criteria for a recommended standard . . . .

OCCUPATIONAL EXPOSURE
TO
SODIUM HYDROXIDE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Center for Disease Control
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 sodium hydroxide by members of my staff, the valuable and constructive comments presented by the Review Consultants on Sodium Hydroxide, by the ad hoc committees of the American Conference of Governmental Industrial Hygienists and the American Occupational Medical Association, by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine, and by William A. Burgess on respiratory protection. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on sodium hydroxide. Lists of the NIOSH Review Committee members and of the Review Consultants appear on the following pages.

for

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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 recommended standard for sodium hydroxide. The University of Michigan developed the basic information for consideration by NIOSH staff and consultants under contract No. HSM-99-73-31. Jack E. McCracken, Ph.D., had NIOSH program responsibility and served as criteria manager.

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CRITERIA DOCUMENT: RECOMMENDATIONS FOR AN OCCUPATIONAL EXPOSURE STANDARD FOR SODIUM HYDROXIDE

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I. RECOMMENDATIONS FOR A SODIUM HYDROXIDE STANDARD

The National Institute for Occupational Safety and Health recommends that worker exposure to sodium hydroxide in the workplace be controlled by compliance with the following sections. The standard is designed to protect the health and safety of workers over a working lifetime. Compliance with the standard should prevent adverse effects of occupational exposure to sodium hydroxide. 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.

Occupational exposure to sodium hydroxide is defined as exposure to airborne concentrations of sodium hydroxide exceeding one-half of the recommended workplace environmental limit. Adherence only to sections 4(a), 4(b), 6(a) (1, 2, 7, 8, and 9), and 7(a) is required when workplace environmental concentrations of sodium hydroxide are not greater than one-half of the recommended workplace environmental limit. Synonyms for sodium hydroxide include caustic soda, lye, and white caustic.

Section 1 - Environmental (Workplace Air)

(a) Concentration: Occupational exposure to sodium hydroxide shall be controlled so that no worker is exposed to sodium hydroxide at a concentration greater than 2.0 mg/cu m of air for any 15-minute sampling period.

(b) Sampling and Analysis: Procedures for sampling, calibration of equipment, and analysis of sodium hydroxide samples shall be as provided in Appendices I and II, or by any method shown to be equivalent to the methods specified.

Section 2 - Medical

Medical surveillance shall be performed as outlined below for all workers occupationally exposed to sodium hydroxide, including maintenance personnel periodically or occasionally exposed during routine maintenance or emergency repair operations.

(a) Comprehensive preplacement medical examinations shall be provided to all workers subject to exposure to sodium hydroxide. The examinations shall include an evaluation of the advisability of the workers' using negative or positive pressure respirators.

(b) Medical examinations shall be made available promptly to all workers with signs or symptoms of skin, eye, or upper respiratory tract irritation from exposure to sodium hydroxide.

(c) If clinical evidence of injury from exposure to, or local contact with, sodium hydroxide is developed from these medical examinations, the worker shall be kept under a physician's care until the worker has completely recovered or maximal improvement has occurred.

(d) Examinations of current workers shall be performed within 6 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, of the employee or former employee, and of the employer shall have access to all pertinent medical records.

(f) Medical records shall be maintained for all persons with exposure to sodium hydroxide and for maintenance personnel with occasional exposure. Applicable medical records, including information on all required medical examinations, shall be retained for at least 5 years after the termination of the individual's employment.

Section 3 - Labeling (Posting)

(a) All shipping and storage containers of anhydrous or hydrated sodium hydroxide (solid caustic soda) shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

CAUSTIC SODA
(Sodium Hydroxide)
DANGER! CAN CAUSE SEVERE BURNS OR BLINDNESS

Before using, secure information on procedure and
  protective measures for safe handling.
Do not get in eyes, on skin or clothing.
Avoid breathing dusts or mists.
Do not take internally.
When handling, wear goggles or face shield. While
  making solutions, add slowly to surface of solution
  to avoid spattering.
In case of contact, immediately flush eyes or skin
  with plenty of water for at least 15 minutes; for
  skin and eye burns, call a physician.
Remove contaminated clothing and shoes and wash before reuse.
Spill or leak: Thoroughly flush area with water.

(b) All shipping and storage containers of solutions of sodium hydroxide (liquid caustic soda) shall bear the label in 3(a) except that LIQUID CAUSTIC SODA shall replace CAUSTIC SODA, and (Sodium Hydroxide Solution) shall replace (Sodium Hydroxide).

(c) In areas or equipment where contact with, or inhalation of, sodium hydroxide (solid or solution) is likely, the following warning signs shall be posted in readily visible locations, particularly at entrances to these areas:

EXTREMELY DANGEROUS CHEMICAL
(CAUSTIC SODA, SODIUM HYDROXIDE)
USED IN THIS AREA
CAN CAUSE BURNS OR BLINDNESS
Unauthorized Persons Keep Out

Any special precautionary requirements for safety equipment or practice in the area should also be noted on the sign.

If respiratory protective devices are to be used, add to the warning sign a statement specifying the requirements for use of such equipment and describing the location of the respirators.

(d) During any loading, unloading, or transfer of sodium hydroxide solution (liquid caustic soda) through temporary transfer lines or lines with temporary connections, the following sign shall be prominently displayed in the area, particularly at points of potential release of, or exposure to, this chemical.

EXTREMELY DANGEROUS CHEMICAL
(CAUSTIC SODA, SODIUM HYDROXIDE)
CAN CAUSE BURNS OR BLINDNESS
TRANSFER IN PROGRESS
Unauthorized Persons Keep Away

If the area or equipment is posted as provided in section 3 subsection (c), the temporary sign is not required.

(e) During loading or unloading of a tank car or tank truck with sodium hydroxide solution (liquid caustic soda), caution signs as follows:

STOP!
TANK CAR
CONNECTED

shall be displayed at least 50 ft fore and aft of the car or truck in addition to applicable signs described in Section 3, subsections (c) and(d).

In Section 3, subsections (c), (d), and (e), signs shall also be printed in the predominant language of non-English-speaking workers, if any, unless they are otherwise informed. All illiterate workers shall be so informed.

Section 4 - Personal Protective Equipment

Engineering controls shall be used to maintain airborne sodium hydroxide concentrations at or below the prescribed limit. Requirements for personal protective equipment shall be as approved under provisions of 29 CFR 1910.132.

(a) Eye and Face Protection

Eye protective equipment shall be provided by the employer and used by the employee where eye contact with sodium hydroxide is likely.

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

(2) At all operations where there is danger of sodium hydroxide (solid or in solution) coming in contact with the eyes, chemical safety goggles with resistant glass or plastic lenses and adequate air vents that do not allow entry of liquids shall be worn. Plastic chemical goggles may be worn over metal or plastic frame safety spectacles with prescription safety lenses. Safety spectacles may not be used alone for

protection from splashes, mists, or dust of sodium hydroxide.

(3) At any operation where splashes of sodium hydroxide solution are likely to occur and there is danger of such splashes striking the face, a full-length (8-inch minimum) plastic face shield shall be worn in addition to chemical safety goggles.

(4) Protective hats with brims shall be worn by workers at operations or in areas where there is a likelihood of overhead splashes or leaks. Where there is also danger of falling objects, hard hats with brims shall be worn. (Aluminum hard hats shall be excluded because they are incompatible with strong caustics.)

(b) Skin Protection

(1) Sodium hydroxide will produce skin burns at the site of contact. Impervious protective clothing made of rubber, neoprene, or other caustic-resistant material, such as gloves, aprons, suits, hoods, boots, and overshoes, shall be provided by the employer and worn by the employee when there is a likelihood of body contact with sodium hydroxide.

(2) Sodium hydroxide-wetted clothing, unless impervious, shall be removed promptly.

(3) Work clothing should not be made from wool; cotton is preferred because it is not rapidly affected by sodium hydroxide. Pant legs should cover the tops of boots. Shirts should be long-sleeved and buttoned at the collar. Leather footwear does not provide adequate protection against spills of sodium hydroxide.

(c) Respiratory Protective Equipment

Engineering controls shall be used wherever feasible to maintain airborne sodium hydroxide concentrations below those recommended in Section

1 above. Compliance with the permissible exposure limit by the use of respirators is only allowed when airborne sodium hydroxide concentrations are in excess of the workplace environmental limit while required engineering controls are being installed or tested, when nonroutine maintenance or repair is being accomplished, or during emergencies. When a respirator is thus permitted, it shall be selected and used in accordance with the following requirements:

(1) For the purpose of determining the type of respirator to be used, the employer shall measure, when possible, the airborne concentration of sodium hydroxide in the workplace initially and thereafter whenever process, worksite, climate, or control changes occur which are likely to increase the airborne concentration of sodium hydroxide.

(2) The employer shall ensure that no worker is occupationally exposed to sodium hydroxide because of improper respirator selection, fit, use, or maintenance.

(3) A respiratory protection program meeting the requirements of 29 CFR 1910.134 which incorporates the American National Standard Practices for Respiratory Protection Z88.2-1969 shall be established and enforced by the employer.

(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 the provisions of 30 CFR 11.

(6) The employer shall ensure that respirators are adequately cleaned, and that employees are instructed on the use of

respirators assigned to them and on how to test for leakage.

(7) Respirators specified for use in higher concentrations of airborne sodium hydroxide may be used in workplaces with lower concentrations of airborne sodium hydroxide.

(8) Where an emergency may develop which could result in employee injury from sodium hydroxide, the employer shall provide an escape device as listed in Table I-1.

TABLE I-1

RESPIRATOR SELECTION GUIDE

Multiples of Ceiling	Respirator Type
Less than 5X	Single use respirator with dust filter, half or quarter mask, valveless.
Less than 10X	(1) Single use respirator with dust filter, quarter or half mask, with valves.
	(2) Quarter or half mask respirator with replaceable dust, mist, or high efficiency particulate filter.
	(3) Type C supplied air respirator, demand (negative pressure) mode with quarter or half mask facepiece.
Less than or equal to 100X	(1) Full facepiece respirator with chin style or front or back mounted canister with high efficiency particulate filter.
	(2) Powered air-purifying respirator with half or full facepiece, hood, or helmet, with high efficiency particulate filter.
	(3) Supplied air respirator with full facepiece, hood, or helmet in continuous flow mode or with full facepiece in demand (negative pressure) or pressure-demand (positive pressure) mode.
	(4) Self-contained breathing apparatus with full facepiece in demand (negative pressure) mode.
Greater than 100X (Immediately dangerous to life or health)	(1) A combination respirator which includes a Type C supplied air respirator with a full facepiece operated in continuous or pressure-demand (positive pressure) mode and an auxiliary self-contained breathing apparatus.

TABLE I-1 (CONTINUED)

RESPIRATOR SELECTION GUIDE

Multiples of Ceiling	Respirator Type
	(2) Self-contained breathing apparatus with full facepiece operated in pressure-demand (positive pressure) mode.
Emergency Entry or Escape from Unknown Concentration	Self-contained breathing apparatus with full facepiece operated in pressure-demand (positive pressure) mode.
Escape	(1) Gas mask with full facepiece with chin style, front or back mounted canister with high efficiency particulate filter. (2) Self-contained breathing apparatus with full facepiece operating in demand (negative pressure) or pressure-demand (positive pressure) mode.

Note: Wearers of quarter or half mask devices may find it necessary to use full facepiece devices if eye irritation is noted.

Section 5 - Informing Employees of Hazards from Sodium Hydroxide

At the beginning of employment or assignment for work at operations or in an area which may involve exposure to sodium hydroxide (dry solids or solutions), each employee shall be informed of the hazards and possible injuries associated with occupational exposure. He shall be instructed in the proper procedures for the safe handling and use of this compound, in the operation and use of protective systems and devices, and in appropriate emergency procedures.

Instructions shall include, as a minimum, all relevant information in the pertinent Material Safety Data Sheet(s) (Appendix III). This information shall be posted in the work area and kept on file readily accessible to the worker at all places of employment where exposure may occur. The worker shall be apprised of the location and availability of this information.

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

The worker must be apprised of the need for rapid removal of sodium hydroxide from skin and eyes and should be informed that severe damage can occur without irritation or pain. The worker must also be cautioned on ways of preventing accidental ingestion such as storage of sodium hydroxide only in designated labeled containers.

Section 6 - Work Practices

(a) Control of contact with skin and eyes

(1) Each employee working in an area where sodium hydroxide (solid or solution) is used shall be instructed in safe work procedures and in the proper use of all protective and process equipment.

(2) Each employee working in such areas where contact with sodium hydroxide is likely shall wear full-body protective clothing, close-fitting chemical goggles, and gloves, all of a caustic-resistant material. In areas where splashes of caustic solution are likely, a full-length plastic face shield shall be worn in addition to chemical goggles. Broad-brim hats shall be worn. Boots or overshoes of caustic-resistant material shall be worn in all areas where there is a likelihood of spills or of other causes of serious sodium hydroxide contamination of the floor and

walkways.

(3) Transfer of solutions of sodium hydroxide (liquid caustic soda) from tank cars, tank trucks, and other portable tanks shall be done only by fully trained employees under adequate supervision. All applicable requirements of the US Department of Transportation (DOT) shall be followed (49 CFR Chapter I) in regard to:

(A) Positioning of cars or trucks, blocking wheels, setting hand brakes, and otherwise securing before connecting transfer or steam lines.

(B) Inspection of tanks and posting of warning signs before transfer of the solution.

(C) Venting of tanks before connection.

(D) Heating of solution and lines to proper temperature to melt or prevent crystallization of sodium hydroxide must be done carefully to prevent overheating. No open fires may be used.

(E) Inspection of valves, lines, and joints after connection and before the transfer is started.

(F) Attendance of operator throughout the period of transfer.

(G) Assuring that the storage tank has adequate space to accomodate the contents of the tank car or truck.

(H) Flushing of tank and lines before, and flushing and draining after, disconnecting.

(I) Securely covering partially or fully filled tanks before moving them.

(4) In the handling of drums of sodium hydroxide the following practices shall be observed:

(A) Open or unsealed containers of caustic solution shall be handled only by workers wearing proper personal protective devices and using appropriate mechanical assistance which provides for protection from splashes and spills.

(B) Open or unsealed containers of solid sodium hydroxide shall be handled only by persons wearing proper personal protective devices and using adequate mechanical assistance.

(C) Emptied containers shall be flushed free of sodium hydroxide before being returned, stored, or discarded.

(D) Drums shall be stored so there will be no accumulation of water. Drums containing anhydrous or hydrated, solid sodium hydroxide may be stored on their side to minimize external corrosion around the bottom seam. Drums of anhydrous flake, granular, or ground sodium hydroxide should be stored in an upright position. Tiers of drums shall be separated by planks or other means to provide stability.

(5) In the preparation of solutions from sodium hydroxide, the following practice shall apply:

(A) Sodium hydroxide flakes, beads, chunks, or other forms capable of being added by hand shall be added to the water slowly and with agitation to prevent a dangerous rise in temperature causing boiling and spattering. Localized, highly concentrated solutions may form which will cause overheating when mixed with water. Do not attempt to increase the concentration of sodium hydroxide in solution by more than 5% sodium hydroxide with any single addition of sodium hydroxide.

(B) Sodium hydroxide cylindrical cake (molten sodium hydroxide solidified in a drum) shall be handled by mechanical equipment and dissolved in equipment designed for this purpose with protection of the workers from splashes or other skin contact with sodium hydroxide. In some situations anhydrous solid sodium hydroxide may be dissolved without first removing it from the steel drum. This may be accomplished by punching holes in the ends and sides of the drum with an axe or chisel lowering the drum in a perforated basket into an appropriate quantity of water and stirring the solution.

(C) The employee shall not add water to solid sodium hydroxide or to concentrated solutions thereof.

(D) Adequate respiratory protection shall be used in this process.

(6) Spills of sodium hydroxide solids or solutions shall be cleaned up immediately. Spilled solids may be taken up by careful shoveling followed by thorough flushing of the area with water. Spills of solution or of small amounts of solid shall be flushed away with water. Spills of sodium hydroxide on walkways create a serious slip and fall hazard; footwear used where spillage has resulted shall be appropriately slip-resistant. Residual sodium hydroxide on walkways shall be flushed or chemically neutralized to eliminate the hazard of fall on a slippery floor or walkway. Dry materials should not be cleaned by sweeping with a broom; vacuum-cleaning or wet-mopping may be used where appropriate.

(7) If sodium hydroxide in any form gets into an employee's eyes, it must be flushed out immediately with copious quantities of water for at least 15 minutes. The employer shall ensure that the

exposed employee receives immediate attention by medical personnel and subsequently by an ophthalmologist. Safety fountains for flushing the eyes shall be conveniently located in all areas where there is likelihood of sodium hydroxide splashes or dust.

(8) An employee who gets sodium hydroxide solid or solution on his skin or clothing shall immediately wash with a copious flow of water under an emergency shower or an equally effective washing facility. It may be necessary to scrub areas of skin under flowing water to remove sodium hydroxide. In cases of skin contact, there is often considerable delay before an irritation is noticeable. Attention must be directed to this latent period to prevent skin damage. Goggles shall not be taken off until the adjacent area has been thoroughly flushed. Contaminated clothing shall be removed during the shower flushing which shall be continued for as long as 1 hour or more, and the services of a physician shall be obtained. Safety showers shall be provided in all areas where serious contact with sodium hydroxide is likely.

(9) Severe burns of the lips, mouth, throat, esophagus, and stomach will result if sodium hydroxide is taken internally. Do not induce vomiting if sodium hydroxide is swallowed. If the victim is conscious, give milk or water, then egg white in water or cooking oil, followed by more water, vinegar, or lemon juice. Call a physician.

(b) Control of airborne contamination

Any operation where dusts or mists of sodium hydroxide may be dispersed into the air in concentrations exceeding the recommended workplace environmental limit shall be provided with local exhaust ventilation, shall be fully enclosed, or shall be controlled by other means equally effective to keep the airborne concentration below the recommended workplace environmental limit.

(c) General practices for safe handling

(1) All process equipment shall be constructed of alkali-resistant material, shall be regularly inspected for leaks, and shall be maintained in a safe operating condition.

(2) Pressure tanks or other apparatus shall not be used at pressures in excess of their safe rating and shall be regularly tested for safety at the pressures used.

(3) Tanks shall be provided with overflow openings, baffled to prevent obstruction, and shall be provided with troughs to conduct any overflow away from the employees and walkways.

(4) Air release lines for venting pressure from a line or vessel in which sodium hydroxide is used shall be directed into a pit or a trap, or directed straight down with the end of the line close to the ground so the discharge when venting cannot strike employees or walkways.

(5) The employer shall ensure that all safety equipment, personal protective devices, and work clothing are regularly cleaned, inspected, and maintained in good condition.

(A) Contaminated protective clothing shall be laundered before reuse.

(B) When respiratory protective devices are provided and required for wear in an area or at a task, they shall be worn and maintained in accordance with the principles given in Section 4 and with any requirements for obtaining a variance.

(6) Good personal hygiene shall be encouraged.

(7) Good housekeeping practices shall be observed to prevent or minimize contamination of areas and equipment and to prevent build-up of such contamination.

(8) Electrical equipment used in sodium hydroxide service shall be designed to prevent deterioration or electrical shorting which can result from accumulations of sodium hydroxide on wiring and terminals. Protective enclosures or splash walls shall be provided in heavy use areas. Pneumatically operated equipment may be substituted for electrical equipment in some areas.

(9) Precautions shall be taken to:

(A) Prevent contact of molten anhydrous sodium hydroxide with combustible containers, pallets, and other organic materials.

(B) Avoid contact of sodium hydroxide with chemically reactive metals such as aluminum, tin, zinc, magnesium, copper, bronze, brass, chromium, and others because flammable, explosive hydrogen gas may result, or structural defects may occur.

(C) Avoid accidental mixing of sodium hydroxide and concentrated acids.

(10) Attention shall be directed to the danger of embrittlement which may result from contact of steel with sodium hydroxide at elevated temperatures.

(11) Sodium hydroxide shall be stored or transferred in appropriately designated and labelled containers which cannot be mistaken for food or beverage containers.

Section 7 - Sanitation

(a) Eye flushing fountains and emergency showers with adequate pressure of cool water shall be provided as specified in Section 6.

(b) Clothing change and locker room facilities shall be provided in a nonexposure area. Workers should be encouraged to change work clothing daily. Contaminated clothing or personal protective equipment shall be cleaned before being reused.

Shower and basin washing facilities shall be located in the locker room area.

(c) Food storage and preparation and eating facilities, if provided, shall be located in nonexposure areas.

Section 8 - Monitoring and Recordkeeping

Workroom areas will not be considered to have occupational exposure to sodium hydroxide if environmental levels, as determined on the basis of an industrial hygiene survey or by the judgment of a compliance officer, do not exceed half of the workplace environmental limit. Records of these surveys, including the basis for concluding that airborne concentrations of sodium hydroxide are not above half of the workplace environmental limit, shall be maintained until a new survey is conducted. Surveys shall be repeated when any process change indicates a need for reevaluation or at the discretion of the compliance officer. Requirements set forth below apply to areas in which there is sodium hydroxide exposure.

Employers shall maintain records of accidental sodium hydroxide releases. In addition, records of workplace environmental exposures to sodium hydroxide shall be maintained based upon the following sampling and analytical schedules except as otherwise indicated by the judgment of a professional industrial hygienist. Samples representative of the exposure in the breathing zones of at least 25% of the employees in each operation or process shall be collected. Every employee shall be included in the sampling at least once every 2 years.

(a) Initial and Recurrent Sampling and Analytical Procedures

(1) The first environmental sampling and analysis shall be completed within 6 months of the promulgation of a standard incorporating these recommendations.

(2) Samples shall be collected and analyzed at least every 6 months in accordance with Appendices I and II to evaluate whether or not the work environment conforms with the recommended workplace environmental limit.

(b) Special Sampling and Analytical Procedures

(1) Monitoring of the airborne sodium hydroxide in the workplace shall be repeated at 15-day intervals when the concentration has been found to exceed the recommended workplace environmental limit. In such cases, suitable controls shall be initiated, and monitoring shall continue at 15-day intervals until 2 consecutive surveys indicate that exposures are at or below the recommended workplace environmental limit.

(2) Sampling and analysis of airborne sodium hydroxide shall be accomplished within 30 days after installation of a new process or process change.

(c) Recordkeeping procedures

Applicable medical records and records of all sampling and chemical analysis of airborne sodium hydroxide shall be maintained for at least 5 years after termination of employment. Records shall indicate the type of personal protective devices, if any, in use at the time of sampling. Each employee shall be able to obtain information on his own workplace environmental exposure.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational injury and disease arising from exposure to sodium hydroxide. 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 or 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 for a recommended standard should enable management and labor to develop better engineering controls resulting in more healthful work environments and mere compliance with the recommended standard should not be used as a final goal.

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

These criteria were developed to ensure that the standard would (1) protect against the development of acute and chronic sodium hydroxide poisoning and damage from local contact, (2) be measurable by techniques that are valid, reproducible, and available to industry and governmental agencies, and (3) be attainable with existing technology.

From the health hazard standpoint, sodium hydroxide must be handled with utmost care because of its highly damaging effect on the eyes, skin, alimentary tract, and respiratory tract. The importance of good work practices is emphasized.

The standard was not designed for the population at large and any extrapolation beyond general occupational exposure may not be warranted.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Sodium hydroxide, or caustic soda, is a strongly alkaline substance, which is soapy to feel, dissolves freely in water with the evolution of heat, is deliquescent, and in the moist state absorbs carbon dioxide from the air to form sodium hydrogen carbonate and sodium carbonate. [1,2] The chemical and physical properties of concentrated solutions of sodium hydroxide and anhydrous sodium hydroxide are shown in Table X-1.

In the United States sodium hydroxide is manufactured either by an electrolytic process or by a combination of lime and soda ash, the latter process becoming uncommon. [3] The electrolytic process consists of passing an electric current through a sodium chloride solution in specially designed cells. [3] The salt, which serves as the basic raw material can be obtained from natural brines, mines, or by the evaporation of sea water. Once in solution, the brine is heated and treated to remove calcium, magnesium, and sulfates. The salt brine is then decomposed by electrolysis to form a 10-12% sodium hydroxide solution while hydrogen is liberated at the cathode and chlorine is liberated at the anode.

Sodium hydroxide is one of the most widely used chemicals in industry. During 1974, 10.9 million tons of sodium hydroxide were produced in the United States. [4] It is used in the manufacture of rayon, mercerized cotton, soap, paper, aluminum, petroleum, chemicals, and dyestuffs. It is also used in chemical industries, in metal cleaning, electrolytic extraction of zinc, tin plating, oxide coating, laundering, and bleaching. [3,5] The commercial uses are listed in Table X-2.

Sodium hydroxide is sold in various grades: USP, CP, reagent, and commercial. The common solid forms are flakes, granules, grinds, sticks, lumps, and drops (pellets). [3,6] Common assays of sodium hydroxide in marketed solids are in the range of 77-98%. Aqueous solutions are usually either 50% or 70-74% sodium hydroxide. Solids are sold in drums, bags, barrels, cans, bins, and bottles. Liquids are marketed in insulated tank cars, trucks, barges, ocean-going tankers, drums, and barrels. Most of the sodium hydroxide produced in the United States is made by the electrolytic process [3,7,8] and sold as a solution. [3]

The occupations in which workers may have exposure to sodium hydroxide are listed in Table X-3. [9,10]

The number of workers with potential exposure to sodium hydroxide has been estimated by NIOSH to be 150,000.

Historical Reports

In 1713, Ramazzini [11] reported occupational injuries from sodium hydroxide. He found that laundresses and washerwomen developed fissures, sometimes deep and troublesome, in their hands, followed by inflammation and fever. [11] He further noted that the feet and other parts of soap boilers were excoriated when in contact with the "strong and acrid water," presumably an impure sodium hydroxide-potassium hydroxide solution.

In the early part of the 20th Century, an Austrian factory inspector [12] reported to the International Labour Office (ILO) that a workman got caustic soda in his eye which resulted in corneal opacity.

Kober [13] wrote that over 13,000 people were engaged in the manufacture of soap in the United States in 1910. He reported a high incidence of morbidity and mortality among female tallow and soap workers.

In 1925, Hinkel [14] cited leaky valves, bursting tanks, fume line leaks, and poor recovery equipment as major culprits in producing injury from sodium hydroxide. Although he presented no data he noted that engineering and accident prevention programs had been effective in markedly reducing the number of cases.

Later Terry [15] reported that on-the-spot eye wash and treatment stations in British alkali plants were beneficial, but presented no data. He also mentioned that the application of bicarbonate of soda to form sodium carbonate, one of the forms of skin treatment for alkali burns prior to 1930, was unsatisfactory. He found that despite early treatment of sodium hydroxide burns of the eye, ie, washing with a boric acid solution for 2-5 minutes, there was a prolonged period of inflammation, the formation of granules over the sclerotic and inner surfaces of the eyelid, and an adhesion between the tarsal and bulbar conjunctivas. Even more serious consequences followed corneal burns. It was recommended [15] that there be immediate irrigation (within 30-40 seconds) of skin or eye injuries with aqueous 5% ammonium chloride solution from gravity-fed containers placed about the plant, educational and medical programs, and the use of personal protective equipment. For eye burns, irrigation with ammonium chloride solution was followed by treatment with a warm boric acid-saline solution in the clinic for 1 hour with subsequent shorter rinses with other agents and water as required. He reported that this program reduced the severity of eye and skin injury markedly during the period 1930-42 and shortened the recovery periods 5- to 7-fold as compared to older methods.

Effects on Humans

Eye injury has probably been the most severe effect from contact with sodium hydroxide. [12,14-19] Damage to the skin, [11,12,14,15,20-25] loss of hair, [23] and injury of mucous membranes have also been severe. However, only in rare instances were the concentrations of airborne sodium hydroxide reported. [2,26, TR Lewis, written communication, November 1974] Ingestion of sodium hydroxide, although infrequently reported in the occupational setting, [27,28] has had severe consequences. [27-33]

(a) Effects on Eye

In the early part of the 20th Century, a workman was reported [12] to have suffered corneal opacity following exposure to sodium hydroxide dust. Other reports [14-19] have also described the extreme hazard of eye contact with sodium hydroxide, with blindness a frequent consequence. Terry [15] observed some of the long term sequelae as a result of contact of the eye with sodium hydroxide. These included formation of granulation tissue over the sclerotic and inner surfaces of the eyelids and sticking of the eyelid to the eyeball. He also reported the development of tough bands of adhesion between the eyelids and the eyeball, thereby limiting eye movement. He also commented on the severity of corneal burns.

Hughes [16,17] compiled a general chronology of events following contact of the eye with sodium hydroxide; it is presented in Table III-1. He concluded that the alkalinity and not the specific cation determined the severity of the eye burn.

TABLE III-1

CHRONOLOGY OF THE PROMINENT CHARACTERISTICS OF SEVERE ALKALI BURNS OF THE EYE*

Time	Characteristics
1-10 min	Rapid penetration of alkali through cornea into anterior chamber; diminished tactile sensitivity of cornea; disintegration and sloughing of conjunctival and corneal epithelium; opalescent opacification of cornea; washed-out appearance of substantia propria with beginning of disintegration of stromal cells; fragmentation of corneal endothelium; hyperemia of iris
2 hr	Edema and ischemia of conjunctiva and limbal (corneoscleral) region of the eyeball; infiltration of polymorphonuclear cells into conjunctiva; episcleral tissues and periphery of cornea; corneal edema, giving rise to opalescent haziness of cornea, with wrinkling of Descemet's membrane ("striate keratitis"); exudation of serum into anterior chamber; Greef blebs and edema of ciliary processes
18 hr	Beginning regeneration of corneal epithelium; marked edema, loss of metachromatic staining of corneal mucoid, disappearance of stromal cells; increase of purulent infiltration into conjunctiva, cornea, and anterior chamber; opacity of anterior capsular and subcapsular region of lens
24-48 hr	Moderate mucopurulent discharge in cul-de-sac; intensification of opacification, edema, and purulent infiltration of cornea; appearance of spindle-shaped cells at periphery of lesion; regeneration of corneal endothelium
3-6 days	Petechial hemorrhages in ischemic areas of conjunctiva; varying amounts of superficial corneal ulceration, without apparent progression of corneal infiltration or opacification; persistence of iritis

TABLE III-1 (CONTINUED)

CHRONOLOGY OF THE PROMINENT CHARACTERISTICS OF SEVERE ALKALI BURNS OF THE EYE*

Time	Characteristics
7-13 days	Stage of gradual recovery or progression of corneal opacification and ulceration; varying amounts of mucopurulent discharge from eye; formation of adhesions between severely burned portions of bulbar and palpebral conjunctivas, localized corneal infiltrates of polymorphonuclear and mononuclear cells, with ulceration over such areas; beginning vascularization of cornea from limbal vessels, superficial loops from unthrombosed conjunctival vessels or brush-like projections from deep scleral plexus in ischemic regions; continued proliferation of spindle-shaped cells in cornea; subsidence of corneal edema; improvement of iritis
14 days and over	Abatement or progression of symptoms previously described; great resistance of Descemet's membrane to perforation; healing of corneal ulceration by proliferation of opaque fibrous tissue and blood vessels Complications of severe burns: Symblepharon with overgrowth of cornea by a vascularized membrane; progressive or recurrent corneal ulceration, occasionally leading to perforation; permanent corneal opacification; staphyloma of cornea; persistent or exudative iritis, at times ending in phthisis bulbi, secondary glaucoma or cataract

* Derived from reference 16

In 1954, Dennis [19] reported a case of occupational eye burns from alkalis. A 63-year-old textile worker was splashed in the face and eyes with sodium hydroxide. Affected areas were immediately irrigated with water for an unspecified time and the worker was later treated in a hospital. Examination showed excessive edema of the conjunctivas, photophobia, and pain. Both corneas were gray. Treatment consisted of irrigations with saline, neutralization with acetic acid solution, topical anesthetics and antibiotics, and removal of all devitalized tissue. The patient's eyes healed well, but he developed a wing-like overgrowth of conjunctival tissue in the area of the deepest corneal burn.

The value of prompt treatment in order to alter the course of events in eye burns was demonstrated in a case reported by Horwitz [18] in 1966. In this case, a 28-year-old member of an oil-well drilling crew sustained extensive splash burns of the left eye from sodium hydroxide and received emergency care from a general physician prior to being hospitalized. At the hospital, initial examination showed vision limited to light perception, corneal clouding to such an extent that iris markings were not discernible, necrosis of most of the bulbar conjunctiva, some sloughing in the nasal area of the cornea, blanched and necrotic cul-de-sac, and some involvement of the lids and adjacent skin.

The treatment for the patient at the hospital consisted of daily debridement of necrotic areas, local atropine, antibiotics, and steroids, systemic ACTH, vitamins, antacids, and proteolytic enzymes.

The treatment produced some improvement with time so that usual, late sequelae such as vascular invasion and symblepharon did not occur, and the cornea cleared sufficiently within 7 weeks that vision returned to near normal.

(b) Effects on Skin

Cutaneous exposure has resulted in severe damage to skin. [11, 12,14,15,20-25] Davidson, [21] in an effort to determine the latent period between the exposure of skin to sodium hydroxide and the sensation of irritation, put aqueous 50% or 25% solutions on the skin of 3 human volunteers and noted that neither concentration of sodium hydroxide caused any sensory stimulation within 3 minutes after application. Acids were used as positive controls; an aqueous 50% solution of either nitric or sulfuric acid promoted responses in all 3 persons in 22.6-50 seconds, and a 37% hydrochloric acid solution elicited a response in 2 people in 15 and 17 seconds, respectively.

Later Terry [15] also described a similar latent period in his observations of sodium hydroxide burns in an alkali plant in England.

Chiego and Silver [22] found that keratin material in the skin underwent rapid decomposition in sodium hydroxide above pH 9.2. In their in vitro experiments, they mixed aliquots of washed human hair and fingernails with various amounts of sodium hydroxide solution and measured the extent of keratin breakdown by estimating the cystine produced. They found that the cystine portion of the keratin complex of human hair or nails was readily cleaved by sodium hydroxide in the S-S bond. After 20 hours of contact with 0.1N or 0.25N sodium hydroxide, 61.4% and 97.6%, respectively, of the nail keratin were decomposed. Thus a high degree of destruction of tissue even by a dilute sodium hydroxide solution can occur from prolonged contact.

An occupational accident involving hair was reported by Morris. [23] A 42-year-old man was working at a bench under a clogged pipe. A sodium hydroxide solution of pH 13.5 had been put into the pipe in an effort to unclog it. This solution had destroyed part of the pipe and dripped on the worker's head. He experienced neither burning nor pain at that time and merely wiped the material off with his hand. The next morning, when combing his hair, he noticed that some of the hair came loose from the roots and he became aware of a burning sensation on his scalp. The lesion consisted of erythematous skin studded with minute pustules in the areas of baldness. After washing with water, the burn subsided and in time the hair grew back. This incident demonstrates that there is not necessarily an immediate sensation of pain or irritation following cutaneous exposure to sodium hydroxide. In this case, however, abundant flushing with water, even several hours after exposure, seems to have limited the injury.

In an effort to relate injury from sodium hydroxide to rate of water loss from tissue, Malten and Spruit [24] cemented a small cylindrical plastic cup with cover to the forearm of a human volunteer. In a series of experiments, sodium hydroxide or potassium hydroxide solutions of various concentrations were placed in the cup for various time periods. Clinical observations were made and water vapor loss was measured as a function of time in each of the experiments. After every exposure the cup was removed. It was placed on the same spot in serial experiments. The authors observed perceptible erythema of the skin with 0.0675N (0.27%) sodium hydroxide within 1/2 hour, and less marked erythema with 0.03N (0.12%) sodium hydroxide after 1 hour. The rate of water vapor loss from injured skin was greater than from normal skin, but decreased with time. The authors proposed the use of this decrease as an index of damage. Their experiment with an aqueous potassium hydroxide solution indicated that 0.0675N potassium hydroxide produced damage equivalent to that caused by 0.045N sodium hydroxide. They suggested that this difference was significant and that damage might not be governed solely by the hydroxyl ion concentration and that, based on the rate of water vapor loss, damage from 0.0675 N potassium hydroxide was only half as severe as that produced by 0.0675 N sodium hydroxide. The authors also found that, as skin injured by sodium hydroxide or potassium hydroxide regenerated, the rate of water vapor loss approached that of normal skin. In a later experiment [34] using the same technique, these authors showed that adhesive-tape stripping of the skin produced reactions equivalent to treatment with sodium hydroxide.

In this later study, Spruit and Malten [34] noted that following exposure to sodium hydroxide solutions in a manner similar to that described above, [24] at pH's 11.5-11.7, injury to the horny layer was sufficient to cause approximately 8 times the rate of water vapor loss as was caused by a solution of pH 11.3. Basing their evaluation of skin injury on the increase in water vapor loss rate, the authors found that injury to skin from sodium hydroxide of pH 11.75 was equal to injury to skin which had been pretreated with petrolatum and exposed to sodium hydroxide of pH 11.95.

In order to simulate a normal exposure to alkali, the authors [34] exposed the same patch of skin of each of 2 volunteers to 0.5 ml of 0.03 N sodium hydroxide/sq cm for 1 hour/day for 6 successive days. In general, repeated applications of sodium hydroxide produced increasing damage to the skin. Because of variation of response during various times of the year and the differences in the skin textures in the 2 individuals tested, the authors concluded that various climates and skin textures may influence the seriousness of skin injury.

In 1972 Nagao et al [25] reported a study of human primary irritant dermatitis. Part of the experiment used sodium hydroxide as the irritant. Twenty microliters of 1N sodium hydroxide was applied 1, 2, or 3 times at 30-minute intervals to the flexor surface of the forearms of 7 healthy volunteers, aged 21-31. The subjects included Caucasian, Negro, and Japanese males and one Caucasian female. Under local anesthesia, 4-mm punch biopsies were taken 15, 30, 45, and 60 minutes after application of the sodium hydroxide. Control specimens were prepared from each subject. One-half of each specimen was fixed in a 10% formalin solution, embedded in paraffin, stained with hematoxylin and eosin, and examined under light microscopy. The other half was fixed in cacodylate-buffered osmium tetroxide for 2-3 hours, dehydrated, embedded in resin, sectioned, stained with toluidine blue, and examined by electron microscopy. Some thick sections were also prepared in the above manner and examined with light microscopy. Clinical observations made during and after sodium hydroxide application showed a slight erythema 25-30 minutes after application, then a "waxy" appearance, and swollen hair follicles in several test sites. With light microscopy, it was apparent that 1N sodium hydroxide produced changes more rapidly than 1N HCl. After 15 and 30 minutes, the sodium hydroxide caused the horny layer to be swollen and the prickle-cell layer to display a few pyknotic nuclei. At 45 and 60 minutes, intercellular edema was pronounced and cleft formation was seen in the middle and lower prickle-cell layers. The entire epidermis in the test areas of several subjects was destroyed at 60 minutes. The authors believed that it was possible that partially neutralized sodium hydroxide that failed to cause visible changes in the relatively insoluble lower horny layer cells could be of sufficient concentration to affect living cells of the stratum malpighii.

(c) Effects on Alimentary Tract

In 1965, Moeschlin [27] reported the case of a 37-year-old carpenter who accidentally drank a concentrated solution of sodium hydroxide from a Chianti bottle, which he thought was apple cider. Signs and symptoms included violent pain in the esophagus and stomach, severe corrosion of the lips, mouth, pharynx, and tongue, and the vomiting of large pieces of mucosa. Because he received prompt on-the-spot treatment and follow-up medical treatment there were no sequelae.

Palmer [28] reported about 1,500 serious casualties incurred by the drinking of schnapps that had been adulterated with lye. The boobytrapped schnapps had been left in France and Germany by the retreating German army or given to inebriated Allied soldiers during the later stages of World War II. Most injured soldiers obtained medical help months after consuming the adulterated spirits and the most serious sequela was esophageal stenosis with a few cases severe enough to lead to antropyloric stenosis.

Several reports [29-33,35] have implicated the massive ingestion of sodium hydroxide as causing esophageal cancer. None of these cases were of occupational origin and all were cases involving severe stricture of the esophagus requiring a gastrostomy. Latent periods ranged from 12 years [35] to 42 years. [30] All identified tumors were classified as squamous-cell carcinomas. It should be pointed out that carcinoma at the site of damage is also an even more frequent late sequela to severe thermal burns. [30] While there seems no question that the various cases of cancer were causally related to sodium hydroxide ingestion, it seems clear that these cancers were sequelae of tissue destruction and possibly scar formation and not from a direct carcinogenic potential of sodium hydroxide itself.

(d) Effects on Respiratory Tract

Most authors concerned with hazards from sodium hydroxide have emphasized the prevention of contact with eyes and skin, and of its ingestion. Inhalation of sodium hydroxide has received little attention. [2,26, TR Lewis, written communication, November 1974] It may be presumed that the irritating nature of the aerosol on mucous membranes has prompted the maintenance of airborne concentrations of sodium hydroxide at tolerable levels. Patty [2] made reference in his 1949 review of the literature to the concentration of sodium hydroxide in workroom air. After commenting that he was unable to find any published record of measurements of airborne sodium hydroxide in industry, he stated, apparently based upon his own experience, that "from the irritant effects of caustic mists encountered in concentrations of 1 to 40 mg per cubic meter of air, 2 mg sodium hydroxide per cubic meter is believed to represent a concentration that is noticeably, but not excessively, irritant." He further suggested that this figure be used as a "bench mark" until further information is presented.

In May 1974, NIOSH [26] reported an investigation of the possible hazards associated with a chemical degreasing operation. The degreasing vat was 11 x 11 x 3 ft and contained a caustic solution maintained at 200 F by steam bubbling through it. The caustic solution contained primarily sodium hydroxide, but also sodium gluconate, tetrasodium pyrophosphate, and minor amounts of nonsodium compounds otherwise unspecified. The pH of the bath was 12.5-13.5. (This pH is equivalent to a hydroxyl ion concentration of 0.032-0.32 moles/liter or a sodium hydroxide concentration of 0.13-1.3

g/liter). Operations adjacent to the vat involved the use of other substances (eg Ensis 254 oil, Stoddard solvent, Zyglo, and Magna flux).

In September 1972, 2 employees experienced irritation of the nose and throat and frequent chest pains associated with shortness of breath. One was treated with antibiotics. A week later a third person, a vat operator, experienced nausea, vomiting, and nose and throat irritation. Antibiotic therapy was an effective treatment; the vat operator was transferred and experienced no recurrence of these signs and symptoms. The other 2 employees remained in the vat area and intermittently had irritation of the nose and throat. In December 1972 NIOSH made a preliminary survey of the establishment. In May 1973 NIOSH found the airborne concentration of Stoddard solvent to be 14-780 mg/cu m; other solvent vapors (undescribed) were 276-725 mg/cu m, reported as Stoddard solvent, according to a written, internal NIOSH laboratory report series. Airborne sodium concentration, reported as sodium hydroxide, was <0.1-0.7 mg/cu m; airborne sulfuric acid concentrations were 0.3-2.2 mg/cu m. Another survey was made in September 1973, but no data were reported.

In October 1973, a more comprehensive survey was made by NIOSH. At this time the airborne concentrations of sodium, reported as sodium hydroxide, were 0.005-0.12 mg/cu m. The airborne Stoddard solvent concentrations were <10-62 mg/cu m and the airborne n-butyl acetate concentrations were <0.2-0.4 ppm.

Fifteen workers (aged 21-63) in the vicinity of the degreasing vat which contained sodium hydroxide and 10 workers (aged 24-59) from another unspecified area of the plant filled out questionnaires and were given medical examinations limited to the skin and upper respiratory tract structures. Employees in both groups were in good health. All personnel who participated in this study had worked for at least 16 months. The employees supplied information relating to symptomatology, that is, the occurrence of any given symptom at a minimum frequency of 4 times/year while on the job. Of the 15 who worked in the vicinity of the vat, 8 reported burning/redness of the eyes, 9 burning/redness of the nose, 7 burning/dryness of the throat, 2 burning in the chest, 1 headache, 1 rhinorrhea, and 3 skin eruption. There were no reports of sneezing or wheezing. None of the control group reported any of these symptoms at a frequency greater than 4 times/year. Apparently, half the workers in the vicinity of the vat experienced some symptoms of irritation of the upper respiratory tract. The authors concluded that the 3 persons with skin eruptions did not develop them as a result of in-plant factors, but presented no supporting data. They also concluded that caustic mist exposure was responsible for the symptoms reported.

Two possibly significant factors the authors presented, but did not fully evaluate, were that (1) the temporal occurrence of symptoms during the normal work shift did not correlate well with the degree of ventilation in effect at these times and (2) some of the effects may have been caused by Stoddard solvent. There was a greater incidence of sneezing and burning/dryness of the nose when the vat cover was on than when it was off. Burning/redness of the eyes occurred with equal frequencies with the vat cover on or off, and burning/dryness of the throat occurred only slightly more frequently with the vat cover on than off. These observations are not entirely consistent with the conclusion reached by the investigators that the mist from the vat produced the signs and symptoms.

Another factor which may have been important was the presence of rather high airborne concentrations of Stoddard solvent in the workplace.

In 1974, in another study by NIOSH designed for purposes not directly relevant to the determination of sodium hydroxide aerosol dose-response relationships, 9 persons recorded their responses while they used a spray oven-cleaner which contained sodium hydroxide, among other ingredients (TR Lewis, written communication, November 1974). Personal samples of airborne sodium were taken with 0.8 μm pore size filters, both during a spray application and during the manual cleaning process which followed. Samples were analyzed for total sodium by atomic absorption spectrophotometry and reported as sodium hydroxide. Subjects used the spray cleaner on their home ovens, so exposures and breathing-zone samplings were unsupervised.

Some of the persons who cleaned their home ovens with the aerosol reported symptoms of irritation of the respiratory tract. Because the study was not designed for the purpose of evaluating the irritancy of sodium hydroxide, but rather to evaluate the general irritancy of the aerosol, air sampling and chemical analysis for sodium hydroxide and other ingredients was not extensive enough to allow identification of the specific agents responsible for this irritancy.

Animal Toxicity

Two studies [21,36] have evaluated the effects of sodium hydroxide on skin, and the effectiveness of treatments. In 1927 Davidson [21] studied the various treatments for alkali burns of the skin and described the etiology of these burns. In his first experiment, he used 3 groups of

3 rats each, all anesthetized with ether. The hind legs of all 9 animals were dipped into a solution of 50% sodium hydroxide for 1 minute with no treatment for the next 5 minutes. One group of 3, regarded as a control, then had the excess sodium hydroxide wiped away with cotton. In the second group, the sodium hydroxide was neutralized with 1% acetic acid. Rats in the third group were treated by vigorous washing with water. Control animals over an 18-hour period gradually developed edema and maceration of the skin with the formation of thick, edematous sloughs. The author also performed similar experiments with nitric, sulfuric, hydrochloric, and trichloroacetic acids and noted that damage from sodium hydroxide was unlike that produced by acids. Rats whose lesions were treated by neutralization developed edema and redness of the foot at the end of 24 hours; gradually the skin of the thigh and flank sloughed but the animals recovered. The hair of the rats treated with water remained intact and there was no sloughing of the skin. The only evidence of a burn in these animals was moderate edema of the toes and excoriation of the skin of the foot; healing took place promptly and without deformity. Based on these observations, the author concluded that the preferred treatment for sodium hydroxide burns was vigorous washing with water followed by neutralization of the residual alkali.

Bromberg et al [36] in 1965 published a study in which the clipped backs of anesthetized, A/He, and C57 black adult mice weighing 25-35 g were painted with 50% sodium hydroxide on a 3-sq cm area. The animals were treated in various manners, as shown in Table III-2. All mice except those treated immediately developed a rapidly progressive burn in both extent and depth. The severity of the burn increased with delay in treatment. Two hours after application, 2 untreated mice were dead, and after 24 hours a hard, dark brown eschar had developed in both the untreated group and in the group treated 2 hours after the burn. The group irrigated 30 minutes after the burn showed a rather limited, spotty, superficial burn compared to the burn in untreated animals. Groups irrigated 1 and 2 hours after the burn developed progressive changes in both depth and extent of burn, with severity increasing with time to treatment. The group irrigated 2 hours after sodium hydroxide application exhibited changes similar to those of the untreated group but with less local edema in the area peripheral to the burned zone. Biopsy sections obtained 24 hours after application exhibited some edema and cellular infiltration in the mice given immediate irrigation. In biopsy of untreated mice severe necrosis was found.

TABLE III-2

MORTALITY IN MICE FROM TOPICAL APPLICATION OF SODIUM HYDROXIDE
(50% SOLUTION OF SODIUM HYDROXIDE APPLIED TO A 3-SQ-CM AREA)

Treatment	Time of Treatment	Number of Animals	Mortality
Continuous irrigation with water for 1 hour	Immediately	5	0/5
"	30 minutes after application	5	1/5
"	1 hour after application	5	2/5
"	2 hours after application	5	4/5
None	--	7	5/7

Derived from reference 36

Several studies [17,37-49] have evaluated the effects of sodium hydroxide on the eye. Cosgrove and Hubbard [37] placed a drop of 40% sodium hydroxide solution in the eyes of an unspecified number of anesthetized rats. One group of rats received 2% acetic acid to neutralize the base. Another group was treated by washing the eye with water. Eyes of both positive controls (untreated) and of those treated with acetic acid were completely degenerated at the time of death 2-3 days later. Fifty percent of the eyes treated by washing with water had cloudy corneas and the remainder had complete degeneration of the cornea. Results were similar with lesser concentrations of sodium hydroxide and none of the eyes treated by neutralization were saved; only about 50% of the eyes treated by washing were saved. Unlike skin damage, [21] the authors [37] found there was no detectable latent period for eye damage.

In 1937 Hubbard [38] reported instilling 20% sodium hydroxide into the eyes of an unspecified number of rabbits where it remained for 10 seconds. One eye of each animal was irrigated with water for an unspecified time; the other was irrigated with an aqueous 2% solution of acetic acid. The author reported that in 75% of the eyes tested, washing with dilute acetic acid resulted in less damage than washing with only water, but he presented only limited supporting data.

In another experiment, Hubbard [39] introduced an amount of aqueous 20% sodium hydroxide into the eyes of rabbits sufficient to fill the conjunctival sac and allowed it to remain for 10 seconds. Eyes of all rabbits were irrigated with water for an unspecified time. This was followed by no further treatment, or by irrigations with: (1) 5% tannic acid solution, or (2) 5% tannic acid solution followed by 2% silver nitrate solution, or (3) 1% methylrosaniline solution followed by 2% silver nitrate solution, or (4) 1% methylrosaniline solution followed by 5% tannic acid solution and additional methylrosaniline solution, immediately and once on the following day. After treatment (1), the eyeball had degenerated 19 days later; after (2), (3), and (4) necrosis of the cornea occurred 27-29 days later. In the case where there was no further treatment, the cornea ruptured in 18 days. Although corneal rupture was delayed by the various treatments, it eventually occurred.

In 1946 Hughes [17] irrigated a rabbit eye for 3 minutes with 0.2% sodium hydroxide made isotonic by the addition of sodium chloride. A moderately severe lesion which healed in about 10 months was produced. He observed and described in detail the progress of the lesion with time; it was similar to that outlined in Table III-1.

In 1955 Grant and Kern [40] dropped test solutions in the eyes of rabbits for 15 minutes at room temperature after scraping off the corneal epithelium. Sodium hydroxide, 0.23M, was adjusted to pH 11 and produced slight and reversible injury; when adjusted to pH 12, it produced severe injury with opacity. The authors did not describe the method of adjusting pH. Other alkaline materials, namely, potassium hydroxide, calcium hydroxide, barium hydroxide, strontium hydroxide, ammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, trimethylamine, triethylamine, tributylamine, diethanolamine, and piperidine produced similar injuries, indicating that injury was likely caused by the hydroxyl ion at high concentration and not by cations.

In a series of experiments by Brown and co-workers [41-46] in which a solution of 0.5N sodium hydroxide (2.0%) on cotton pads was applied to the eyes of anesthetized albino rabbits for 30 seconds, severe corneal burns resulted. In each report, ulcerated or perforated corneal tissue developed within 3 weeks of exposure, and the ulcerated tissue was shown to produce collagenase while normal tissue of control animals did not. In their more recent works, [45,46] subsequent application of cysteine proved beneficial in 13-16 eyes so treated. In similar experiments, the presence of collagenase after application of 0.5N (2.0%) sodium hydroxide to eyes of rabbits was also noted by Francois and Feher [50] in 1972.

In 1971 Chiang et al [47] reported applying 0.05 ml of 0.125N (0.5%), 0.5N (2.0%), and 2.0N (8.0%) sodium hydroxide, respectively, into the eyes of 3 anesthetized albino rabbits and finding that the intraocular pressure increased 5, 18, and 37 mm Hg, respectively, within 2.5 minutes.

Geeraets et al [48] reported a study in which 0.5 ml of 0.5N sodium hydroxide was added to both eyes of 62 rabbits after the nictitating membrane had been sutured open. Half of the animals had both eyes irrigated with 1 liter of tap water starting 1 minute after the injury, while the other half was treated similarly 4 minutes after injury. After the water wash, some eyes were treated with 10% neutral ammonium tartrate (NAT) solution and some with water. The results appear in Table III-3. Although neutral ammonium tartrate was not more effective than water in preventing descemetoceles or perforations, the repeated washing at intervals was decidedly more effective than single washes in preventing damage.

TABLE III-3

OBSERVED DESCEMETOCELES AND PERFORATIONS IN EYES TREATED SINGLY OR HOURLY FOR 8 HOURS WITH NAT AND CONTROL EYES TREATED IN A SIMILAR MANNER WITH TAPWATER

Alkali-cornea Interaction	Hourly Application	Total No. of Eyes	Descemetocele or Perforation
1 minute	NAT	19	6
	Water	19	7
4 minutes	NAT	19	6
	Water	19	6
	Single Application		
1 minute	NAT	12	8
	Water	12	10
4 minutes	NAT	12	10
	Water	12	11

It should be noted that even 1 minute of exposure to 0.5 N sodium hydroxide was sufficient to produce descemetoceles or perforations of corneas in 65-91% of the eyes which were inadequately washed.

Shapiro [49] immersed the corneas removed from rabbits in 1N (4.0%) and 0.2N (0.8%) sodium hydroxide solutions and found immediate clouding and an increase in both their size and weight which continued for 200 minutes; at that time the weight had more than tripled. In experiments with living rabbits, 4-mm circles of filter paper were soaked in 1N sodium hydroxide and the excess solution was removed. They were then applied to the center of the cornea of living rabbits for 1- to 60-second periods after which the eye was irrigated with running tap water for 14 minutes. Animals were killed and their corneas examined microscopically. Shapiro found that significant swelling had occurred in as little as 2 seconds and that the amount of swelling was directly proportional to the contact time.

Dluhos et al [51] in Poland reported a later study dealing with the inhalation of sodium hydroxide aerosol. White, female, 5-months-old rats with an average weight of 150 g were used. Ten rats were exposed to a sodium hydroxide aerosol for 30 minutes, twice daily, for 2.5 months. Another 10 rats exposed to sodium hydroxide in the same manner and also to an aerosol generated from an aqueous 8% ammonium chloride solution for 30 minutes immediately after each exposure to sodium hydroxide. A group of 5 rats served as controls and were not exposed. This routine was interrupted for 10 days 3 weeks into the experiment because the animals tolerated it badly and 2 from the second group died. The airborne concentration of sodium hydroxide was not determined; however, the sodium hydroxide aerosol was generated from a 40% solution of sodium hydroxide and 80% of the particles were less than 1 μm in diameter. The animals were killed 1 week after the last exposure. The lungs of the first group were grayish-brown, but resembled those of the control group; those of the second group were more strongly brownish-discolored. Undescribed, isolated tumors were found in 3 animals exposed to sodium hydroxide aerosols.

Rats in the first group had what was described as inflated pulmonary tissue. In places the chamber barriers (presumably alveolar walls) were thickened, with cell proliferation, and congested. The bronchial epithelium was damaged, flattened, and ulcerated; there was thickened lymphadenoidal tissue, penetrating the muscle under the epithelium in several places. At other points, the proliferated lymphadenoid tissue adhered to the bronchial lumen. In the bronchial lumen there often were stripped epithelia, dystrophic to a great extent, thoroughly mixed with amorphous protein substances and leukocytes. In several areas on the lung parenchyma very small, often fused together beds of bronchial pneumonia were observed.

The second group of rats suffered greater damage. Bronchi were more dilated and had markedly flattened epithelium with progression to apparent metaplasia of the epithelium. The walls of the bronchi had granulation tissue structurally alternating with the formation of fibroblasts. The bronchial wall was entirely destroyed in places and elsewhere epithelium was completely absent. Animals in this group died exhibiting interstices significantly infiltrated with round cells of the lymphocyte type, plasma cells, and histiocytes. The control group appeared to be normal.

In another experiment, Vyskocil et al [52] found that 27 white rats died within a month, mostly from bronchopneumonia, after twice-weekly exposures to an aerosol of unknown airborne concentration generated from an aqueous 40% sodium hydroxide solution. When exposed to an aerosol generated from aqueous 20% sodium hydroxide solution, the septa were emphymatously (sic) dilated and cracked, the bronchi were dilated and their epithelial cover was thin and frequently desquamated, and a light round-cell infiltration of the submucous membrane tissue occurred. Other rats were exposed to aerosols generated from 10% and 5% solutions of sodium hydroxide. In the group exposed to aerosols from 10% sodium hydroxide, little change occurred. In the group exposed to aerosols from 5% sodium hydroxide, rats had dilatation of the bronchi and a slight degeneration of the mucous membrane and thickened strata of the lymphadenoid tissue surrounding the bronchi. All rats in these experiments were exposed to quartz dust at a concentration of 10 g/cu m. It is unclear what effect this exposure may have had on the results.

Correlation of Exposure and Effect

There are 4 principal occupational hazards associated with the manufacture and use of sodium hydroxide: (1) contact with the eyes, [2,15-21,53,54] (2) contact with the skin, [2,11,12,14,15,20,21] (3) ingestion, [27,28] and (4) inhalation of sodium hydroxide aerosol. [2] All these hazards reflect the destructive action of sodium hydroxide on tissue. [2,12,14-21,27,28,53,54]

When sodium hydroxide comes into contact with the eye, even for a matter of seconds, some damage results. [15-19,36-40,42-47,49,53,54] One of the shortest contact times recorded [49] as capable of inducing ocular injury from 1N (4%) sodium hydroxide was 2 seconds. Contact with 0.5 N (2%) sodium hydroxide [48] for 1 minute, the shortest period used, caused descemetoceles or perforations in 65-91% of the corneas tested. Immediate availability of treatment for accidental eye contact consisting of sufficient flushing with water, followed by appropriate clinical therapy, is of the greatest importance.

Sodium hydroxide of sufficient concentration produces damage if it remains in contact with the skin for a long enough time. [2,11,12,14,15,20-22,24,25,34] Damage to healthy skin has been reported [24] following contact with sodium hydroxide solutions as weak as 0.03N (0.12%) for 1 hour. Contact with 50% sodium hydroxide, followed by immediate irrigation with water for 1 hour, [36] produced some edema and cellular infiltration, but no apparent destructive damages. Regardless of the concentration, the severity of the damage and the extent of its irreversibility increase with increasing contact time. [15,21,22,24,25,34,36] There is a latent period [15,21,23] following skin contact with sodium hydroxide during which no sensation of irritation occurs, about 3 minutes with 25-50% solutions [15,21] and several hours with 0.4-4% solutions. [23] Because damage to the skin will occur before the sensation of irritation, good work practices including prompt attention to accidental skin contact are of paramount importance.

Ingestion of sodium hydroxide has rarely occurred as a result of exposure in the occupational setting. [27,28] Accidental ingestion has caused violent pain in the esophagus and stomach, severe corrosion of the lips, mouth, pharynx, and tongue, and vomiting of large pieces of mucosa, [27] and esophageal and antropyloric stenosis. [28] In other isolated case reports, [29-33,35] burns resulting from ingestion of sodium hydroxide have apparently led to squamous-cell carcinomas of gastric tissue. As previously commented on these cancers were undoubtedly caused by the tissue destruction and regeneration and not by a direct carcinogenic action of the compound.

The inhalation of sodium hydroxide can result in irritation and damage [2,51, TR Lewis, written communication, November 1974] of the tissue of the respiratory system. As the concentration of sodium hydroxide in the inhaled aerosol increases, the extent of irritation or damage evidently increases. [51] At present, probably the only reports in the literature which discuss either human or animal response to a known, low concentration of sodium hydroxide are (1) a NIOSH Health Hazard Evaluation, [26] (2) a written communication from TR Lewis describing the irritative effects on the upper respiratory tract from oven cleaners, and (3) a statement by Patty [2] which was: "Judging from the irritant effects of caustic mists encountered in concentrations of 1 to 40 mg per cubic meter of air, 2 mg sodium hydroxide per cubic meter is believed to represent a concentration that is noticeably, but not excessively, irritant." No further description of what led Patty to this conclusion was given, but Smyth [55] in his critical review of Threshold Limit Values avouched that it was based upon observations of exposed workmen.

The authors of a NIOSH Health Hazard Evaluation [26] reported that some of the employees tending a cleaning vat had upper respiratory irritation such as burning/redness of the nose and throat, and also burning/redness of the eyes from sodium hydroxide exposure. Airborne concentrations of sodium were found to be 0.005-0.7 mg/cu m (as sodium hydroxide). The Stoddard and other unspecified solvents in the workplace were assumed not to have been responsible for the upper respiratory and eye irritation, but based on the information presented by the authors, this assumption is not necessarily valid. They found airborne concentrations of Stoddard and other unspecified solvents as high as 780 mg/cu m. These solvents may have played an important role in the production of upper respiratory irritation. The Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists [56] recommended a Threshold Limit Value (TLV) for the Stoddard solvent of "approximately 800 or 1100" mg/cu m on the basis of its similarity in composition to unleaded gasolines. The TLV documentation [56] cited the work of Davis et al [57] in which men were exposed to unleaded gasoline at airborne concentrations of 150-220 ppm (800-1210 mg/cu m) for 30 minutes and reported itching or burning of the throat and of eyes and headaches. Because of these effects of gasoline and the probable similarities between gasoline and Stoddard solvent, it is unlikely that sodium hydroxide was conclusively and solely responsible for the effects the authors found.

In the study by TR Lewis, reviewed in the section on Effects on Humans, 1 person felt throat irritation when the airborne sodium concentrations, as sodium hydroxide, were 0.24 and 1.86 mg/cu m. Another person developed watering eyes when exposed at 0.80 mg sodium/cu m, reported as sodium hydroxide. Another person did not experience irritation when the airborne sodium concentration was 0.28 mg/cu m as sodium hydroxide. It is apparent that since these were all short-term exposures, of 2-15 minutes duration, irritation may result in a rather short period of time. Two factors limit the extent of correlation that can be made between the amount of exposure and effect. One of these is the uncertainty that the irritation from the use of the oven cleaner was due to sodium hydroxide. One subject, for example, noted that other sprays (eg spray deodorant) also caused a choking feeling. The other factor is the possibility that the sampling process, being unsupervised, was not accurate enough to allow a meaningful conclusion to be drawn.

IV. ENVIRONMENTAL DATA

Sampling

In view of the usual forms and uses of sodium hydroxide as discussed in Chapter III, it is likely introduced into the workplace air as a dust or mist. Dusts of sodium hydroxide are hygroscopic and deliquescent, [58,59] and in humid air would be expected to become mists.

Carbon dioxide, an acidic ambient gas, probably interacts to some extent with airborne sodium hydroxide to decrease its alkalinity. Carbon dioxide, usually present at 330 ppm, [60] is in nearly a 300-fold excess of sodium hydroxide at 2 mg/cu m, the current (1975) federal standard (29 CFR 1910.1000). Other acidic gases, such as nitrogen oxides and sulfur oxides would also tend to decrease the alkalinity of a sodium hydroxide aerosol. It is significant that the hydroxyl ion in the sodium hydroxide is responsible for the alkalinity of the substance, because sodium ions do not hydrolyze to any appreciable extent. [61] Although the reactions with ambient gases decrease the alkalinity of the aerosol (ie amount of hydroxyl ion/cu m), they do not change the sodium ion concentration.

In the usual workplace air, the sodium hydroxide in an aerosol is almost completely dissociated into sodium and hydroxyl ions. [58] This dissociation precludes the ready determination of sodium hydroxide as a compound, but does allow one or both of the resulting ions to be determined.

Sampling and analysis of sodium hydroxide in air is troublesome and has been reported on rare occasions. [26, TR Lewis, written communication, November 1974, BJ Gunter, written communication, April 1974] In these instances, aerosols were collected by filters and impingers.

When an aerosol of sodium hydroxide is collected for determination of its airborne concentration, the method to be used for chemical analysis must be considered in selecting an appropriate sampling technique. As mentioned above, sodium hydroxide may be determined by the sodium content of the sample, alkalinity, or both, but under some circumstances sampling may decrease the validity of calculations of the airborne sodium hydroxide concentration on the basis of chemical analysis. Instances in which this validity may be diminished are likely the result of inadequate samples or chemical reactions which occur during sampling.

If the concentration of a sodium hydroxide aerosol is to be determined, the aerosol must be sampled accurately and the samples must be transported to a laboratory for analysis without disrupting the contents of the sample. For the purposes of discussing the advantages and disadvantages of each of the 2 alternative methods of sodium hydroxide determination, assume for a moment that analysis for alkalinity is to be accomplished. Sampling for the alkalinity of an aerosol, ie the number of moles of alkaline substances in excess of chemical neutrality, if intended to exclude alkaline gases, eg ammonia and amines, would appear to be an instance where particulate-collecting devices should be used. Industrial hygienists have often used filters or impingers for collection of dusts and mists, and by analogy alkaline dusts and mists should be collectable in either manner. There is some tendency to prefer filters instead of impingers in current industrial hygiene practice because they are more convenient to use; the combination of a filter and holder is smaller, less cumbersome, more compatible with personal breathing-zone sampling, and somewhat easier to ship to a laboratory. Impingers may be excellent collecting devices. However, they are often used only when filters are not adequate, such as in the case of gas sampling. [62]

Regardless of whether filters or impingers are used to remove airborne sodium hydroxide from the air for subsequent analysis, it is well to consider that all dusts and mists will be concomitantly sampled, and that large quantities of air will be drawn through the sampling devices. When air contaminants are collected and thereby concentrated, reactions between constituents are more likely to occur in the sample than in the air, based on general principles of reaction kinetics. [63]

The most alkaline substance which can exist, except momentarily, in water, the hydroxyl ion, tends to react with acidic components of the air. [64] All of these components react to decrease the apparent alkalinity of an aerosol, but ambient carbon dioxide is probably the most significant reactant in view of its high concentration (v.s.). [60]

When hydroxyl ions are collected in an impinger solution or on a filter, it is uncertain how much neutralization by acidic gases is likely to occur. [65,66] Nevertheless, during collection hydroxyl ions would probably be neutralized by ambient carbon dioxide to some extent [66-69] forming carbonate and hydrogen carbonate ions and carbonic acid. Because of this reaction, an analysis of the sample for total hydroxyl ion content must take into account an indeterminate factor--the degree of neutralization which occurred during collection. Of course, dusts and mists of carbonates and hydrogen carbonates which are collected in the collecting device would be indistinguishable from those formed in the device by this acid-base reaction.

On account of this yet undetermined variable--the degree of neutralization which occurs during collection of a hydroxyl ion-containing aerosol--measurement of net alkalinity in a sample is not likely to give an accurate indication of airborne hydroxyl ion concentration.

Because of this variable and the difficulties likely to be encountered when collecting an aerosol for total alkalinity determination, it is appropriate to examine whether or not the sodium hydroxide aerosol can be effectively sampled if the analysis is to be based, instead, on a total sodium assay. Reactions which occur in the sampling process which change the apparent sodium hydroxide concentration in a sampled aerosol, by altering the hydroxyl ion concentrations, are not likely to occur; even if constituents were collected concomitantly with the sodium to decrease the solubility in solution (the only likely reaction), [58] an analysis for total sodium content and not ion activity (viz alkalinity measurement) would alleviate any such difficulties. [70]

In a possibly simplistic, exemplary, situation in which a source of sodium hydroxide is sampled, on the basis of the above arguments, samples would be produced which have a sodium content proportional to the airborne sodium hydroxide concentration, but an alkalinity which would be less than that of the aerosol.

Regardless of whether sodium or alkalinity is to be determined, sampling will introduce errors because the analytical method to follow is not selective. Other sodium compounds will provide sodium contamination, and other alkalies will contribute alkalinity indistinguishable from that due to sodium hydroxide. Other alkalies would be capable of being neutralized by acidic gases, especially carbon dioxide [66] and so analyses of total alkalies are likely to err. There is a possible means to diminish the extent to which other sodium compounds interfere, however; the fraction of sodium in a source of air contaminants which is sodium hydroxide may be reasonably assumed to approximate the fraction of sodium in collected samples which is due to airborne sodium hydroxide introduced by the source.

As discussed in Chapter III, it was probably not the airborne sodium concentration which was responsible for upper respiratory tract irritation and eye irritation on those rare occasions when reports were made. The reported irritation was probably related to the amount of alkaline substances deposited on tissue, using the data on injury to eyes and skin from direct contact with aqueous solutions of sodium hydroxide [36,48,49] as a guide to inferences. However, the limited inhalation and response data as discussed in Chapter III do not support the contention that the determination of alkalinity of samples of airborne sodium hydroxide aerosols can be positively correlated with the severity of irritation of eyes and the upper respiratory tract. The presence of carbon dioxide is likely to play a significant role in moderating the effects on mucous membranes from sodium hydroxide aerosols, if the arguments used above for explaining probable reactions on filters and in impingers [59,65-69] are applicable. In the above description of the advantages of using the collection of sodium as a more accurate means than using collected alkalinity for monitoring sodium hydroxide aerosol concentrations, it was implicit that engineering controls are more effectively monitored by this method; airborne sodium concentrations are not likely to decrease [58] while being transported by the air from a source of contamination to the sampling device. Therefore, airborne sodium concentration should serve to determine whether the recommended workplace environmental limit is being complied with.

Analysis

Although sampling sodium hydroxide aerosols is difficult (v.s.) and there is no entirely satisfactory technique currently (1975) available, analysis is comparatively straightforward, provided either alkalinity or sodium determination can be related to sodium hydroxide content. It is appropriate to discuss methods for determining alkalinity in samples and for determining sodium in the samples. [71-74]

Alkalinity of an aqueous sample is its capacity to accept protons. [64,75] It may be imparted to a sample by anions of any weak acids, such as hydroxyl, carbonate, phosphate, silicate, and others. [76] Alkalinity is usually determined by titration with a strong mineral acid to an endpoint indicated electrometrically or by a change in indicator color. [75] The alkalinity of a sample depends on the equivalence point selected and on how well the end point correlates with the equivalence point. [75-77]

Standard methods of water analysis have been developed for surface streams, domestic sewage, anaerobic digester supernatants, industrial wastes, and other waste waters. [75] In general, potentiometric titrations are recommended [75] when colored or turbid samples are encountered causing a colorimetric indicator to be less reliable; the use of potentiometric titration also avoids the errors due to the personal judgments of end-point color. In the presence of unknown amounts of anions of weak acids, it is often more useful and fail-safe to plot the actual potentiometric titration curve rather than titrate to a predetermined end point. [75,76] This plot should reveal a shift in the equivalence point due to temperature, ionic strength, or the presence of interfering weak acid anions. [75]

The equivalence point in a titration of total alkalinity (the point at which the sample's ability to accept protons is judged to be null) must be determined in view of the concentration of carbon dioxide present at the end of the titration. [75] In the presence of carbon dioxide or one of its precursors (carbonate or hydrogen carbonate) the equivalence point, and thus the end point to titrate to, also depends on the total alkalinity of the sample; this factor is often difficult to estimate before a titration is begun. [75-77]

If samples are to be determined for total alkalinity, it is important that they be analyzed as soon as practicable, preferably within 1 day. [75] NIOSH has not developed a standard method for analysis of sodium hydroxide by total alkalinity, so further description of exact specifications to be used for routine analysis is inappropriate at this time. When a method for determining alkalinity of aerosols is developed and tested, these recommendations for an appropriate analytical method for airborne sodium hydroxide will be reevaluated by NIOSH.

Determinations of sodium hydroxide aerosols by collection and analysis of sodium have been reported on several occasions. In a NIOSH Health Hazard Evaluation [26] samples were collected on filters and analyzed for total sodium using emission photometry. In another written report by BJ Gunter in 1974, samples were taken with impingers and analyzed for total sodium by emission photometry. When NIOSH investigated the effects of sodium hydroxide-containing aerosols generated by a spray oven-cleaner, samples were collected on membrane filters and analyzed for total sodium by atomic absorption spectrophotometry. [74] The NIOSH manual on recommended sampling and analytical methods describes recommended procedures (Appendix II) which may be used for atomic absorption analysis of sodium. [74] Perkin-Elmer [73] and the Environmental Protection Agency [78] have published methods for the analysis of water samples for sodium using atomic absorption spectrophotometry.

Other methods for determining sodium have been used. Zinc uranyl acetate [71] has been used in a gravimetric method for sodium, but to be effective this technique requires amounts of sodium larger than those expected in samples of airborne sodium hydroxide. Ion-selective electrodes have been used [72] for analysis of sodium and other ions; analysis with these electrodes generally increases in difficulty when samples having unknown matrices are to be analyzed. Ion-selective electrodes have the further disadvantage of responding to sodium-ion activity but not to total sodium-ion concentration.

In contrast to the very short lives of samples if total alkalinity is to be determined (ie 1 day), [75] samples which are to be analyzed for total sodium are probably indefinitely chemically stable.

On the basis of available information, it is recommended that airborne sodium hydroxide be sampled and analyzed on the basis of airborne sodium concentration, and that when necessary, an evaluation of a source be made to determine that fraction of total sodium contributed by sodium hydroxide in an aerosol. Because of the convenience associated with their use, filters are recommended for collecting sodium hydroxide aerosols. Analysis of sample's contents for sodium should be accomplished using emission or atomic absorption photometers, because methods using these instruments generally have high specificity, sensitivity, and speed of analysis, and because these instruments are likely already in widespread use in laboratories capable of analyzing samples from industrial hygiene surveys.

NIOSH has published a method for analyzing sodium with atomic absorption spectrophotometry, [74] but has not published a method for determining sodium using flame photometry. For this reason, Appendix II comprises the atomic absorption spectrophotometric method.

Control of Exposure

The hazards to workers exposed to sodium hydroxide (caustic soda) arise from the destructive action of this chemical on living tissue. The prevention of injury to employees working in areas where sodium hydroxide is used, handled, or stored must be based nearly entirely on measures and practices to prevent or minimize all contact of sodium hydroxide with any external or internal tissue of the body. The hazards of sodium hydroxide are usually the result of local contact and therefore the use of control methods and work practices is an appropriate means of preventing injury.

Insofar as possible, solutions of sodium hydroxide should be handled in closed systems which will prevent either contact with, or inhalation of, the chemical. Because of the highly corrosive action of sodium hydroxide, all such process, transfer, and storage equipment must be constructed of resistant materials and must be regularly inspected to prevent leaks and other failures.

Carbon steel is the material generally used for containment of sodium hydroxide; contamination of solutions with iron may result from such contact, however. [79] At temperatures above 140 F stress corrosion cracking called caustic embrittlement may occur, so the temperature should be held below 140 F. If temperatures above 140 F are used, containers must be stress-relieved or made from materials more resistant than carbon steel. Nickel affords resistance superior to carbon steel and may be used as nickel-cladding or nickel-plating on steel; nickel alloys give nearly as resistant a coating as nickel. Stainless steel is occasionally used where external corrosion may occur. Copper, brass, chromium, and bronze are moderately attacked by caustic soda and should not be used. Zinc, tin, magnesium, and aluminum are rapidly attacked, liberating hydrogen gas and thereby creating a possible explosion hazard, and must not be used. Nonmetallic materials such as epoxy resins and some synthetic elastomers such as neoprene have been successfully used as tank linings.

Emissions of airborne sodium hydroxide as dusts or mists should be controlled by enclosure of the process or by application of suitable exhaust ventilation equipment. The exhaust ventilation should be designed, installed, operated, and maintained in accordance with the principles given in the 1974 [80] or subsequent edition of _Industrial Ventilation--A Manual of Recommended Practice_ and _Fundamentals Governing the Design and Operation of Local Exhaust Systems_. [81]

All process, transfer, and storage equipment should be designed to minimize possibilities of employee contact with sodium hydroxide and of dispersal dusts or mists of sodium hydroxide into the air. [79,82-85] The use of remote control and mechanical handling equipment can do much to reduce the hazards.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

The American Conference of Governmental Industrial Hygienists was the first organization in the United States to recommend an environmental limit for sodium hydroxide. That recommendation, introduced in 1948, [86] specified a Threshold Limit Value (TLV as a time-weighted average) of 2.0 mg sodium hydroxide/cu m, and remained until 1973 [87] when ACGIH gave notice that revision to a ceiling value was intended. The only reference given to substantiate the ACGIH TLV recommendation [2] was the observation made by Patty, presumably based upon his experience, that "from the irritant effects of caustic mists encountered in concentrations of 1 to 40 mg per cubic meter of air, 2 mg sodium hydroxide per cu m is believed to represent a concentration that is noticeably, but not excessively, irritant." [2] No data or reference to substantiate this statement were given. Patty further clarified his recommendation of 2 mg per cu m as a "temporary bench-mark of permissible atmospheric contamination until further information is presented."

The present (1975) federal standard for sodium hydroxide is also 2 mg/cu m as a time-weighted average (29 CFR 1910.1000) and is based upon the 1968 ACGIH Threshold Limit Value.

Six other countries have also recommended standards for sodium hydroxide which appear in Table V-1. The limits in this table were compiled from several sources, [88-90] but explanations of how they were derived were not given.

TABLE V-1*

STANDARDS FOR SODIUM HYDROXIDE

Country	Substance	Standard (mg/cu m)
USA	Sodium hydroxide	2 (TWA)
Finland	Sodium hydroxide	2 (Ceiling)
West Germany	Sodium hydroxide	2 (Ceiling)
Yugoslavia	Sodium hydroxide	2 (Ceiling)
Rumania	Hydroxides (alkaline)	1 (Ceiling)
Bulgaria	Alkalies (sodium hydroxide, etc)	0.5 (Ceiling)
USSR	Alkaline aerosols (as sodium hydroxide)	0.5 (Ceiling)

*Derived from references 88-90

Basis for Recommended Environmental Standard

Sodium hydroxide has been found to cause blindness after just a few seconds of contact with the eye. [49] Sodium hydroxide in solutions as dilute as 2% have caused [48] blindness in 65-91% of the animals whose eyes were in contact with it for only 1 minute.

Sodium hydroxide has caused irritation of the skin in rats after only a few moments of contact followed by extensive irrigation [36]; there is a latent period between contact of sodium hydroxide with the skin and the sensation of irritation. [15,21,23]

Ingestion of sodium hydroxide has produced esophageal stenosis and antropyloric stenosis [28] and, in several cases, massive injuries to the gastrointestinal system from sodium hydroxide have apparently promoted the development of esophageal cancer. [29-33,35] While, as previously commented on, this does not demonstrate a direct carcinogenic action of sodium hydroxide, it does nevertheless demonstrate the need for rigorous precautions against the accidental ingestion. An appropriate practice is to recommend that specifically labelled, capped containers be used which cannot be mistaken for something else, eg soft-drink bottles. Solutions of sodium hydroxide also may constitute an attractive nuisance because they resemble milk by appearance, lack an objectionable odor, and lack a warning taste; this is another example of the reasons to keep unauthorized persons, especially small children, out of the workplace.

The effects of inhalation of sodium hydroxide aerosols have been reported only on rare occasions. [2,51, TR Lewis, November 1974] When the airborne sodium hydroxide concentration was 2.0 mg sodium hydroxide/cu m it was observed to be "noticeably, but not excessively, irritant." [2]

In the recent report by TR Lewis, [written communication, November 1974] of the irritation produced among healthy volunteers when they sprayed an oven cleaner containing sodium hydroxide, among other undescribed ingredients, it appeared that upper respiratory tract irritation was produced in a very short period of time (2-15 minutes). The concentration of airborne sodium hydroxide, the only agent sampled, was 0.24-1.8 mg/cu m.

In view of the report by Patty [2] in which he mentioned that noticeable irritation occurred at 2 mg sodium hydroxide/cu m, and the reports describing damage to skin and eyes from local contact in a very short period of time, [36,48,49] it is reasonable to suggest that the current (1975) federal standard, (29 CFR 1910.1000) 2 mg sodium hydroxide/cu m as an 8-hour TWA, may be inadequate to prevent irritation from sodium hydroxide aerosols, and that it should be altered to provide a ceiling environmental limit. Although the study by TR Lewis [written communication, November 1974] may suggest that irritation from sodium hydroxide aerosols occurs at concentrations below 2 mg/cu m, the number of uncontrolled variables in the study, including questions about the reliability of the estimates of airborne sodium hydroxide, are such that confirmation and extension of this study should first be accomplished. In the interim, it is recommended that extensive procedures be undertaken to ensure that local contact with sodium hydroxide be prevented, and that an environmental limit of 2 mg sodium hydroxide/cu m as a 15-minute ceiling be applied to limit to a reasonable extent the effects of airborne sodium hydroxide.

It is recognized that many workers handle small amounts of sodium hydroxide or work in situations where, regardless of the amount used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with many of the provisions of this recommended standard, which has been prepared primarily to protect worker health under more hazardous circumstances. Concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below this limit. For these reasons "occupational exposure to sodium hydroxide" has been defined as exposure above half the workplace environmental limit, thereby delineating those work situations which do not require the expenditure of health resources, of environmental and medical monitoring, and associated recordkeeping. Half the workplace environmental limit has been selected on the basis of professional judgment rather than on quantitative data that distinguish nonhazardous areas from areas in which a hazard may exist. However, because of the nonrespiratory hazards such as those resulting from contact with eye or skin or from ingestion it is recommended that appropriate work practices and protective measures be required regardless of the airborne concentration of sodium hydroxide.

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VII. APPENDIX I

AIR SAMPLING PRACTICES FOR SODIUM HYDROXIDE

General Requirements

In order to evaluate conformance with the workplace environmental limit, 15-minute breathing-zone samples representative of the individual worker's exposure shall be collected. Sampling data sheets shall include:

(a) The date and time of sample collection

(b) Sampling duration

(c) Volumetric flowrate of sampling

(d) A description of the sampling location

(e) Other pertinent information

Air Sampling

(a) Fifteen-minute breathing-zone samples representative of worker exposure shall be collected to characterize the exposures of workers in each job or specific operation in each production area.

(b) Samples shall be collected using a portable sampling pump plus a cellulose membrane filter with a pore size of 0.8 μm or less mounted with backup pad in a 2- or 3-piece closed-face cassette.

(c) The sampler shall be operated at a flowrate of 2 liters/min and samples shall be taken for 15 minutes.

(d) A minimum of 3 samples shall be taken for each operation or process.

(e) If 20 or fewer samples are taken, 3 blank filters shall be carried in closed cassettes to the sampling site and shall be provided to the analytical laboratory for determination of the background correction which must be applied to the results of analysis. One additional blank shall be provided for each 10 samples in excess of the first 20.

Calibration of Sampling Trains

Since the accuracy of an analysis can be no greater than the accuracy of the measurement of the volume of air which is sampled, the accurate calibration of a sampling pump is essential for the correct interpretation of the volume indicator. The necessary frequency of calibration is dependent on the use, care, and handling to which the pump has been subjected. In addition, pumps should be recalibrated if they have been subjected to misuse, received from a manufacturer, or repaired. If the pump receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and at frequent intervals if they are used to collect numerous field samples. The accuracy of calibration is dependent on the type of calibrating instrument used as a reference. The choice of calibrating instrument may depend largely upon where the calibration is to be performed. For laboratory testing, a 1- or 2-liter buret or a wet-test meter is recommended, although other standard calibrating instruments such as a spirometer, Marriott's bottle, or dry-gas meter can be used.

Instructions for calibration with the soapbubble flowmeter follow. However, if an alternative calibration device is selected, equivalent procedures should be used. The calibration setup for personal sampling pumps with a cellulose membrane filter is shown in Figure X-1. Since the flowrate indicated by the flowmeter of the pump is dependent on the pressure drop across the sampling device, a membrane filter with appropriate backup pad, the pump flowmeter must be calibrated while operating with a representative filter and backup pad in the line.

(1) While the pump is running, the voltage of the pump battery is measured with a voltmeter to assure that the battery is charged adequately for calibration.

(2) Place the cellulose membrane filter with backup pad in the filter cassette.

(3) The calibration setup is assembled as shown in Figure X-1.

(4) The pump is turned on and the inside of the soapbubble meter is moistened by immersing the buret in the soap solution and drawing bubbles up the tube until they are able to travel the entire length of the buret without bursting.

(5) The pump is adjusted to provide a flowrate of 2.0 liters/min.

(6) The water manometer is checked to ensure that the pressure drop across the sampling train does not exceed 13 conventional inches of water at 2 liters/min.

(7) A soapbubble is started up the buret and the time it takes the bubble to travel a minimum of 1.0 liter is measured with a stopwatch.

(8) The procedure in (7) above is repeated at least 3 times, the results are averaged, and the flowrate is calculated by dividing the volume between the preselected marks by the time required for the soapbubble to travel the distance.

(9) Data for the calibration should include the volume of air measured, elapsed time, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and name of the person performing the calibration.

VIII. APPENDIX II

ANALYTICAL METHOD FOR SODIUM HYDROXIDE IN AIR

Principle of the Method [73,74,78]

Sodium hydroxide collected on membrane filters is dissolved in distilled water and the sodium content is determined by means of atomic absorption spectrophotometry. For maximum sensitivity, the 589.6-nm line is used; for higher concentrations of sodium, the less sensitive 330.2-nm line may be used instead of diluting the sample.

Interferences

Absorption of radiation by sodium is enhanced in the presence of rubidium, potassium, lithium, and cesium, especially in a high-temperature flame. It is unlikely that most industrial exposures to sodium hydroxide will involve more than trace quantities of these metals, so this type of interference will ordinarily be negligible. Any other compounds containing sodium will also be determined by this procedure, and therefore the method cannot be considered specific for sodium hydroxide when sodium chloride or other sodium salts are present. Whenever it is likely that appreciable quantities of other sodium salts are present, it may be appropriate to take bulk samples at the sources of sodium emissions to determine the fraction of sodium present as sodium hydroxide. Such an analysis may be accomplished by acid-base titration and total sodium assay.

Equipment and Reagents

Any suitable atomic absorption spectrophotometer and related accessories suitable for an air-acetylene flame may be used.

Water should be freshly distilled in an all-glass still and stored in polyethylene bottles.

Standard Solutions

Stock solution: Dissolve 2.542 g of NaCl (analytical reagent grade, dried at 140 C) in sufficient distilled water to make up 1 liter of solution. One milliliter equals 1 mg of sodium (1000 mg/liter). Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis.

Procedure

Remove filters from the cassette with tweezers and place them in a clean, dry 25-ml Erlenmeyer flask. Add approximately 5 ml of distilled water, swirl the flask, place it on hot plate, and bring the solution to a boil. Remove the flask from the hot plate, allow it to cool; then transfer the liquid to a 10-ml volumetric flask and dilute to volume. Aspirate the sample into the flame in accordance with appropriate procedures for the instrument used and compare the absorbance of the sample solution with that of standard solutions which have been similarly treated.

Range and Sensitivity

Using the 589.6-nm line, the sensitivity is 0.02 μg sodium/ml, and the optimum concentration range is 0.02-5 μg sodium/ml. If 30 liters of air are sampled, this range corresponds to airborne concentrations of about 12-3000 μg sodium hydroxide/cu m.

Precision and Accuracy

Data on precision and accuracy have not been developed but it is presumed that good precision and accuracy are obtainable.

IX. 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 in as large type size 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 guidelines in Chapter V, Part B, of the NIOSH publication, "An Identification System for Occupationally Hazardous Materials." 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, eg "500 mg/kg-lowest lethal dose published-oral-rabbit" 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 relative to the density of air; solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated whether by weight or by volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to the evaporation rate for 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 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 (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special fire fighting 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 Information

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, adverse effects certain; prolonged or repeated contact, severe damage may result.
>
> Eye Contact--no initial pain, but blindness may result.

"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 to common substances or circumstances such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. 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 anti-pollution 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 the correction of any 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 in 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

X. TABLES AND FIGURE

TABLE X-1

CHEMICAL AND PHYSICAL PROPERTIES OF SODIUM HYDROXIDE

	50% Solution	73% Solution	Anhydrous
Physical state at 25 C	Liquid	Solid	Solid, flake, ground, powdered
Explosive limits	None	None	None
Flash point	None Noncombustible	None Noncombustible	None Noncombustible
Autoignition temperature	None	None	None
Boiling point (760 mmHg)	142-148 C (288-298 F)	188-198 C (370-388 F)	1390 C (2534 F)
Color	Clear and colorless to slightly colored and turbid	Clear and colorless to slightly colored and turbid	White to slightly colored
Corrosivity (all commercial grades)	Noncorrosive to rubber at atmospheric temperatures. Solutions are slowly corrosive to iron and copper; they may pick up quantities of these and other metals harmful for some uses. Attacks wool and leather clothing and a few metals, such as aluminum, tin, and zinc, and alloys containing these metals.		
Deliquescence	Yes	Yes	Yes
Hygroscopicity	Yes	Yes	Yes

TABLE X-1 (CONTINUED)

CHEMICAL AND PHYSICAL PROPERTIES OF SODIUM HYDROXIDE

	50% Solution	73% Solution	Anhydrous
Melting point (freezing point) crystallization begins at	12-15 C (54-59 F)	63 C (145 F)	310-320 C (590-608 F)
Solidifies at	5 C (41 F)	62 C (144 F)	
Reactivity	Considerable heat is generated when water is added to caustic soda; boiling and spattering of hot caustic solution may result. Caustic soda can react violently or explosively with many organic chemicals.		

Derived from reference 91

TABLE X-2

COMMERCIAL USES OF SODIUM HYDROXIDE IN 1969 IN THE UNITED STATES

End Use	Percentage of Total
Chemicals	42.5
Pulp and Paper	13.6
Rayon	5.4
Aluminum	7.4
Textiles	3.9
Petroleum	3.8
Soap and Detergents	4.8
Cellophane	2.1
Export	1.3
Miscellaneous	15.2
Total	100.0

Derived from reference 8

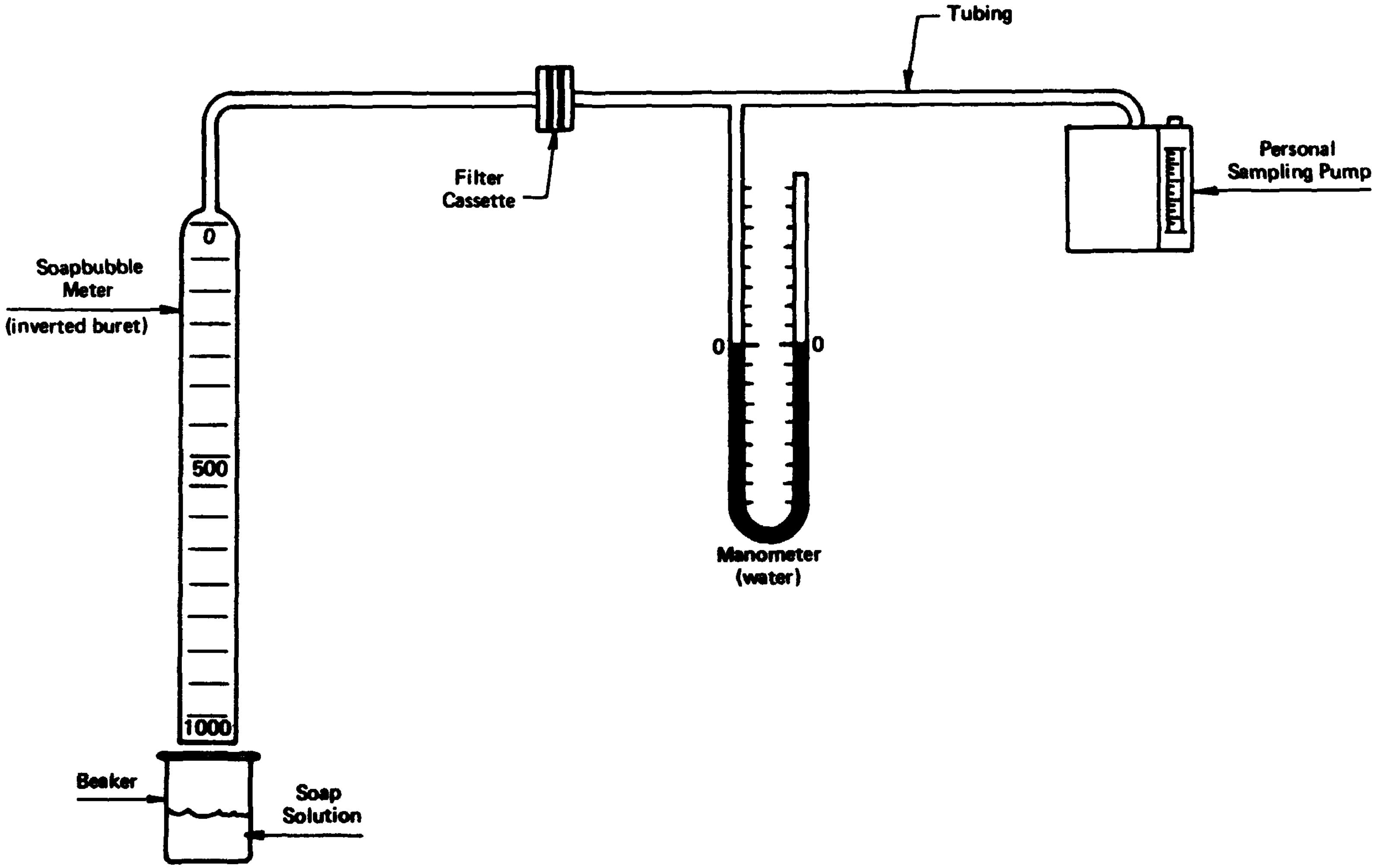
TABLE X-3

OCCUPATIONS WITH POTENTIAL EXPOSURE TO SODIUM HYDROXIDE

- bleachers
- bleach makers
- bronzers
- cellulose workers
- degreasers
- detergent makers
- dye makers
- electroplaters
- enamelers
- engravers
- etchers
- furniture polishers
- glass makers
- housekeepers
- laboratory workers, chemical
- laundry workers
- lithographers
- matchmakers
- mercerizers
- oxalic acid makers
- paint makers
- paint removers
- paper makers
- perfume makers
- petroleum refinery workers
- photoengravers
- pharmaceutical workers
- printers
- printing ink makers
- pulp makers
- rayon makers
- rubber makers
- rubber reclaimers
- soap makers
- sodium hydroxide workers
- tannery workers
- textile bleachers
- transparent-wrapping-material workers
- varnish makers
- vegetable oil refiners

Derived from references 9,10

FIGURE X - 1. CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH FILTER CASSETTE



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