effect of nitric acid on rat lung tissue as revealed by light and electron microscopy was reported by Greenberg et al. [46] A 0.15-ml suspension consisting of dilute nitric acid (1%) and india ink (a suspension of carbon particles) was injected into the bronchial tree of the experimental animals, following a tracheotomy which was performed under ether anesthesia. Animals were killed at various intervals ranging from 2 hours to 7 days after instillation of the suspension. The preparation was administered to 16 rats; 5 others were used as controls. Sections of the lungs were then processed by routine histological procedures for light and electron microscopic examination. The lungs of rats killed 2 and 4 hours after intrabronchial instillation of the nitric acid suspension apparently showed no significant histological changes as revealed by light microscopy. Lungs processed 8 hours after instillation showed evidence of alveolar cellular hyperplasia. An increase in the number of alveolar macrophages was also observed. Within 2-3 days following injection, these 2 reactions were heightened and there was evidence of bronchiolitis, some pneumonia, and obliterative bronchiolitis. However, electron-microscopic examination revealed more subtle cytological changes in the lungs after the shortest time interval. Thus, after only 2 hours, there was evidence in focal areas of marked edema of the cytoplasm of the membranous pneumonocytes. There was also marked degenerative change in the alveolar wall as well as fibrin in the alveolar space. The Type 2 cells showed regressive alteration with dissolution of the cytoplasm and nucleus, leaving only "ghosts" of cells and residual lamellar bodies. After 8 hours, there was a marked prominence of the endothelial cells of the alveolar capillaries. In addition, cytoplasmic processes of membranous pneumocytes (Type 1) covered partially, or completely, some degenerated granular pneumocytes (Type 2). Some Type 2 cells lacked microvilli, and free lamellar bodies and cellular fragments were seen within the alveolar spaces. Four days after injection, the damaged Type 2 cells showed accumulation of osmiophilic material in a large portion of the cytoplasm. The microvilli were absent and the osmiophilic material was randomly dispersed in the cytoplasm.

A series of interrelated studies, under the broad general heading "Toxicity of the Oxides of Nitrogen," was published by Gray and his associates. [8,17,18,26] In the 1952 study, Gray et al [26] investigated toxicity to rats by exposing several groups to the vapors of red fuming nitric acid (RFNA) for 4 hours/day. The nitrogen dioxide content of RFNA to which the animals were exposed ranged between 9 and 14 ppm. Groups of rats were exposed to RFNA for 40, 56, or 96 hours. Some animals were examined shortly after the inhalation exposure. Visual examination of the respiratory tract indicated widespread inflammation, particularly in the upper portion. Rhinitis, tracheitis, and pneumonitis were diagnosed. Other animals were examined several weeks after their inhalation exposure. In many of the latter, the respiratory inflammatory process subsided; however, localized areas of what the authors described as emphysema were evident in all lobes of the examined lungs. Moreover, these findings were not a function of the duration of exposure, since rats that were exposed to the RFNA for only 40 hours showed the same pathologic changes as those that were exposed for 96 hours. The authors concluded that exposure of rats to nitrogen dioxide greater than 8 ppm may also be injurious.

During the course of their experiments on RFNA, Gray and his associates [8,17,18,26] encountered the problem of maintaining a constant level of nitrogen dioxide in the environment. [8] This problem was due to the differences in the vapor pressures of the two components of RFNA, namely, nitric acid and nitrogen dioxide. They thus developed a new method for dispensing RFNA which made it possible to supply nitrogen dioxide from RFNA to experimental animals at a constant and reproducible rate. [8] This new dispersion method was subsequently used in two other studies. [17,18] In one of these studies, [17] acute exposures of male rats to nitrogen dioxide, RFNA, and white fuming nitric acid (WFNA) were investigated. The RFNA contained from 8 to 17% nitrogen dioxide and WFNA contained from 0.1 to 0.4% nitrogen dioxide. The animals were exposed in groups of 10 to RFNA or nitrogen dioxide, and in groups of 5 to WFNA for various periods of time. The LC50's (median lethal concentration) data reported on rats exposed to RFNA, WFNA, and nitrogen dioxide for 30 minutes are shown in Table XI-5. In terms of total concentration, the LC50 for nitrogen dioxide gas (174 ppm) was below the LC50's for RFNA and WFNA, the latter computed by NIOSH to be approximately 310 ppm and 334 ppm, respectively. The data indicated that, on an acute basis, nitric acid vapor is approximately 1/2 as toxic as nitrogen dioxide. In addition, comparison of LC50 ppm levels for WFNA (334 ppm) and RFNA (310) suggest the possibility of a synergistic toxic effect between nitric acid vapor and nitrogen dioxide since RFNA has a higher nitrogen dioxide content by weight. This latter conclusion is further supported by the authors' own evidence which showed that the LC50 for RFNA was at a lower concentration than for nitrogen dioxide when the concentration of each was expressed in ppm nitrogen dioxide. In all cases, death was due to pulmonary edema; however, burns were noted on the skin of animals exposed to the high concentrations of WFNA.

The other study [18] determined the effect of chronic exposure to low concentrations of vapors from RFNA on mice, rats, and guinea pigs. Ninety rats, 30 mice, and 10 guinea pigs were exposed to RFNA at a concentration of 4 ppm for 4 hours/day, 5 days/week, for up to 6 months. The results indicated that animals exposed to the vapors of RFNA showed no significant increase in pathologic changes, such as pulmonary congestion, when compared with control animals. As a result of the findings of this study and of those of a previous study, [26] Gray et al [18] recommended that the MAC for the oxides of nitrogen be set at 5 ppm.

Correlation of Exposure and Effect

No laboratory or epidemiologic reports of the respiratory effects of human exposures to nitric acid vapor per se have been discovered. However, it can be inferred from the limited amount of available animal data that nitric acid vapor or mist is irritating to the respiratory tract.

It is probable that direct exposure of the teeth to nitric acid vapor or mist causes erosion of those teeth and parts of teeth most exposed in the natural oral cleft. [41, 42] There is evidence that the longer the duration of exposure the more severe the extent of the dental erosion, but, in the absence of any environmental data, it is difficult to estimate the minimal concentration of nitric acid mist or vapor necessary to produce this effect. However, in both the reports in which dental erosion was attributed to nitric acid,[21,22] there was concomitant exposure to sulfuric acid, which is well known to cause dental erosion. [42] In the mixture of acids employed in both studies [41, 42] sulfuric acid was the major acid constituent, and nitric acid the minor.

The severity of injury caused by the corrosive effects of liquid nitric acid upon the skin [13, 14], the eyes, [15] and the gastrointestinal tract [24, 37, 38, 39] is clearly dependent upon the concentration of the acid, the duration of contact, and the absolute quantity of acid involved.

The limited animal data reported indicate that the 30-minute LC50 for WFNA in rats is approximately 334 ppm (224 ppm measured as nitrogen dioxide), and that death in these animals appeared to be due to pulmonary edema. [17] However, a single exposure of rats to 25 ppm of nitric acid vapor for an unstated duration of time had no apparent effect. [44] Toxic effects of exposure to oxides of nitrogen, particularly nitrogen dioxide, have been reported for humans and research animals at much lower concentrations (See _Criteria for a Recommended Standard_....._Occupational Exposure to Oxides of Nitrogen_). At low concentrations, therefore, the 2:1 ratio of toxicity between nitrogen dioxide and nitric acid may not exist. A small amount (0.15 ml) of a 1% solution of nitric acid instilled directly into the bronchial tree of rats caused subtle cytological changes in the alveolar epithelial cells 2 hours following instillation. These changes were detectable only by electron microscopy. Within 3-4 days after instillation, gross pulmonary complication occured as evidenced by bronchiolitis, some pneumonia, and obliterative bronchiolitis. [46] However, it is difficult to relate such instillation dosage to doses of nitric acid vapor which are inhaled.

IV. ENVIRONMENTAL DATA

Environmental Concentrations

Published data concerned with airborne exposures involving nitric acid have been limited, for the most part, to measurements of the total oxides of nitrogen. Elkins [47] reported that in 6 studies of acid dipping by the Massachusetts Department of Labor and Industries, the maximum concentration of nitrogen dioxide found was 14 ppm with an average of 5 ppm. Wade et al, [25] in another report from the same organization, presented the following data on "acid dip fumes":

TABLE IV-1

AIRBORNE LEVELS OF NITROGEN OXIDES FROM ACID DIPPING

Acid Strength		Tests	Range of Concentration of Total Nitrogen Oxides ppm
Unknown		2	5-7
Concentrated:	Operator's exposure	4	2-6
	Over tank	1	110
Ten percent		3	3-8

Concentrations of airborne nitric acid and nitrogen dioxide associated with production of nitric acid at the Tennessee Valley Authority's National Fertilizer Development Center have been presented in an unpublished report by Myers (written communication, April 1975). The following table summarizes results of measurements made during the past 30 years:

TABLE IV-2

AIRBORNE LEVELS OF NITRIC ACID AND NITROGEN DIOXIDE ASSOCIATED WITH FERTILIZER PRODUCTION

Date	Type of Processing	No. of Units Operating	Airborne Agent	Measurement Location	Concentration in ppm
Unknown	Atmospheric	12	NOX*	Area around absorption tower	30-75**
1945	"	12	"	Plant vicinity	Mean=10.5** Max=35
1945	"	12	NO2	Work area	0.1-12.2 Mean=2.3
1945	"	12	HNO3	"	0.7-3.2 Mean=1.2
1961	"	6	NO2	"	0.8-3.0
1966-67	Pressure	3	NOX*	"	0.6-2.6**
1975	"	1	"	"	0.5**

* Refers to a mixture of airborne nitric acid, nitrogen dioxide, and nitric oxide

** Expressed as nitrogen dioxide

Engineering Controls

Since the use of nitric acid presents potential inhalation hazards and also dangers arising from skin contact with the acid in its liquid form, careful attention must be given to engineering controls as well as to work practices.

The control of nitric acid vapor and mist, as well as nitrogen oxides evolved from operations or processes conducted in fixed locations, may generally be effected under normal situations through use of conventional enclosure or local exhaust ventilation practices. [1, 2]

It is particularly important that all equipment be adequately resistant to the strengths of nitric acid involved and constructed so that leaks cannot develop. Failure to meet such criteria can result in serious, even fatal, consequences. [48] The Manufacturing Chemists' Association [7] points out the need for electrical fixtures to be of vaporproof type, and for all wiring and other electrical equipment to be suitable for corrosive atmospheres. The Association also recommends that operations in which large scale formation of nitrogen oxides may occur should be housed in one-story buildings from which rapid escape would be possible, or if taller structures must be used, means for rapid exit from upper floors should be provided.

Buildings, floors, and other structural elements should be of such design and materials as to minimize adverse effects which could result in the event of spills, leaks, or other accidents. This should include the provision of readily accessible water supply in adequate quantity for rapid flushing away of the maximum amount of acid which could be lost.

Sampling and Analytical Methods

Chemical methods for the analysis of nitric acid fall into two general categories: acid titration and nitrate methods. Both suffer from the same problem, lack of specificity to differentiate between oxides of nitrogen and nitric acid.

Acid titration is a simple procedure which is carried out routinely in any laboratory. A sample is collected in an impinger containing a known amount of alkaline solution. The excess base is then determined by titration, and from this total, acidity can be calculated. Since total acidity is determined, the presence of any other acids in the atmosphere may yield artificially high results which would not be indicative of the true nitric acid concentration.

A number of colorimetric nitrate methods have been used for both air and water analyses. These include the phenoldisulfonic acid method, [49,50] the 2,4-xylenol method, [51] and the brucine method. [50]

The phenoldisulfonic acid method was first used for determination of nitrates in water. It has since been adapted as an air pollution method and is recommended by the Intersociety Committee [49] for determination of total nitrogen oxides including nitric oxide (NO), nitrous anhydride (N2O3), nitrogen dioxide (NO2), nitrogen tetroxide (N2O4), vapor or mist of nitric acid (HNO3), and nitrous acid (HNO2). The method depends on the oxidation of these compounds to the nitrate ion by hydrogen peroxide in an acidic medium, and subsequent reaction of the nitrate with phenoldisulfonic acid to form a yellow compound which is measured spectrophotometrically at 410-420 nm. Possible interferences include nitrites, reducing compounds such as sulfur dioxide, and chlorides. It is a time-consuming method and accuracy below 50 ppm is questionable.

For sampling and analysis of nitrates in atmospheric particulate matter, the Intersociety Committee [51] recommends the 2,4-xylenol method. As presented, it calls for collection of a 24-hour sample on an 8" by 10" glass fiber filter attached to a high-volume sampler. Although it is theoretically possible to adapt personal sampling with smaller membrane filters to shorter duration, recent experiments indicate that nitric acid vapor penetration of the filters may be a problem (L Doemeny and J Holtz, written communication, August 21, 1975). This method is subject to interference by nitrites, chlorides, and oxidizing agents.

The brucine method, [50] a colorimetric determination simpler than the phenoldisulfonic acid method, was also initially developed for the determination of nitrates in water. It has been successfully adapted to the analysis of air samples from occupational exposures. The reaction of brucine and nitrate at a controlled temperature produces a yellow color. The intensity of the color is measured spectrophotometrically at 410 nm. Among the disadvantages of this method are the facts that brucine is highly toxic and that the analysis procedure calls for heating the sample.

Another nitrate method utilizes the specific ion electrode. Nitrates must be collected in an aqueous solution into which an ionic strength adjustor (potassium fluoride) and a preservative solution (phenylmercuric acetate) are added. Interference by bicarbonate and chloride may be removed by acidification of the sample and by substitution of AgF for KF in the ionic strength adjustor, respectively. The electrode is then placed in the sample solutions, and a reading is obtained on either a pH/mV meter or a specific ion meter. [52,53,54] If a pH/mV meter is used, a calibration curve must be constructed by measurement of standard solutions (usually 10 and 100 ppm nitrate). If the specific ion meter is used, a direct reading of sample concentration is made following calibration of the meter using standard solutions. In both cases, determinations below 1 ppm are difficult. Leakage of the electrode has also been found to be a problem (L Doemeny and J Holtz, written communication, July 28, 1975).

In 1964, a spectrophotometric analytic method with good specificity for nitric acid was reported in the Russian literature. [55] It distinguishes nitric acid from other nitrates in the atmosphere and eliminates interference by sulfur dioxide under the conditions described. It is sensitive to levels well below the current workroom environmental limit. However, there has been no testing of the efficiency of the sampling method.

The recommended method for sampling is collection via an impinger containing distilled water. This is a convenient field method, but efficiency of absorption by distilled water as opposed to an alkaline solution is questionable. Current NIOSH tests, not yet complete, of a collection method using glass fiber filters indicate that the filters have poorer collection efficiency and recovery for nitric acid than the impinger.

In conjunction with the above sampling method, an ultraviolet spectrophotometric analytic method is being recommended. It is based upon a method published for analysis of nitrates in natural and treated waters. [50] This method is simpler and faster than any of the colorimetric methods and has acceptable sensitivity (0.177 ppm) and good accuracy.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

The first recommended environmental limit for nitric acid was 10 ppm (about 25 mg/cu m) as an 8-hour TWA, suggested as a tentative Threshold Limit Value (TLV) by the American Conference of Governmental Industrial Hygienists (ACGIH) [56] in 1956. The following year, this tentative value was adopted as the ACGIH recommendation, although the value cited was misprinted as "5 ppm" or approximately 25 mg/cu m. [57] The following year, this misprint was corrected [58] and the ACGIH recommended that the TLV for nitric acid remain 10 ppm through 1963. In 1964, the TLV was tentatively revised downwards to 2 ppm (about 5 mg/cu m), [59] and in 1966, 2 ppm was adopted as the definite recommendation of the ACGIH. [60]

The basis for these ACGIH recommendations appears, from the ACGIH Documentation of the Threshold Limit Values, [61] to have been largely analogous to the other mineral acids. It was pointed out that the proposed value of 2 ppm for nitric acid was intermediate between the 5 ppm TLV for hydrogen chloride and the 0.25 ppm for sulfuric acid, and the opinion was expressed that 2 ppm is low enough to prevent pulmonary irritation and corrosive effects on the teeth, but possibly not low enough to prevent potentiation of the effects of nitrogen dioxide. However, the papers cited as documentation were those of Lynch and Bell [42] in 1947, Diggle and Gage [44] in 1954, and Fairhall's textbook [28] of 1957, all of which have been reviewed in this document and none of which contains any environmental data. Furthermore, the ACGIH Committee recommended a higher TLV for nitrogen dioxide than for nitric acid, although the documentation for the latter substance states that nitrogen dioxide is more toxic. Therefore, the recommended ACGIH TLV for nitric acid must be regarded as that Committee's judgmental recommendation.

There is no American National Standard Institute (ANSI) recommended standard for nitric acid.

The current federal standard for nitric acid is 2 ppm or 5 mg/ cu m as an 8-hour TWA (29 CFR Part 1910.93 published in the <u>Federal Register</u> 37:22139, October 18, 1972). This is based upon the ACGIH TLV.

The Maximum Acceptable Concentration for nitric acid as of 1970 was 10 ppm in Finland, the Federal Republic of Germany, Japan, Poland, and Rumania, and 25 ppm in Yugoslavia, according to the International Labour Office. [62]

Basis for the Recommended Environmental Standard

Concentrated liquid nitric acid is corrosive and produces severe chemical burns on contact with the skin, [13,14] with the eyes, [14,15] and with the gastrointestinal tract. [24,37,38,39] Furthermore, nitric acid vapor or mist has been found to be a pulmonary irritant to man [28] and animals. [17,45]

Nitric acid vapor or mist may cause dental erosion to those parts of the incisor and canine teeth exposed in the natural oral cleft, and this effect may develop within three months of occupational exposure to levels of acid not reported as causing other symptoms. [40,42] However, in almost all occupational exposures to nitric acid, there is concomitant exposure to oxides of nitrogen, especially to the dioxide, because these gases are evolved when nitric acid decomposes or when the acid reacts with the materials with which it comes in contact, whether metal or organic material. [14,20,21,22,23]

Very little is known quantitatively about the effects of inhalation of nitric acid vapor in experimental animals. Data on human exposure have not been found. According to Diggle and Gage, [44] single exposures of rats, for an unstated period of time, to 63 mg/cu m (about 25 ppm) had no apparent effect. Gray et al [17] exposed rats to the vapor of white fuming nitric acid, containing less than 0.5% dissolved nitrogen dioxide, and found the 30-minute LC50 to be variable, but averaging 334 ppm (244 ppm measured as nitrogen dioxide). No animal data have been found on exposures between about 25 and 244 ppm.

In parallel experiments with pure nitrogen dioxide and with red fuming nitric acid (containing from 8 to 17% of dissolved nitrogen dioxide), Gray et al [17] found that the red fuming acid vapor was slightly more toxic than acid-free nitrogen dioxide at the same measured concentration of nitrogen dioxide. At the same time, they found that nitric acid vapor alone was "much less toxic" than either the vapor of red fuming nitric acid or nitrogen dioxide. They therefore concluded that with mixtures of nitric acid vapor and nitrogen dioxide gas, the latter is the primary toxic constituent, but that nitric acid might slightly potentiate the effects of nitrogen dioxide.

At the present time, it is known that contact with concentrated liquid nitric acid has corrosive effects on the skin [13,14] and on mucous membranes. [24,37,38,39] However, only minimal quantitative data are available on the pulmonary effects resulting from inhalation of nitric acid vapor or mist as distinct from the effects of the oxides of nitrogen. In the absence of data showing toxic effects in humans and animals exposed to nitric acid at and below 2 ppm, it is recommended that the current federal standard of 2 ppm be continued as a TWA for up to 10 hours/day and 40 hours/week. It is interesting to note that the recommended workplace limit for nitric acid is twice that recommended for nitrogen dioxide in Criteria for a Recommended Standard...Occupational Exposure to Oxides of Nitrogen, and that the relative toxicity from acute exposures, as measured by experimental animal mortality, [17] is approximately twice as great for nitrogen dioxide as for nitric acid. However, future research should be conducted to determine chronic effects of inhaling low concentrations of airborne nitric acid independent of exposure to nitrogen dioxide as well as determination of the toxic potentiation of nitrogen dioxide by nitric acid vapor or mist.

In an industrial environment, the occupational hazard associated with the production, use, and handling of nitric acid is in two forms, namely topical contact with the liquid form of nitric acid and inhalation of nitric acid vapor and mist. Available workplace data suggest that workers in some occupations are exposed to extremely low concentrations of airborne nitric acid. Under such conditions, it should not be necessary to comply with many of the provisions concerned with airborne hazards associated with nitric acid vapor and mist. Concern for worker health requires that protective measures be instituted below the airborne workplace limit in order to ensure that exposures to the vapor and mist of nitric acid do not exceed the standard. Therefore, "occupational exposure to nitric acid" has been defined as exposure to airborne nitric acid equal to or exceeding one-half of the workplace environmental (workroom air) limit. However, since a significant topical hazard exists from contact of the skin or eye with concentrated nitric acid, it is recommended that appropriate work practices and protective measures be required regardless of the airborne concentration of nitric acid. Furthermore, since the combination of nitric acid with metals, oxidizable substances, or air results in the release of oxides of nitrogen, it is imperative that sampling for oxides of nitrogen be done concomitantly with the sampling for airborne nitric acid.

VI. RESEARCH NEEDS

Epidemiologic Studies

Available animal research indicates that exposure to nitric acid may result in the same or similar changes in the pulmonary system as exposure to the oxides of nitrogen, ie, pulmonary edema, [17] bronchiolitis, pneumonia, and obliterative bronchiolitis. [46] However, as stated in Chapters III and V, no reports have been found on chronic effects in humans resulting from long-term exposure to low concentrations of nitric acid vapor. Therefore, cross-sectional studies of pulmonary function, including measures of ventilatory mechanics and spirometry, should be conducted on selected groups of workers routinely exposed to nitric acid vapor in order to discover and evaluate any effects from such exposure. Posterior-anterior chest X-ray films should also be studied for signs of chronic obstructive pulmonary diseases.

Further research is also needed to determine the incidence of dental erosion in workers employed in the manufacture, use, and handling of nitric acid.

Acute Effects of Exposure to Nitric Acid Vapor in Humans

Reports of acute effects of exposure to nitric acid vapor in humans have been limited to industrial accidents [19,20,21,22,23] in which exposures were to unknown but presumably high concentrations of the oxides of nitrogen and nitric acid vapor. Research is needed to determine if nitric acid vapor per se at concentrations at and below the recommended environmental limit can produce acute changes in pulmonary function.

Chronic Animal Exposure Studies

Several different animal species should be exposed to concentrations of nitric acid vapor between 0.05 and 25 ppm for 8-10 hours/day, 5 days/week, for 18-24 months in order to evaluate:

(a) long-term physiologic effects with particular emphasis on macro- and microscopic changes in the pulmonary system;

(b) dose-effect relationships on selected dependent variables, and

(c) interspecies variation of effects.

Similar studies should be conducted using combined oxides of nitrogen-nitric acid vapor exposure in order to assess potentiation of the toxic effects of the oxides of nitrogen by nitric acid.

Mutagenicity and Teratogenicity

Nitrous acid has been shown to be a potent mutagenic agent. [63] Presumably, nitrates from nitric acid serve as a reservoir of nitrates via reduction. [63] However, no evidence has been found of the direct mutagenic properties of nitric acid. Therefore, studies of the possible mutagenicity of nitric acid, including microbial screens, should be conducted. In addition, research should be conducted to determine possible teratogenic effects of exposure to nitric acid vapor.

Risk of Tumor Formation Following Nitric Acid Exposure

The formation of certain carcinogenic agents such as nitrosamines from their precursors may occur in acidic environments. Laboratory studies should be undertaken to determine the kinetics and thermodynamics of nitrosamine formation from secondary amines and low concentrations of nitric acid vapor. Environmental studies should be initiated in occupations where both nitric acid and secondary amines exist in order to determine if nitrosamines are formed in the workplace air. Furthermore, laboratory animals should be examined for neoplastic lesions following lifetime exposure to nitric acid vapor. If such changes do occur, the dose-response relationship should be determined at concentrations in the neighborhood of the proposed environmental limit. Finally, animal experiments using exposures to nitric acid vapor in combination with other occupational contaminants, such as hydrocarbons, fibrous dusts, and other pulmonary irritants should be conducted to investigate potential additive, synergistic, or inhibitory effects of nitric acid on neoplastic dose-response relationships.

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VIII. APPENDIX I

METHOD FOR SAMPLING NITRIC ACID

Introduction

The recommended sampling method employs a 25-ml midget impinger filled with distilled water sorbent. Concentrations of airborne nitric acid are determined by measuring the ultraviolet absorption at 220 nm by means of an ultraviolet spectrophotometer. The National Institute for Occupational Safety and Health (NIOSH) is currently evaluating the collection efficiency and recovery of a number of filters including a Gelman Type A (glass-fiber filter) or equivalent for use in sampling airborne nitric acid. It was believed that the filter collection device would be superior to the impinger because the former would have greater durability in the field and lower interference from ambient oxides of nitrogen. However, preliminary findings indicate that 4 filters tested thus far have poorer collection efficiency and reliability than the impinger method. However, results are incomplete at this time. A final report will be published in a future edition of the *NIOSH Manual of Analytical Methods*.

General Requirements

In order to evaluate compliance with the standard, half-hour breathing zone samples, representative of the individual worker's exposure, shall be collected. The sample data sheet shall include:

(a) Date and time of sample.

(b) Sample duration.

(c) Volumetric flow rate of sampling.

(d) Description of sampling location.

(e) Other pertinent information.

Air Sampling Requirements

(a) Half-hour breathing zone samples representative of the worker's exposure shall be collected to characterize the exposure from each job or specific operation in each production area.

(b) Samples shall be collected using personal sampling pumps and a 25-ml midget impinger containing 20 ml of doubly distilled water sorbent. A teflon baffle should be installed on the impinger stem at the 25-ml level.

(c) The sample shall be taken at a flow rate of 2.8 liters/minute (lpm). A sample size of 200 liters is required.

(d) A sufficient number of samples shall be taken to allow determination of compliance or noncompliance with the recommended limit at the 95% confidence level. Determination of compliance or noncompliance given the sampling accuracy, analytic accuracy, and type of sampling (eg, full-period consecutive sampling, partial-period consecutive sampling), has been described by NIOSH. [64]

(e) Blank impingers, filled from the same distilled water source as the used bubblers, shall be carried to the sampling site to provide a background correction which must be applied to the analytical results. The number of blank impingers required shall be as follows: 3 for 20 or fewer samples, and 1 for each additional 10 samples.

Sample Procedure

(a) Connect the impinger to the pump with a piece of flexible tubing. If personal sampling is being done, the midget impinger is placed in a midget-impinger holder and fastened to the worker in his breathing zone.

(b) Turn on the pump and set the flow rate to 2.8 liters/minute according to the manufacturer's directions. Periodically check the flow rate and readjust as needed. Terminate sampling if unable to readjust. In addition, check the level of solution in the impinger. If less than 5 ml of solution remains in the impinger, fill the impinger back up to the 20-ml mark.

(c) After sampling, quantitatively transfer the impinger solution to the glass vial. Use 1 or 2 ml of solution to wash the impinger. Transfer the wash to a glass vial. Tightly screw on the cap and seal with vinyl tape.

(d) Record ambient temperature and pressure. If ambient pressure is unavailable, record the elevation.

(e) Use one impinger as a blank. Handle it the same way as any other impinger but do not draw air through it. Label this solution as a blank.

Interferences

The following substances will interfere with NO3 analysis: nitrite, dissolved organic matter, hexavalent chromium, surfactants, suspended particles, hydroxide, and carbonate.

Shipping

Ship in a container designed to prevent damage in transit.

Calibration of Sampling Trains

Accurate calibration of sampling pumps is essential for correct interpretation of the measured concentration. Sampling pumps should be initially calibrated or recalibrated if subjected to misuse, repair, or frequent hard usage.

Ordinarily, pumps should be calibrated in the laboratory both before and after they are used to collect large numbers of field samples. The accuracy of the calibration is dependent on the quality of the standard reference instrument. For laboratory calibration, a 1-liter buret is recommended. Other standard calibrating instruments can be used for field calibration.

XI. APPENDIX II

ANALYTICAL METHOD FOR NITRIC ACID

The recommended analytical method is based on an ultraviolet spectrophotometric procedure described by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation. [50]

Principle of the Method

Measurement of the ultraviolet absorption at 220 nm enables a rapid means of determining nitrate. The nitrate calibration curve follows Beer's law up to 15.5 μg NO3/ml nitrogen. Because dissolved organic matter may also absorb at 220 nm and nitrate does not absorb at 275 nm, a second measurement is made at 275 nm to correct the nitrate value. The extent of this empirical correction is related to the nature and concentration of the organic matter.

Interferences

Dissolved organic matter, suspended particles, hydroxide, carbonate, nitrite, chromium(VI), and surfactants interfere. The latter three substances may be compensated for by the preparation of individual correction curves.

All glassware must be thoroughly cleaned and rinsed in order to reduce the errors which might result from streaks or particles on the outside of the cuvettes, as well as traces of surfactants or dichromate cleaning solution which might adhere on the interior glass surfaces.

The ultraviolet method yields best results in the presence of very low color interference and appreciable nitrate content. Colored samples should accordingly be treated with aluminum hydroxide, or diluted to minimize color interference.

Apparatus

(a) Spectrophotometer: A spectrophotometer for use at 220 nm and 275 nm with matched silica cells having 1-cm or longer light path. A Beckman Model DU spectrophotometer with a photomultiplier attachment and hydrogen lamp source, or equivalent.

(b) Impinger: A midget impinger, 25-ml size, containing 20 ml of redistilled water.

Reagents

(a) Redistilled water: Use redistilled water for the preparation of all solutions and dilutions.

(b) Standard nitrate solution: Dissolve 850.0 mg of anhydrous sodium nitrate and dilute to 1000 ml; 1.00 ml = 620 μg NO3.

(c) Aluminum hydroxide suspension: Dissolve 125 g of aluminum potassium sulfate or ammonium sulfate redistilled water. Warm to 60C and add 55 ml concentrated NH4OH slowly, with stirring. After 1 hour, transfer to a large bottle and wash the precipitate by successive additions (with thorough mixing) and decantations of distilled water until free from ammonia, chloride, nitrate, and nitrite. Finally, after settling, decant off as much clear liquid as possible, leaving only the concentrated suspension.

Analysis Procedure

(a) Midget impinger: Absorbance can be measured directly from the solution. However, if the solution has a high color or contains organic substance, decant the solution into a 15 ml graduated centrifuge tube and add 0.5 ml aluminum hydroxide suspension into the sample. Cap the centrifuge tube with a parafilm strip and mix thoroughly. Centrifuge at 2,000 rpm for 5 minutes.

(b) Preparation of standard curve: Prepare nitrate calibration standards in the range 0-15.5 μg NO3/ml by diluting to 50 ml the following volumes of the standard nitrate solution: 0, 0.05, 0.1, 0.2....1.25 ml. Treat the nitrate standards in the same manner as the samples.

(c) Spectrophotometric measurement: Read the absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Use a wavelength of 220 nm to obtain the nitrate reading and a wavelength of 275 nm to obtain the interference due to dissolved organic matter.

(d) Preparation of correction curves for nitrite, chromium(VI) and surfactants: When nitrite, chromium(VI) and anionic surfactants are known to be present in the sample, prepare correction curves for each of these substances at 2 mg/liter intervals up to 10 mg/liter. Use potassium nitrite, potassium dichromate, and linear alkylate sulfonate, with redistilled water for this purpose. Measure the absorbances given by each substance at a wavelength of 220 nm against redistilled water and plot a separate curve for each of these interfering materials.

Calculations

(a) Correction for dissolved organic matter: Subtract 2 times the reading at 275 nm from the reading at 220 nm to obtain the absorbance due to nitrate. Convert this absorbance value into equivalent nitrate by reading the nitrate value from a standard calibration curve obtained at 220 nm.

(b) Correction for nitrite, hexavalent chromium, or surfactants: Deduct the equivalent nitrate values for each of these interfering substances from the gross nitrate result.

(c) Calculations: Plot absorbance against concentration, and obtain the concentration from the standard curve.

$$\mu g \ HNO3 = (\mu g/ml \text{ from the curve}) x (\text{sample vol}) x (1.016)$$

Convert the volume of air sampled to standard conditions of 25(C) and 760 mmHg.

$$Vs = V \times \frac{P}{760} \times \frac{298}{T+273}$$

Vs = volume of air in liters at 25 C and 760 mmHg.

V = volume of air in liters as measured.

P = barometric pressure in mmHg.

T = temperature of air in centigrade.

$$\frac{mg \ HNO3}{cu \ m \ air} = \frac{\mu g \ HNO3}{Vs}$$

X. APPENDIX III - MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the procedures described in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. [52] The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, ie, "100 mg/kg LD50-oral-rat," "25 mg/kilo LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flammability or reactivity data could be flash point, shock sensitivity, or other brief data indicating nature of the hazard.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicate if by weight or volume) at 70 F (21.1 C); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation data are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flash point and autoignition temperature in degrees Fahrenheit (Centigrade in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Data

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50, if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact with concentrated acid is painful and burns the skin.
>
> Eye Contact--painful, opacification of cornea, may result in blindness.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed workers.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility with common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc.

"Hazardous Decomposition Products" shall include those products released as a result of fire. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect workers assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," "Suitable for dusts not more toxic than lead," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage.

Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to workers potentially exposed to the hazardous material. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA

BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT
% VOLATILES BY VOL.		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)		AUTOIGNITION TEMPERATURE	

FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER	

EXTINGUISHING MEDIA	
SPECIAL FIRE FIGHTING PROCEDURES	
UNUSUAL FIRE AND EXPLOSION HAZARD	

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS

OTHER HANDLING AND STORAGE REQUIREMENTS

PREPARED BY

ADDRESS:

DATE.

XI. TABLES

TABLE XI-1

PHYSICAL DATA ON CHEMICALLY PURE NITRIC ACID

%HNO3	Sp.Gr.at 15.5 C(60 F)	Melting Points C	F
52.30	1.3303	-19.5	-3
56.52	1.3551	-20.0	-4
61.38	1.3810	-24.5	-12
67.18	1.4078	-33.0	-27
70.33	1.4216	-42.5	-45
80.04	1.4610	-39.0	-38
85.70*	1.4796	-47.0	-53
95.11	1.5026	-52.0	-62

* Considered "fuming acid" above this strength. "Red fuming acid" is high strength nitric acid containing varying percentages of oxides of nitrogen in solution at normal temperatures. At elevated temperatures all nitric acid will give off gaseous oxides of nitrogen (commonly called "nitrous fumes").
From reference 7

TABLE XI-2

PROPERTIES AND CHARACTERISTICS OF NITRIC ACID

	100%	Aqueous Solution
Physical state	Liquid	Liquid
Explosive limits	Nonflammable	Nonflammable
Boiling point	86 C (186.9 F)	Constant boiling mixture 68 to 68.5% HNO_3 121.6 C (251 F)
Color	Colorless	Colorless to light brown
Corrosivity	Will vigorously attack most metals	
Hygroscopicity	Yes	Yes
Light sensitivity	Water white acid becomes amber to brown depending upon strength of acid and exposure	
Odor	HNO_3 vapors acrid--Oxides of nitrogen sweet to acrid	
Reactivity	Will react readily with most chemicals. Strong nitric in contact with wood and some other organic materials may cause fire	

From reference 7

TABLE XI-3

VAPOR PRESSURES OF HNO_3 AND NO_2

HNO_3		NO_2	
Temp, C	Vp, mm Hg	Temp, C	Vp, mm Hg
20	42	21.3	760
30	77	30	1125
40	133	40	1733
50	215	50	2599
60	230	60	3823

From Gray et al [8]

TABLE XI-4

POTENTIAL OCCUPATIONAL EXPOSURES TO NITRIC ACID

Aircraft workers
Ammonium nitrate makers
Bleachers
Brass cleaners
Bright-dip workers
Cellulose nitrate makers
Drugmakers
Dyemakers
Electroplaters
Etchers
Jewelers
Laboratory workers, chemical
Lithographers
Mirror makers
Nitration workers
Nitric acid workers
Nitrobenzene makers
Nitro-compound workers
Ore flotation workers
Organic chemical synthesizers
Photoengravers
Rocket fuel handlers
Steel etchers
Sulfuric acid makers

From reference 12

TABLE XI-5

EXPOSURE OF MALE RATS TO NITRIC ACID FUMES AND NITROGEN DIOXIDE

Chemical Agent	No. of Runs	LC50 in ppm NO2 (Total Concentration)
Red Fuming Nitric Acid	9	138 (310)*
Nitrogen Dioxide	10	174 (174)
White Fuming Nitric Acid (WFNA)	16	244 (334)*

*Total concentration computed by NIOSH. Based upon molecular weights and the percentage of nitrogen dioxide in white and red fuming nitric acid.

Adapted from Gray et al [17]

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