

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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