

#### IV. ENVIRONMENTAL DATA

##### Environmental Concentrations

Few data have been found on the concentrations of airborne vinyl acetate in either industrial or ambient air. Gordon and Meeks [49] found ambient (grab-sample) vinyl acetate concentrations ranging from 0.07 to 0.57 ppm (0.25-2.0 mg/cu m) at four locations in the Texas City, Texas, area. Pervier et al [50] considered air emissions of vinyl acetate from production facilities to be less significant than emissions from other processes surveyed and therefore did not recommend that the Environmental Protection Agency conduct further (in-depth) study of vinyl acetate air emissions.

Deese and Joyner [18], in the course of an epidemiologic study of vinyl acetate workers, reported industrial air sampling results. "Short-term" samples were collected in a midget bubbler and an impinger in series, with toluene (near 5 C) as the collection medium, and "long-term" samples were collected similarly with standard Greenburg-Smith impingers; analyses were performed by gas chromatography. Deese (DE Deese, written communication, May 1978) indicated that the midget impinger samples were breathing-zone samples. The vinyl acetate concentration averaged about 8.6 ppm (30 mg/cu m), ranging from nondetectable to 49.3 pp m (173 mg/cu m). TWA concentrations in three production areas were reported as 8.2, 7.7, and 5.2 ppm (29, 27, and 18 mg/cu m).

Investigators for EI du Pont de Nemours and Company [16] collected air samples in the breathing zones of workers in a vinyl acetate production area. Vinyl acetate was collected in midget impingers containing dimethylformamide and was analyzed by gas chromatography. Samples were collected during two separate periods in summer and winter. The reported TWA concentrations ranged from 0.4 to 4.9 ppm (1.4-17 mg/cu m) with no systematic seasonal variation.

##### Sampling

Vinyl acetate has been collected by integrative sampling methods such as solid sorbent tubes [51] and midget impingers [18] and by grab-sampling methods, such as sampling bags [49].

Ambient air samples have been collected in polyvinyl fluoride bags for analysis by gas chromatography or infrared absorption spectroscopy [49]. Samples were collected with a 12-volt DC centrifugal blower, in 100-liter and 500-liter bags, requiring sampling periods of 2 minutes and 18-20 minutes, respectively. Two possible disadvantages of this method were noted: contamination of sample by diffusion of bag material and loss of sample by sorption, decomposition, or permeation. An additional disadvantage of this method is that the large sampling bags and the associated pumps are not suitable for personal sampling.

Although often used, midget impingers may be inconvenient for personal sampling because it may be necessary to recharge them with collecting medium frequently (depending on its vapor pressure) and because they may interfere with the movements of the worker, especially when used in series. Handling and transporting absorber solutions is difficult because of the possibility of spills and leaks.

Deese and Joyner [18] used two standard Greenburg-Smith impingers in series or a "fritted glass midget impinger bubbler and a standard midget impinger" in series to collect vinyl acetate. The standard impinger series was used to collect 2-hour samples at a flowrate of 1.5 liters/minute. The midget impinger series was used to collect 10-minute samples at the same flowrate. The temperature of the toluene collecting medium was kept near 5 C with aqueous methanol and dry ice, and vacuum was provided by a portable constant-rate sampler or a sequential sampler. The mean collection efficiency for the first impinger of each series (midget or Greenburg-Smith) was 86.3% at 0 C; mean collection efficiency for the first absorber near 5 C was 84.2%. Gas chromatography was used to analyze the samples.

Solid-sorbent devices are well suited for personal sampling; they are relatively small, and persons wearing them quickly adjust to their presence. They require less careful handling than liquid sorbents and are efficient and easy to use. Charcoal is a widely used general sorbent because it is nonpolar and has an affinity for organic vapors and gases. However, its collection and desorption efficiencies vary from batch to batch, so that it is necessary to determine the collection and desorption efficiencies for each batch.

Celanese Chemical Corporation investigators [51] have developed a method that utilizes a low-flow air sampler pump in conjunction with a collection tube packed with Porapak Q to sample for vinyl acetate. Basically, an air sample is collected in the worker's breathing zone at a flowrate of 40-60 ml/minute; the sample passes through a 3-inch collector tube with a 1-inch backup tube, both packed with Porapak Q (50/80 mesh). The collector tube is removed from the pump connection and locked into the programmed thermal desorber, eg, Century PTD-132, and the sorbent in the collector tube is immediately convection-heated with purge gas, eg, air, drawn through the tube by a device similar to a large stainless steel syringe. After desorption, the "syringe" retains the analyte reconcentrated in a fixed 300-ml volume of purge gas. At any later time, replicate analytical size samples of this gas may be manually or automatically withdrawn from the "syringe" and injected into a gas chromatograph for analysis without sample dilution, since the syringe piston adjusts itself to maintain a constant sample concentration by compensating for the volume of sample withdrawn. The sampling equipment is portable, automatic, and easy to use. Desorption and analysis with a portable gas chromatograph can be performed by on-site (field) personnel, thereby minimizing both the chances of mixup of tubes during transportation to a laboratory and the typical transportation and laboratory delays. Desorption can also be performed at a site remote from that of sample collection.

NIOSH [52] has proposed a solid-sorbent sampling method for vinyl acetate. It is recommended that the sampling rate and volume not exceed 0.1 liter/minute and 3.0 liters, respectively. Chromosorb 107 is the recommended sorbent. Vinyl acetate has been successfully collected by this method over the concentration range of 8.2-206 mg/cu m at a relative humidity of over 80%, but the method is known to be capable of collecting much smaller amounts of vinyl acetate (quantitative limit is 0.5  $\mu$ g of vinyl acetate/300 mg of solid sorbent). This method, described in Appendix I, is the recommended sampling method.

### Chemical Analysis

Vinyl acetate has been determined by polarography [27,53], infrared absorption spectroscopy [49], bromometry [54], paper chromatography [55,56], colorimetry [3,57-59], and gas chromatography [4,16,18,36,51,60-63].

Horacek [53] hydrolyzed vinyl acetate in an alkaline (LiOH) medium and determined the resulting acetaldehyde by polarography. The method was useful for concentrations of vinyl acetate of 0.01-1 mg/ml. The author stated that the method was simple, rapid, and sufficiently precise (not further defined), but interferences included aldehydes and many alkaline cations, eg, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Rb<sup>+</sup>, and Ba<sup>++</sup>. Filov [27] also used a polarographic method to analyze for vinyl acetate, but he did not describe the method in detail.

Long-path infrared Fourier transform absorption spectroscopic analysis was used to measure vinyl acetate at concentrations ranging from 0.07 to 0.57 ppm (0.25-2.0 mg/cu m) [49].

Bokov et al [54] used bromometry to determine vinyl acetate in air. This method was based on the addition of bromine across the double bond of vinyl acetate. The quantity of bromine consumed was indicative of the concentration of vinyl acetate.

Several colorimetric methods have been used for determination of small amounts of vinyl acetate in air. The complexation of mercuric acetate with vinyl acetate was the basis of one colorimetric method [57]. Mercuric acetate was added to a solution containing vinyl acetate in ethyl alcohol; after 1 hour, diphenylcarbazide in ethanol was added to form a violet complex with the excess mercuric acetate. The sensitivity was reported as 0.05 mg/liter of sample. To determine the concentration of vinyl acetate in air in the presence of aldehydes, Andronov and Yudina [58] mixed a sample with hydroxylamine hydrochloride and ferric chloride and used phenolphthalein as the colorimetric agent. The sensitivity of this method was stated to be 1  $\mu$ g in 3.5 ml. Another colorimetric method [59] was based on vinyl acetate's oxidation to formaldehyde by permanganate or periodic acid. Chromotropic acid was then used for colorimetric determination of the formaldehyde at 574 nm. Gofmekler [3] mixed a sample of vinyl acetate with alkaline hydroxylamine to

form acetohydroxyamino acid, which produced a color ranging from light yellow to purple in the presence of ferrous chloride. The sensitivity of the method was reported to be 0.025  $\mu\text{g}/\text{ml}$ .

Horacek [55] used paper chromatography to separate the hydroxamate derivatives of caprolactam, vinyl acetate, acrylic acid, and metacrylic acid esters. The method was described as rapid and relatively sensitive; the amount of monomer in the aliquot was determined colorimetrically by adding a ferric salt.

Osokina and Erisman [56] described an analytical method for vinyl acetate that involved reacting a salt of mercury with the vinyl acetate, followed by separation of the resulting mercury compound by paper chromatography. The addition of the mercury was found to proceed more rapidly in an alcoholic medium. The minimum amounts of vinyl acetate detectable in various alcohols ranged from 0.3 to 1.0  $\mu\text{g}$ .

The most widely used method for analyzing vinyl acetate is separation by gas-liquid chromatography with flame-ionization detection. Analysis by gas chromatography generally involves either direct injection of a portion of the sample from a sampling container or injection of an aliquot of sample desorbed from a suitable sorption material. The choice of column materials and operating parameters for vinyl acetate analysis depends on the relative retention times of the possibly interfering compounds.

West et al [61] reported using a U-shaped 5-mm x 2-meter glass tube containing 20% beta,beta'-oxydipropionitrile on 30/60 mesh Chromosorb to measure vinyl acetate retention times at a column temperature of 53 C. In another retention behavior study of vinyl acetate, Germaine and Haken [63] used a gas chromatograph with a 12-foot x 1/4-inch aluminum column packed with 10% methyl silicone polymer (SE-30) on 60/80 mesh, acid-washed, and silanized Celite 560 and operated at 150 C.

Bollini et al [62] used gas-liquid chromatography with flame-ionization detection to determine the amount of vinyl acetate monomer in a mixed aqueous suspension of polyvinyl acetate and butyl acrylate-vinyl acetate copolymer. They used a 1/8-inch x 6.6-foot steel column containing 10% polyphenylether OS-138 on Chromosorb W-AV (80/100 mesh) at 90 C. The authors' major criticism of this system was that the injection chamber of the chromatograph might become encrusted after approximately 10 injections.

To separate vinyl acetate from other organic compounds, Smith and Dahlen [60] used a column of tetraamylsilane and dimethyldioctylsilane on 60/100 mesh Celite 545 at a column temperature of 95 C. Values obtained with this method had only a 0.4% error when compared with the known amounts of vinyl acetate used.

Deese and Joyner [18] also used a gas chromatograph equipped with a flame-ionization detector to measure vinyl acetate concentrations. A 6-foot x 1/4-

inch stainless steel column packed with 80/100 mesh Porapak Q was used at 200 C. Preliminary evaluation using known concentrations of vinyl acetate showed a 99.2% mean accuracy (range, 80.9-110.2%) with this method; it was stated to be accurate and reliable for the low concentrations (0.4-49.3 ppm) encountered in the study.

A 4-foot x 1/8-inch stainless steel column packed with Chromosorb 101, 80/100 mesh, has been used at 110 C for monitoring vinyl acetate in air by Celanese Chemical Corporation investigators [51]. May et al [64] found Porapak Q to be a suitable packing in a pyrolysis gas chromatographic system for a 5% vinyl acetate-vinyl chloride copolymer. Two other reports [4,16] noted that airborne vinyl acetate was analyzed by gas chromatography, but details of the analytical methodology were not presented.

NIOSH [52] has proposed a method for analyzing vinyl acetate in workplace air samples by gas chromatography with flame-ionization detection. Samples are collected on Chromosorb 107 and thermally desorbed with helium at 150 C. The desorbed vapors are injected onto a chromatographic column packed with 10% FFAP on 80/100 mesh Chromosorb W AW. This method has been found suitable for quantifying vinyl acetate in concentrations as low as 0.5  $\mu\text{g}/300 \text{ mg}$  of Chromosorb 107. The pooled relative standard deviation of the sampling and analytical method was 8.1% for 50 samples over the concentration range of 8-200 mg/cu m. This method is described in detail in Appendix I.

There are a number of direct-reading devices that can be used to determine vinyl acetate in workplace air. Combustible gas meters and colorimetric tubes, although they are not sensitive enough to determine vinyl acetate at concentrations as low as the recommended ceiling limit, may be useful for leak detection and other emergency situations.

NIOSH [65] has evaluated nine commercially available, portable combustible gas meters. These instruments are not specific for vinyl acetate, but their utility for measuring concentrations of vinyl acetate can be enhanced by calibrating them under temperature and other conditions resembling as closely as possible those at the sampling site.

Colorimetric tubes capable of semiquantitative measurements of vinyl acetate in air are manufactured by Draeger [66] and by Gastec [67]. The Draeger tubes are sensitive to vinyl acetate at 50 ppm with 10 strokes of the pump, and the Gastec tubes can detect vinyl acetate at 10 ppm with a single stroke of the pump. This sensitivity can be increased by increasing the number of strokes, down to about 5 ppm, the minimum detection limit for these devices. Ethyl acetate and other esters of acetic acid will interfere.

NIOSH [68] has also evaluated several portable, direct-reading analyzers. At least three of these are suitable for determination of vinyl acetate concentrations at or below the recommended occupational exposure limit. The Wilks-Miran infrared analyzer is capable of detecting vinyl acetate down to about 0.02 ppm [69]. The Century organic vapor analyzer is capable of

detection over the range of 1-10,000 ppm, depending on the scale selected [70]. The photoionization meter produced by HNU Systems, Inc, can detect vinyl acetate, as well as many other gases and vapors, over the concentration range of 0.1-2,000 ppm, using energy sources of 10.2 and 9.5 electron volts (eV) [71]. Although none of these devices is specific for vinyl acetate, the HNU photoionization meter with 9.5-eV energy source will discriminate out all compounds with ionization potentials above 9.5 eV; this includes most potential interferences, eg, ethyl acetate (10.11 eV), methane (12.6 eV), vinyl chloride (9.996 eV), acetic acid (10.36 eV), ethylene (10.5 eV), acrylonitrile (10.91 eV), and acetonitrile (12.2 eV) [9].

NIOSH recommends a gas chromatographic method with flame-ionization detection for analysis of vinyl acetate in workplace air. The recommended method is described in detail in Appendix I. This method has the advantage of permitting analysis by a quick instrumental method either on-site or in a laboratory remote from the site of sample collection. It is efficient and economical, since sampling tubes may be reused after analysis is completed. Most potential interferences can be eliminated by altering chromatographic conditions. Although this analytical method has not yet been approved or validated by NIOSH, it shows promise of being suitable for determination of vinyl acetate in workplace air at the concentrations required by the recommended standard, with acceptable precision and accuracy.

## Hazard Control By Process and Design Engineering

### (a) Ventilation

Engineering design of operations and process equipment involving vinyl acetate should be oriented toward controlling inhalation and skin and eye contact with the liquid or vapor. Properly designed and maintained ventilation systems should prevent dispersal of vinyl acetate into the workroom atmosphere and the accumulation of vinyl acetate on surfaces. These goals can be met with properly constructed and maintained closed systems. If closed systems are not feasible, local exhaust ventilation systems should be provided at potential contamination sources to direct airflow away from the employees' breathing zones. These systems should be designed to remove the vapor with proper allowance for makeup air and should prevent mere recirculation of contaminated air. Guidance for design of such systems can be found in Industrial Ventilation--A Manual of Recommended Practice [72], in Fundamentals Governing the Design and Operation of Local Exhaust Systems (ANSI Z9.2-1971) [73], and in NIOSH's Recommended Industrial Ventilation Guidelines [74].

Ventilation systems require regular inspection and maintenance to ensure effective operation. Inspections should include measurements of system function, eg, airflow at collection hoods, static pressure at branch ducts, or pressure drop across filters and fans. Whenever measurements indicate unacceptable functional decrements in a system, the equipment should be

inspected more closely and immediately repaired or otherwise restored to an acceptable state of function. A water or oil manometer can provide a convenient, continuous method for evaluating airflow. The manometer should be marked to indicate design airflows. The continued effectiveness of vapor control systems should be evaluated by sampling and analyzing air in the general workroom, in operators' breathing zones, and around potential contamination sources whenever the ventilation system or work operations or processes are changed.

Ventilation systems, as well as all other equipment in vinyl acetate manufacture or use facilities, must be designed and operated in a manner cognizant of the high flammability of this compound. Electrical motors and other electrical components must be explosion-proof. Moving parts of the system, eg, fan blades, must be constructed of nonsparking materials.

#### (b) Storage and Handling Areas

Manufacturing, processing, storage, and transfer equipment must be constructed of materials resistant to corrosion by vinyl acetate. One vinyl acetate manufacturer recommends carbon steel, lined carbon steel, or aluminum and has noted that brass, bronze, or lead compounds are not acceptable construction materials [51]. Small samples should be stored in brown bottles [12]. Storage in outdoor or detached bulk storage areas is preferable to indoor storage. Bulk storage areas must be diked to contain any spills, and sump pumps in these areas must be explosion-proof. Storage and manufacturing areas must be constructed so that spilled or leaked vinyl acetate does not run into sanitary sewers, where it may present an explosion or fire hazard. Facilities in which large quantities of vinyl acetate are processed or stored should be protected by automatic sprinkler or deluge systems [5,51].

Vinyl acetate storage areas should be separated from areas containing oxidizing and polymerization-initiating compounds. Vinyl acetate should also contain a suitable polymerization inhibitor, such as hydroquinone or diphenylamine, when stored [8,12]. Any recommendations of the manufacturer regarding the necessity for the presence of dissolved oxygen should be followed [12].

The storage of vinyl acetate poses certain problems related to vent size, diking, and separation distances, which, in turn depend on other variables, such as tank size or design. Storage areas should therefore be designed in consultation with qualified fire protection engineers [5].

Loading and unloading operations are particularly hazardous because of the high flammability hazard associated with vinyl acetate. Moving liquids, especially bulk liquids, produce buildups of static electricity. These must be controlled by bonding and grounding barge, railroad car, and tank truck terminals.

## V. WORK PRACTICES

### Storage, Handling, and Use

Vinyl acetate is extremely flammable and potentially explosive; its flashpoint has been reported as -5.5 C (22 F) [5], and the explosive limits, in air by volume, have been reported as 2.6-13.4% [5]. Other pertinent physical and chemical properties are listed in Table XI-1. Because of this extreme flammability, smoking and the unregulated use of open flames or other ignition sources, including matches, must be prohibited in vinyl acetate work areas. Flashlights, if used, must be of a type approved by the Mine Safety and Health Administration for use in hazardous atmospheres [12].

Electrical systems and all electrical equipment in vinyl acetate work areas must conform with the provisions of 29 CFR 1910, Subpart S [75].

Storage areas must be operated in accordance with the regulations applying to flammable liquids in 29 CFR 1910.106. Containers should be stored safely to minimize breaks and leakage. Vinyl acetate should be stored at temperatures below 37.8 C (100 F) to prevent acid buildup [12]. Storage areas should not contain sources of high temperature or be exposed to sunlight or other penetrating electromagnetic radiations [12]. Vinyl acetate polymerization can be retarded by adding a suitable inhibitor, such as diphenylamine or hydroquinone [5,8]. The maximum safe storage period depends on the amount and type of inhibitor added [5] and the amount of dissolved oxygen present [12]; the manufacturer's recommendations for oxygen content and maximum storage periods should be observed. The US Department of Transportation (DOT) compatibility guide for bulk liquid chemical transportation by water lists vinyl acetate as incompatible with nonoxidizing mineral acids, sulfuric acid, nitric acid, ammonia, aliphatic amines, and alkanolamines [76]. Vinyl acetate has been found to react with certain desiccants such as silica gel and alumina gel [5]. When desiccants are used, they should be tested for reactivity with vinyl acetate.

During the transfer of vinyl acetate from metal tanks or containers to other metallic vessels, the two vessels must be bonded and grounded to prevent the buildup of static electricity and possible spark generation. Failure to do so has caused explosion resulting in fatal injuries [77,78]. Inert gas purging of enclosed containers should be performed during transfer operations to prevent formation of explosive mixtures of air and vinyl acetate. Pressurized air should never be used for emptying vessels containing vinyl acetate [5].

Containers used to transport vinyl acetate should bear labels warning of the possibility of irritation to skin, eyes, and respiratory tract and providing information on the proper storage and handling of vinyl acetate.



DOT regulations require that vinyl acetate be tagged with a label classifying it as a flammable liquid (49 CFR 172).

Metal drums and other containers of vinyl acetate should be opened only with nonsparking tools. Fittings should never be struck with anything that may cause a spark [5]. When containers have been emptied, all openings should be closed tightly [5]. Vessels to be discarded should be steamed to remove traces of vinyl acetate and rendered impossible to reuse by crushing or piercing.

### Maintenance of Equipment

The duties of maintenance and repair workers pose special problems with regard to the evaluation of their potential exposure to vinyl acetate. Often the very circumstances that require the maintenance or repair work, and under which work must be done, will negate some of the normal control procedures. Therefore, these activities should be very carefully supervised. Maintenance and repair workers should use and wear appropriate protective equipment and clothing and should follow standard operating procedures or directives provided along with required special work permits (see below). They should be trained to recognize and control the hazards to which they may be subjected.

All tank maintenance and repair work should be performed under a permit system or its equivalent. Immediately before such work begins, the air in the tank should be tested. If the concentration of vinyl acetate vapor is found to be at or below the recommended ceiling limit, a work permit authorizing the maintenance and repair work should be issued, and the work should be started as soon as all potential vinyl acetate sources have been blocked and the work area has been posted with signs saying that work is in progress. If the concentration of vinyl acetate vapor is found to be above the recommended limit, the tank should be steamed to remove residual vinyl acetate [5]. The tank should then be cooled, preferably by rinsing with water and draining, and purged with fresh air. A work permit should not be issued until tests show that the vinyl acetate concentration in the tank is below the recommended limit. If the work is interrupted before completion, the tank air should be retested and a new work permit issued before work is resumed. The tank atmosphere should be tested frequently while the maintenance and repair work is in progress. If the vinyl acetate vapor concentrations are ever found to exceed the environmental limit, the work permit should be revoked and all work should stop until the concentration of vinyl acetate is reduced to the recommended limit or below and a new permit is issued.

Tanks, equipment, pumps, lines, and valves should be drained and rinsed with water or purged with an inert gas before they are opened and repaired; workers performing this task should use proper protective equipment and avoid contact with any liquid draining or dripping from the equipment. Tanks should be steamed and kept above the boiling point of vinyl acetate (72.7 C) until

residual vinyl acetate vapor has been removed; volatilized vinyl acetate in the steam effluent should not be allowed to contaminate the surrounding areas.

Tank entrances should be large enough to admit a person wearing a safety harness, life line, and respirator in case of emergency. An appropriately equipped worker should be stationed outside the tank to keep the workers in the tank under observation at all times. Tank cleaners or repair workers overcome by vapor should be moved to fresh air immediately, and artificial respiration should be applied if breathing has stopped. A physician should be summoned at once.

Exterior repair work should be allowed only after areas are determined to present no hazard from vinyl acetate vapor. All spark- or flame-producing operations in the vinyl acetate work area must be rigidly controlled by a permit system or its equivalent. All outside welding or burning on tanks or equipment that have contained vinyl acetate should be done only after the containers have been completely purged with steam or filled with inert gas. Purging should continue while repair work is in progress [51].

#### General Housekeeping

Areas where spills of vinyl acetate have occurred should be posted to prevent entry by nonessential employees and promptly cleaned by means that will minimize inhalation of, or contact with, vinyl acetate. Large spills should first be contained, then flushed with water into an appropriate drainage system where vinyl acetate can be safely stored and either recovered or destroyed. Supervisors should emphasize to employees the need for prompt cleanup of spills, prompt repair of equipment and leaks, proper storage of materials, and proper functioning of dikes and deluge systems. All collected vinyl acetate should be recycled into the process or disposed of in a manner that meets applicable local, state, and Federal regulations.

#### Emergency Procedures

Specific procedures should be designed for the handling of emergencies involving vinyl acetate, and employees should be trained in these procedures. Complete written procedures for emergencies, revised and updated when necessary, should be readily available to all employees assigned to vinyl acetate work areas. Emergency procedures should provide for transportation of injured personnel to hospitals and should provide for instructions explaining the location, use, and maintenance of first-aid equipment, firefighting equipment, emergency showers, and eyewash fountains. Emergency drills should be held at least annually. All emergency plans should be designed to minimize personal injury.

Properly maintained safety showers and eyewash fountains should be located in or near all areas where exposure to liquid vinyl acetate may occur. In

case of dermal contact with vinyl acetate, the affected area should be flushed promptly with water. In case of ocular contact with vinyl acetate, eyes should be flushed immediately and thoroughly with water at low pressure. Exposed employees should then be taken promptly to the nearest medical facility to determine the need for further treatment. Employees should be made fully aware of these procedures.

For firefighting, carbon dioxide, foam, or dry chemical extinguishers or a spray of water should be used [5]. Use of a stream of water should be avoided to prevent splashing and spreading of fire. Automatic sprinklers and hose lines with spray nozzles should be available for fire control. Appropriate firefighting equipment should also be readily available. It should be noted that vinyl acetate floats on water and that the heat of burning vinyl acetate may initiate violent polymerization which could spread fire [12].

### Respiratory Protection

Engineering and administrative controls, along with good work practices, are the preferred means of keeping vinyl acetate concentrations within the permissible exposure limits. However, respirators may be needed to adequately protect employees in some situations, such as emergencies, during nonroutine maintenance, during the time necessary to install and test engineering controls, and during the time necessary to evaluate the impact of a process change on workplace air. Employers should provide each employee in these situations with appropriate respiratory protective equipment in accordance with Table I-1, and ensure that a respiratory protection program is established and observed. Guidelines for such a program are found in 29 CFR 1910.134. Cleanliness and maintenance of respirators should be emphasized. The interior of the facepiece should not be contaminated. Detailed information on respirator selection and usage may be obtained from the Respiratory Protective Devices Manual [79].

Nelson and Harder [80] evaluated the service life of organic vapor cartridges in a vinyl acetate atmosphere by determining the time necessary for 10% of a vinyl acetate influent (3,500 mg/cu m) to break through the cartridge. The flowrate was 53.3 liters/minute, the relative humidity was 50%, the temperature was 20-22 C, and the cartridge contained 26.25 g of activated carbon. Breakthrough time was 81.1 minutes. Because the concentration tested was so great, this study suggests that organic vapor cartridges provide adequate protection at the concentrations at which they are recommended for use in Table I-1 (up to 1,400 mg/cu m).

### Other Protective Equipment

The employer must provide all employees occupationally exposed to vinyl acetate with gloves and safety glasses with side shields or goggles and must ensure that they are worn when needed. Long-sleeved cotton coveralls may be

provided and worn to minimize skin contact. Disposable coveralls may be used. Fabrics that generate static electricity should be avoided. In areas where liquid vinyl acetate is handled, suits or aprons and boots impervious to penetration by vinyl acetate should also be provided and worn. Gloves should be constructed of materials resistant to penetration by vinyl acetate. No test data on glove materials were found; one vinyl acetate manufacturer provides neoprene gloves [51], and others have recommended "rubber" [5].

Other personal protective equipment should be provided, used, and maintained as specified in 29 CFR 1910.132-137. Proper protective clothing requires a snug, but comfortable, fit around the neck, wrists, and ankles. The protective equipment and clothing should be cleaned or replaced regularly. Personal protective equipment should be kept in suitable, designated containers or lockers when not in use.

#### Sanitation and Personal Hygiene

Plant facilities should be maintained in accordance with sanitation requirements listed in 29 CFR 1910.141. Contaminated clothing should be discarded or cleaned by laundering before reuse. Clothing to be reused should be stored in a container that is impervious to vinyl acetate. Personnel who clean such clothing should be informed of the attendant hazards.

Good personal hygiene, including washing hands thoroughly before using toilet facilities, eating, drinking, or smoking, is important to prevent ocular, respiratory, and dermal irritation.

## VI. DEVELOPMENT OF STANDARD

### Basis for Previous Standards

A Threshold Limit Value (TLV) of 10 ppm or 30 mg/cu m (sic) was recommended by the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) in 1969 [81] and adopted in 1971 [82]. A Short-Term Exposure Limit (STEL) of 20 ppm or 60 mg/cu m (sic) was recommended in 1976 [83]. The Documentation of Threshold Limit Values [84] noted 4-hour LC50 values in rats, mice, and rabbits of 4,000, 1,550, and 2,500 ppm, respectively. No evidence of circulatory abnormalities or evidence of altered metabolism was noted in dogs exposed 6 hours/day to vinyl acetate for about 11 weeks at average concentrations of from 91 to 186 ppm. The documentation stated that Gage [20] had found rats unaffected by repeated exposures at 100 ppm and had recommended 50 ppm as a working standard. The documentation also noted a report of 15 years' industrial experience with 21 vinyl acetate chemical operators in whom hoarseness and coughing ("slight irritation") were observed at around 22 ppm. The medical records and multiphasic examinations were stated to have revealed no evidence of chronic effects from concentrations of 5-10 ppm. The Threshold Limits Committee recommended a TLV of 10 ppm, citing the evidence that irritation may be experienced at around 20 ppm but not at 10 ppm and in the light of evidence that neither acute nor chronic effects occur from repeated daily exposures for many years [83].

According to an International Labor Office (ILO) report [85], Australia, Belgium, Finland, the Netherlands, Sweden, and Switzerland have maximum allowable concentrations (MAC's) for vinyl acetate of 10 ppm, or 30 mg/cu m (sic). The MAC for vinyl acetate in the USSR, Poland, and Yugoslavia is 10 mg/cu m (2.8 ppm). The Rumanian limits consist of average and maximum vinyl acetate concentrations of 50 and 100 mg/cu m (14 and 28 ppm), respectively. The ILO report noted that MAC's or ceiling values are used because time-weighted averages (TWA's) should not be applied to fast-acting substances, eg, irritants and narcotics, or to substances that are particularly toxic.

There is no current US Federal occupational standard for vinyl acetate.

### Basis for the Recommended Standard

#### (a) Permissible Exposure Limits

Exposures to vinyl acetate in the workplace have produced mainly reversible irritation of the upper respiratory tract and eyes, sometimes accompanied by skin irritation [4,16-18]. The available literature indicates that vinyl acetate typically produces only minor irritation and produces only

minor irritation and produces only minor, perhaps inconsequential, changes in internal organs [4,17-21]. No evidence was found of long-term systemic, carcinogenic, mutagenic, or teratogenic or other reproductive effects in humans or experimental animals.

Three of three persons exposed to vinyl acetate for short periods at 75.6 mg/cu m had upper respiratory tract irritation (hoarseness or cough); one of four exposed at 14.7 mg/cu m experienced hoarseness; and one of three exposed at 20.0 mg/cu m reported eye irritation [18]. All of these symptoms were reversible. Volunteers exposed to vinyl acetate at less than 1 mg/cu m showed changes in ocular light sensitivity and desynchronization of the EEG as a conditioned response [3], but there are no indications that these changes were signs of potentially adverse CNS effects.

All of the rats (presumably six) exposed for 2 hours to vinyl acetate at 28,000 mg/cu m died [17]. Four-hour LC50's for rats, guinea pigs, mice, and rabbits exposed to vinyl acetate ranged from about 5,400 to 21,750 mg/cu m [4,17]. A beagle exposed to vinyl acetate at 13,388 mg/cu m [4] and all rats exposed at 3,500 mg/cu m [17] survived. Rats exposed to vinyl acetate at 7,000 mg/cu m for 6 hours/day, 5 days/week, for 3 weeks exhibited respiratory difficulty, eye and nose irritation, and increased numbers of macrophages in the lungs [20]; examination at autopsy showed no visible abnormalities. Dogs exposed to vinyl acetate for 4 hours at 840 mg/cu m demonstrated eye blinking and reddening of the sclerae [4], and those exposed at 651 mg/cu m for 1 week had eye irritation and tearing [19]. No other adverse effects were reported in the dogs.

There is very little information available on the long-term effects of vinyl acetate on humans or animals. Among 21 production workers exposed to vinyl acetate at an average of 30.1 mg/cu m (range, undetectable to 172.6 mg/cu m) for about 15 years, 3 stated that they had experienced skin effects, and there were 6 reports of eye, nose, or throat irritation [18]; no chronic effects were found. Rats exposed 4 hours/day, 5 days/week, for 52 weeks to vinyl acetate at 8,750 mg/cu m and followed for up to 135 weeks did not develop tumors [24,25]; however, their mortality after 26 weeks of exposure was higher than that of unexposed control animals. Although there is some structural identity between vinyl acetate and other vinyl compounds that are known to induce cancer, there is currently no evidence to suggest that vinyl acetate is carcinogenic, mutagenic, or teratogenic, or that it causes reproductive effects in humans or animals.

In contrast to the vinyl halides, vinyl acetate contains an ester moiety. Vinyl acetate appears to be rapidly detoxified by esterases present in mammalian blood [27], ie, by a metabolic route that is not available to the vinyl halides. While it is conceivable that vinyl acetate is oxidized to a reactive oxirane, neither biochemical nor biologic evidence is available to indicate that this pathway plays a significant role in the biotransformation of vinyl acetate.

In the absence of retrospective epidemiologic studies of morbidity and mortality, and because there is no evidence that there are chronic effects in humans resulting from long-term exposure [18], NIOSH concludes that the recommended environmental limit should be based on the reversible irritation that has been associated with workplace exposure to vinyl acetate. The lowest concentration reported to induce any irritant effect (hoarseness) was 15 mg/cu m [18]. Since the toxic action of vinyl acetate, on short-term exposure, is expressed largely by reversible irritation of the respiratory tract and eyes [4,16,18], a ceiling concentration limit is deemed more appropriate than a TWA concentration limit. While hoarseness was experienced by only one of four persons exposed at 15 mg/cu m and eye irritation by one of three at 20.0 mg/cu m [18], the permissible exposure limit for vinyl acetate should protect even the more sensitive workers from these possible adverse effects. Therefore, a ceiling limit of 15 mg/cu m (4 ppm), measured in a 15-minute sample, is recommended as the occupational exposure limit, pending the development of more definitive data.

#### (b) Sampling and Analysis

Personal sampling, using a low-flow air sampler pump, thermal desorption, and analysis by gas chromatography are recommended for the determination of vinyl acetate. This method is described in detail in Appendix I. The sampling equipment is portable, automatic, easy to use, and relatively inexpensive. Gas chromatography offers the necessary sensitivity, precision, and accuracy and can be used in either field or laboratory situations.

#### (c) Medical Surveillance

Employees should be given preplacement medical examinations if occupational exposure to vinyl acetate may occur. Because vinyl acetate is an irritant to the upper respiratory tract, eyes, and possibly to the skin [4,16-18], attempts should be made to identify persons with preexisting upper respiratory, eye, and skin problems at the preplacement examination. Since there is no evidence that a chronic hazard may be associated with occupational exposure to vinyl acetate, chest roentgenograms are suggested only for preplacement examinations.

#### (d) Personal Protective Equipment and Clothing

Several investigators [4,16-18] have reported that vinyl acetate caused dermal and ocular irritation. Reports of dermal effects have mentioned that skin irritation, rash, or blisters resulted from exposure to liquid vinyl acetate and that blisters also occurred from contact with clothing wet with vinyl acetate [17]. Ocular effects from exposure to vinyl acetate included eye irritation or reddened sclerae [4]. None of these reported effects were severe, and all were reversible. Clothing impervious to liquid vinyl acetate, eg, rubber [5], should be worn to prevent skin contact. This clothing should include boots, gloves, coveralls, and face shields (8-inch minimum) with goggles or safety glasses with side shields. Such clothing should be cleaned

inside and out after each use. Emergency showers and eyewash fountains should be readily available in case of accidental contact of the skin or eyes with vinyl acetate. When existing engineering controls are not adequate to reduce concentrations of airborne vinyl acetate to or below the recommended environmental limit, appropriate respiratory protective devices should be used, pending corrective action.

(e) Informing Employees of Hazards

Exposure to vinyl acetate may cause respiratory, ocular, or dermal irritation. The reported irritation has not been severe, but prolonged contact with vinyl acetate may cause blisters on the skin or significant irritation of the eyes [4,17]. Employees who may be exposed to vinyl acetate should be advised of the possible adverse effects of such exposure, methods of preventing exposure, and environmental and medical monitoring and surveillance procedures used to detect hazards. The benefits to workers of participating in these environmental and medical monitoring procedures should be stressed.

(f) Work Practices and Engineering Controls

To minimize respiratory contact with vinyl acetate, engineering controls, preferably process enclosure, should be used when needed to control emissions into the workplace atmosphere. Engineering controls should include local exhaust ventilation for processes known to produce large amounts of airborne vinyl acetate. All vinyl acetate containers should be kept tightly closed when not in use, and should be stored properly, ie, conform to the provisions of CFR 1910.106 for storage of flammable and combustible liquids; this action should prevent breaks, spills, or contact with sources of ignition. Vinyl acetate forms flammable and explosive mixtures with air at temperatures of -5.5 C and above, and has explosive limits, in air by volume, from 2.6 to 13.4% [5], so that it should be kept away from heat, sparks, flames, peroxides, aldehydes, or other agents that might cause a fire or an explosion. Vinyl acetate is incompatible with nonoxidizing mineral acids, sulfuric acid, nitric acid, ammonia, aliphatic amines, and alkanolamines. Spills or leaks should be attended to promptly. Emergency showers or eyewash fountains should be available and used to clean affected areas in case of gross skin or eye contact with vinyl acetate. All employees, including maintenance and repair personnel, should be fully informed of all procedures, routine and emergency, that their specific jobs entail.

The residual vinyl acetate vapor in confined spaces may exceed the recommended environmental limit. To ensure that workers in confined spaces are adequately protected, entry into confined spaces that may contain vinyl acetate vapor should be controlled by a work permit system. Permits should be signed by an authorized employer representative, certifying that the following preventive and protective measures have been taken. The confined space should be cleaned with steam, purged with air, and thoroughly ventilated, inspected, and tested for oxygen deficiency and for vinyl acetate and other contaminants before it is entered. Ventilation should continue while workers are in the



confined space. Personal protective equipment should be readily available to the employee entering a confined space. Another worker stationed outside, equipped with approved personal protective and rescue equipment, should observe and be in communication with the employee working in the confined space.

(g) Monitoring and Recordkeeping Requirements

To minimize exposure of employees to vinyl acetate, employers should analyze engineering controls, work practices, and sanitation procedures on a continuing basis to ensure that they are operating as effectively as possible.

To ensure that concentrations of airborne vinyl acetate in the workplace do not exceed the recommended environmental limit, employers should conduct an industrial hygiene survey at least annually and as soon as possible after any change likely to result in increased concentrations of airborne vinyl acetate. If such a survey shows that concentrations of vinyl acetate in the workplace are above one-half the recommended ceiling limit, a personal monitoring program should be instituted, and both industrial hygiene surveys and personal monitoring should be repeated every 6 months. If personal monitoring shows that an employee is exposed to vinyl acetate at concentrations above the recommended ceiling limit, control measures should be implemented, the employee should be notified of the exposure and of the control measures being taken, and a personal monitoring program should be instituted, monitoring should be conducted weekly until two consecutive samples show that the employee is no longer overexposed to vinyl acetate. Pertinent environmental monitoring and medical records should be retained for 30 years after termination of employment involving exposure to vinyl acetate.

## VII. RESEARCH NEEDS

### Epidemiologic Studies

Only one very limited (cross-sectional) epidemiologic report on employees exposed to vinyl acetate [18] has been found in the literature, so that further research is required to assess the effects of long-term occupational exposure to vinyl acetate. Long-term epidemiologic studies that assess the effects of vinyl acetate on the skin, eyes, respiratory system, and general metabolic processes should be performed. These studies should include medical histories, specific pulmonary function studies, and comparison of the morbidity and mortality of exposed populations with those of appropriate control populations. It is essential that accompanying industrial hygiene surveys accurately determine actual exposures in terms of concentrations, durations, and frequencies. Concomitant exposures to other chemicals should also be considered.

### Experimental Studies

Studies of both short- and long-term exposures to airborne vinyl acetate at low concentrations should be conducted in at least two animal species. Additional toxicologic experiments should be conducted on a variety of species to characterize, both functionally and anatomically, the nature of any changes induced by vinyl acetate and its metabolites. These studies should simulate occupational exposure regimens, in both the exposure schedule and the routes of exposure (inhalation and skin contact). The results of these studies should provide insights into human susceptibility to the effects of low-level exposure to vinyl acetate. Skin absorption of liquid vinyl acetate in humans should be studied.

Well-designed and controlled behavioral studies should be undertaken to determine whether vinyl acetate affects the CNS, as some studies on humans [3] and animals [22,23] have suggested. Electroencephalographic analyses of humans exposed to vinyl acetate should be conducted to determine whether low concentrations can induce adverse neurologic effects, and animal experiments should be conducted to determine whether or not permanent effects on the CNS can result from exposure to vinyl acetate.

The metabolic fate of vinyl acetate as a function of the concentration and duration of inhalation, including possible oxirane (epoxide) formation and the influence of modifiers of metabolism should be studied. Vinyl acetate's possible role as a substrate for esterases and the possible covalent binding of vinyl acetate or its metabolites to macromolecules should also be quantitatively evaluated.

### Carcinogenic, Mutagenic, Teratogenic, and Reproductive Studies

No human or animal studies have been found on the possible teratogenic or reproductive effects of vinyl acetate and, thus, this type of research should be performed. Only one study of mutagenesis using S. typhimurium [26] and one study of carcinogenesis in rats [24,25] have been found. Although the results of these studies showed no mutagenic or carcinogenic potential for vinyl acetate, further studies in several species are recommended because of vinyl acetate's structural similarity to compounds known to induce cancer.

### Sampling and Analysis

Improved methods of sampling and analysis for vinyl acetate should be investigated. An accurate and precise sampling system for airborne vinyl acetate, as well as convenient, portable direct-monitoring devices, should be developed further.