

IV. ENVIRONMENTAL DATA

Sampling and Analytical Methods

The sampling and analysis of air to determine its formaldehyde content has been a matter of concern to industrial hygienists for many years [123,134, 135,136] as a result of the extensive use of formaldehyde as an industrial chemical [137], and its formation by the incomplete combustion of various organic substances. Since about 1960, the desirability of being able to analyze urban air for formaldehyde and total aldehydes has stimulated the development of many new methods [111,138-145] capable of providing the required sensitivity for analysis of formaldehyde in the occupational environment. Formaldehyde has entered community air from sources such as exhausts from gasoline and diesel engines [111,144,145], effluents from incinerators [111,145], and assorted other industrial effluents [111,144,145]. Frequently, the requirements of air quality investigations are satisfied by analytical methods which determine total aldehydes [111,138,139,142,143,146,147] without specific determination of the quantity of formaldehyde present. As a result, many methods are available [105,106,111,138,139,142,143, 146-154] which are general aldehyde methods, performed with reagents capable of reacting with formaldehyde and other low molecular weight aliphatic aldehydes. Such methods may not be satisfactory for the specific determination of formaldehyde in the occupational environment, but may be used if it is known that the only aldehyde present is formaldehyde. Although not usually required, in some instances it may be necessary to perform qualitative analyses to identify the aldehydes actually present, particularly if a method no specific for the aldehyde of interest is used.

Methods for Total Aldehydes

One of the earliest methods [123] used for the estimation of total aldehydes in the air is generally known as the bisulfite method. It was first proposed for estimating formaldehyde in air by Goldman and Yagoda [123] in 1943. Subsequently, it was adopted by the American Conference of Governmental Industrial Hygienists and was published as a recommended method [55] in 1958. Although identified as a method for formaldehyde in air in both references [123,155], it is actually a nonspecific method for aldehydes and ketones [123,155]. The method relies upon the formation of a nonvolatile sodium formaldehyde-bisulfite complex which is stable in neutral or slightly acid solutions. The sampling solution used in impingers is ordinarily a 1% solution of sodium hydrogen sulfite, and the collection efficiency for aldehydes with a single midget impinger has been shown to be about 98% [118]. The reagent-aldehyde complex has the further advantage of being quite stable, thus permitting analyses to be performed several days after collection without loss of sample [123].

Analysis is performed by destroying the unreacted bisulfite with iodine at neutral pH, after which the solution is made alkaline, decomposing the addition compound. The liberated sulfite may then be titrated with a standard iodine solution to give an indirect measure of the quantity of aldehyde originally collected [123,155]. Although no longer considered the preferred method for aldehyde analysis, this method is quite satisfactory whenever formaldehyde is the only aldehyde present in the atmosphere [155], provided that a sufficient quantity of formaldehyde can be collected to allow the titrations to be performed.

In 1940, Kersey et al [134] suggested the use of Schryver's method as a technique for measuring atmospheric formaldehyde. Formaldehyde in air

was collected by means of a Jena glass distribution tube in an absorption bottle containing a dilute solution of phenylhydrazine hydrochloride, thus forming formaldehyde phenylhydrazone [134]. Subsequently, the addition of hexacyanoferrate(III) in acid solution caused the formation of a pink or purple color which was proportional to the amount of formaldehyde present. Barnes and Speicher [135] subsequently modified the method of Kersey et al by collecting formaldehyde in air with a 1.5% solution of potassium hydroxide contained in a standard impinger. These investigators also pointed out that formaldehyde could not be determined specifically by this method in the presence of acetaldehyde and acrolein. Hence, this method is actually an aldehyde method and not a specific formaldehyde method [135]. Hanson et al [156] also recommended the use of phenylhydrazine hydrochloride as a sampling solution, with subsequent color development in the laboratory following addition of potassium hexacyanoferrate(III). A similar method was published in Australia by Lugg and Wright [157]. Fedotov, according to an article translated by Levine [158], used the phenylhydrazine method by impregnating silica gel and making indicator tubes which could be used to quickly estimate the concentration of aldehydes in the field without laboratory analysis.

One of the most useful agents developed for the determination of aliphatic aldehydes was first described by Sawicki et al [105]. The reagent known as 3-methyl-2-benzothiazolone hydrazone (MBTH) reacts [105] with aliphatic aldehydes in the presence of iron(III) chloride to form a blue cationic dye in acidic solutions. In the original paper, Sawicki et al [105] showed that although the reagent responded to a number of aldehydes, it was most sensitive to formaldehyde. Subsequently, Hauser and Cummins [106] modified the method to increase the sensitivity sufficiently

to determine formaldehyde at concentrations as low as several ppb in ambient air. This version of the method was also included in a volume of Selected Methods for the Measurement of Air Pollutants published by the US Public Health Service [148] in 1969. Additional data concerning collection efficiencies and molar absorptivities of several low molecular weight aldehydes were noted by Cohen and Altshuller [149]. Several papers [138,139,159] in which the MBTH method was used to obtain data on aldehyde concentrations in the atmosphere have been published. In 1970, the Intersociety Committee, an alliance of 10 professional societies, including the APHA, AIHA, and ACGIH, devoted to recommending standard methods of ambient air sampling and analysis, adopted the MBTH method as a tentative method [150] of analysis for formaldehyde and other aldehydes. Elfers and Hochheiser [151] described a modification of the MBTH method which made use of a visual color comparator with calibrated color filters. They noted good agreement between the estimates obtained with the comparator and those obtained with the spectrophotometer and suggested that field surveys could be made using the comparator.

Other methods [134,147,152,160] have been used for the estimation of aldehydes, but few of them [134,147] have found application to industrial hygiene sampling and analysis. Several good reviews [111,161-164] should be consulted for information concerning these methods.

Sampling and Analytical Methods for Formaldehyde

The wide usage and occurrence of formaldehyde have led to the development of numerous methods for its sampling and analysis without significant interference from other aldehydes. Although many of the

methods previously described [123,134,135,155,157,161] have been called formaldehyde methods, they are nonspecific methods for aldehydes and are suitable only when no interfering substances are present. By contrast, a number of reagents have been developed [136,141,144,160,162,164,165,166,167,168,169,170,171,172,173,174, 175, 176] which respond only to formaldehyde, or else respond so weakly to other aldehydes that they may be considered as essentially specific for formaldehyde. The most widely used color-forming reagents for formaldehyde are Schiff's reagent, pararosaniline and sulfite [133,136,140,142,143,165,171,176], and chromotropic acid [117,144,153-155,178-180]; others [170,174] include 2-hydrazinobenzothiazole, J-acid (6-amino-1-naphthol-3-sulfonic acid), and phenyl J-acid (6-anilino-1-naphthol-3-sulfonic acid).

One of the earliest reagents for determining formaldehyde, generally referred to as Schiff's reagent [133], has been known since 1866, and one of the earliest uses of this reagent for air analysis was described by Zhitkova [177] in 1936. Versions of the same method were published by Blaedel and Blacet [136] and Ackerbauer and Lebowich [165]. Numerous modifications of the method have been published [140,142,143,160,166,167], but all use reagent mixtures of fuchsin or pararosaniline which, together with sulfite and formaldehyde, yield a rose-violet color. The method was adapted by Rayner and Jephcott [140] to the microdetermination of formaldehyde in urban air, the formaldehyde being collected in a standard impinger containing a 0.005 N hydrochloric acid solution. The Chief State Sanitary Inspector of the USSR has recommended [166] the use of Schiff's reagent, with distilled water as the absorbing medium. A method using a modified Schiff's reagent was published by Lyles et al [141] in 1965. The

reagent is a mixture of dichlorosulfitomercurate(II) complex and acid-bleached pararosaniline hydrochloride. This method [141] is an outgrowth of the West-Gaeke method [181] for sulfur dioxide, in which basically the same chemical reactions occur except that the reacting mixture contains formaldehyde and withholds the sulfite ion. The authors [141] believed that the substitution of bleached pararosaniline hydrochloride for fuchsin improved the method considerably and made it more highly selective for formaldehyde. Essentially the same method was adapted by Yunghans and Munroe [142] and Cantor [143] to the determination of atmospheric formaldehyde by an automated analysis system. Other modifications of methods using Schiff's reagent include those of Brewer [167] and Knight and Tennant [160].

The analytical method which currently appears to be favored [180] for the determination of formaldehyde in air relies upon the production of a purple color by reaction between formaldehyde and 1,8-dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid) in sulfuric acid. The reagent was first proposed [178] in 1937 as a specific reagent for formaldehyde, and various investigators [182-187] have reported its use in the analysis of vital samples. MacDonald [117] was the first to suggest its usefulness for the analysis of formaldehyde in air in 1954, and developed the method in essentially the form in which it is commonly [155,179,180] used today. Altshuller et al [145] studied a modification of the method which was said to result in improved sensitivity, stability, and freedom from interference. Inasmuch as the recommended sampling method [145] used concentrated sulfuric acid as the collection medium, it is obviously impractical to apply the method to personal air sampling in the occupational environment, where there is a chance for contact of the

employees with concentrated sulfuric acid. When sampling air pollution sources such as the effluents from incinerators, Cares [144] noted that oxides of nitrogen interfered with the color development, and recommended that samples be collected in bisulfite solutions to avoid this interference. Other attempts to minimize the effect of interfering substances have included the use of porous polymer adsorbents [168] and a gas chromatographic separation of styrene and cresols [169]. The Intersociety Committee adopted the chromotropic acid method as a tentative method for formaldehyde in 1970 [153]. Essentially the same method was recommended by Levaggi and Feldstein [154] and the Intersociety Committee [153] except that formaldehyde was determined in an aliquot of a sample collected in 1% sodium bisulfite solution in the former method.

Sawicki et al [170] compared the chromotropic acid method with the J-acid and phenyl J-acid methods and pointed out the potential interference from some formaldehyde-releasing compounds which would not normally be present in an occupational setting. They established that J-acid and phenyl J-acid are extremely sensitive and selective reagents that, in some ways, are superior to chromotropic acid [170,172,174]. Numerous papers have outlined the use of chromotropic acid to measure formaldehyde in either ambient air [139,145,146,159,188] or pollution [145] sources. Gladchikova and Shumarina [171] recommended the chromotropic acid method for use in the USSR.

Several color-forming reagents [170,172,174] other than those described have been reported to be useful for formaldehyde analysis, but do not appear to have gained wide acceptance. Acetyl acetone forms a colored compound with formaldehyde [172,189]; because this compound is fluorescent, it may be measured by fluorimetry with much greater sensitivity than by

colorimetry [173]. Other formaldehyde reagents include 5,5-dimethyl 1,3-cyclohexanedione (Dimedone, Methone) [147,152], 2-hydroxycarbozole [175], paraphenylenediamine [176], and an equilibrium mixture of potassium tetracyanonickelate and dimethylglyoxime [190]. Descriptions of even more reagents may be found in the several review articles previously cited.

Barnes and Speicher [135] suggested in 1942 that formaldehyde could be determined conveniently by polarographic analysis, after collecting the samples in dilute potassium hydroxide solution, but the method does not appear to have found favor, as evidenced by a lack of polarographic or electrometric methods in general use since that time.

Although gas-liquid chromatographic (GLC) methods have attained great popularity for most substances, relatively few GLC methods for formaldehyde have been reported. A possible explanation for this lack of GLC methods may be gained from a report issued by the Los Alamos Scientific Laboratory [191] in 1973 in which various problems of interference and sensitivity that had been experienced with the chromatographic conditions tried were noted. A 1975 report by Wood and Anderson [192], stated that attempts to develop a GLC analysis method were unsuccessful. Various authors have described the determination of formaldehyde in various substances by GLC means [193,-197], but have not applied the procedures to the analysis of low concentrations in air. Levaggi and Feldstein [154] have described the determination of the C2-C5 aldehydes by a GLC procedure but did not recommend its use for formaldehyde.

Until recently, there was no published evidence that the collection of formaldehyde on solid adsorbents or absorbents could be relied upon, so that it was necessary to collect formaldehyde in aqueous medium and to rely on analysis by one of the methods stated to be specific for formaldehyde.

Wood and Anderson [192] have described a method of collection on alumina, however, with subsequent analysis by the chromotropic acid method. Because elution of formaldehyde from the alumina must be performed immediately to prevent loss of the aldehyde, this method may not be applicable to use in the field. The most widely used estimation of formaldehyde at this time [117,155,179,180] is the modified chromotropic acid method, which is the method included in NIOSH's 1973 Manual of Recommended Methods [180].

Engineering Control of Exposure

In the manufacture and use of formaldehyde and formaldehyde-yielding substances, the possible routes of exposure to formaldehyde are:

- (1) inhalation of formaldehyde gas and/or formaldehyde-generating dust;
- (2) contact of formaldehyde gas and/or solutions and of formaldehyde-yielding dust and/or solid with the skin, eyes, and mucosal surfaces; and
- (3) fire or explosion of formaldehyde gas or of formaldehyde-yielding solids.

Ingestion would be a potential exposure hazard inasmuch as formaldehyde is toxic by the oral route. However, ingestion in an amount sufficient to be toxic to an adult would occur only by intentional action, extreme carelessness, or an unusual accident. These sources of poisoning can be minimized by informing all employees of the danger and the need for exercising care [198].

Total enclosure of process and materials is the preferred means of control to prevent contact with, or inhalation of, formaldehyde or

formaldehyde-yielding substances [6,97,198]. When total enclosure is used, provision must be made for its safe venting for pressure or vacuum relief. Vents should be designed for easy cleaning to remove any polymeric products which tend to accumulate [6]. Flame arrestors in the vent lines are recommended when concentrations of formaldehyde gas in the flammable range are expected [6,198,199].

When totally enclosed systems must be opened for either service or maintenance, provisions must be made for the exhausting of formaldehyde emissions either by prior purging of the system, by suitable ventilation, or by a combination of techniques, or by providing proper protective clothing and devices.

Total enclosure also applies to the storage of formaldehyde solutions and formaldehyde-yielding substances, whether in small containers, such as, carboys, drums, and barrels, or in tanks for bulk storage. Small containers should be securely closed and have sufficient strength to withstand likely differential pressure between outside and inside. The bulk tanks should be safely vented.

Storage areas should be adequately ventilated to remove any emissions which may arise from transfer operations or spills. Because formaldehyde gas is flammable and explosive, the storage areas should have sprinkler systems or other suitable automatic fire control facilities.

Storage areas should also be temperature-controlled to maintain the temperature always well below the flashpoint of all materials stored within [200]. The flashpoint of 37% formaldehyde solution with 15% methanol stabilizer is 50 C (122 F) and is higher for solution with less methanol [6]. Temperature in storage areas should not exceed 40 C (104 F) and preferably should be lower.

Storage of formaldehyde solutions should be in securely sealed containers. Large vessels or tanks should be safely vented for relief of pressure or vacuum.

Partial enclosure of process equipment, machinery, and containers will restrict the emission of gases or dust, but must be supplemented by ventilation to prevent the dissemination of vapors or dust into the air of the workroom.

Airborne concentrations of formaldehyde gas and of formaldehyde-generating substances can be controlled and kept below the recommended concentration limits by properly designed ventilation systems of adequate capacity [6,97,198-200]. General dilution ventilation can be used in many instances to reduce the airborne concentrations in a workroom to a level well below the recommended limit. Removal of the gas or dust by local exhaust ventilation close to the source of emission is preferred for control by ventilation. Local exhaust ventilation can prevent the emissions from reaching the employees and from being disseminated, even at low concentrations, throughout the work area. In employing exhaust ventilation for such control, certain recommended practices [201] and design and operating fundamentals should be followed [202]. Regular inspection and maintenance of the ventilation system is necessary for its continued effectiveness [97]. Recirculation of exhaust ventilated air in the workplace is prohibited.

Resins derived from formaldehyde, such as melamine-formaldehyde, urea-formaldehyde and phenol-formaldehyde resins, will begin to decompose rapidly with the release of formaldehyde (FM) at temperatures above 250 C (482 F). [203] Such temperatures may occur in injection molding of these resins. Sawing of sheets of these resins by high speed saws will produce

sufficient heat to cause such release of formaldehyde (FM); sawing will also emit formaldehyde-contaminated dust. These and other operations with formaldehyde-derived polymers should be provided with local exhaust ventilation to remove gas and/or dust [97,203].

Waste disposal shall be by burial, flushing, or chemical deactivation. Burial of waste must be in an area of restricted access and where seepage is not likely to produce exposure of employees or other individuals. Small quantities (not more than several gallons) of waste may be flushed down the drain with large quantities of water (in excess of 20 times the volume of waste). Formaldehyde spills may be inactivated by reaction with aqueous solutions of sodium sulfite or bisulfite.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

The United States of America Standards Institute (now the American National Standards Institute Inc) established a standard for formaldehyde in 1967 [204]. The standard specified that:

(1) Acceptable maximum for peaks, undefined, above the acceptable ceiling concentration for continued exposure is 10 ppm for a total of no more than 30 minutes during an 8-hour work period.

(2) Acceptable ceiling concentration for limitation of discomfort exposure is 5 ppm for an 8-hour work period.

(3) Acceptable 8-hour TWA within limits of Sections (1) and (2) above is 3 ppm. However, persons who have been previously sensitized to formaldehyde may experience an allergic reaction when exposed to concentrations lower than 3 ppm.

(4) Minimum level for sensory detection qualified as to tolerance (sensory fatigue) for warning value is as follows:

- | | |
|------------|---|
| 1 ppm | Odor detectable [205] |
| 2 or 3 ppm | Slight discomfort [205] |
| 13 ppm | Eye irritation that wore off in 10 minutes [46] |

(5) Acceptable concentration to avoid discomfort is 3 ppm.

This standard is based largely upon the personal observation of Fassett [205] and the work of Sim and Pattle [46] and was reaffirmed most recently in 1973.

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended an 8-hour ceiling limit of 2 ppm (approximately 2.5 mg/cu

m) for formaldehyde. A TWA limit of 10 ppm was first established in 1946 and was changed to 5 ppm in 1948. In 1963, ACGIH introduced the ceiling limit concept and established a ceiling limit for formaldehyde of 5 ppm which was decreased to the present limit of 2 ppm in 1973. In 1971, the ACGIH supported its limit in their Documentation of the Threshold Limit Values for Substances in Workroom Air [206] as follows: Formaldehyde irritates the eyes, respiratory tract, and skin [116,207]. Elkins [116] suggested that employees develop tolerance to these irritant effects, but Henderson and Haggard [207] noted that persons may also become more susceptible on repeated exposure. The latter authors cited data that indicate that a threshold limit value of 20 ppm would be appropriate. Elkins [116], however, reported complaints from persons exposed to an atmosphere in which the maximum concentration was 5-6 ppm; eye irritation was noted in unaccustomed persons exposed to much lower concentrations. He indicated that regular employees can tolerate without difficulty concentrations that are intolerable to outsiders, and suggested that the maximal acceptable concentration might be based on cutaneous rather than on pulmonary effects.

The threshold limit value of 5 ppm was expected to be low enough to prevent respiratory injury, but not necessarily to prevent subjective evidence of irritation. Irritation, in the form of itching eyes, dry and sore throat, disturbed sleep, and unusual thirst on awakening, has been reported in a few workers at levels of 1-2 ppm formaldehyde [42,50]. The threshold limit of 5 ppm obviously did not prevent irritation in all exposed individuals.

A recent study [58] of formaldehyde gas emissions in the permanent-press fabrics industry (8 plants) made after complaints of workers revealed formaldehyde concentrations between 0.3 and 2.7 ppm (sewing area), with an

average of 0.68 ppm. Employees complained of annoying odor (odor threshold, below 1 ppm) [205], constant prickling irritation of the mucous membranes, and disturbed sleep. Formaldehyde dermatitis was not mentioned as a problem in the report.

Because of complaints of irritation by exposure to formaldehyde at concentrations well below 5 ppm, the ACGIH recommended in 1971 that the TLV be lowered to 2 ppm. The latter figure was entered in the list of adopted values for TLV's 1973. In 1976, a tentative short-term exposure limit (STEL) for formaldehyde also at 2 ppm was appended to the TLV. Although the reports of Bourne and Sefarian [42] and Shipkowitz [58] were the primary references cited for the new TLV, the former authors studied concentrations of formaldehyde in air at 0.13-0.45 ppm, which were associated with complaints of irritated eyes, headaches, and irritated nose and throat. Shipkowitz [58] reported that concentrations of 0.3-2.7 ppm of formaldehyde were found in 8 factories manufacturing permanent-press and crease-resistant clothing and were accompanied by numerous and bitter complaints of irritation.

The present federal standard, adopted from the American National Standards Institute limit [204], specifies an 8-hour TWA limit of 3 ppm formaldehyde, an acceptable ceiling concentration of 5 ppm formaldehyde, and an acceptable maximum peak above the acceptable ceiling concentrations of 10 ppm for a total of no more than 30 minutes during an 8-hour shift.

Other countries and various states in the United States have set standards for formaldehyde. These standards are listed in Table XII-7.

In evaluating the literature, the Czechoslovak Committee of MAC in their Documentation of MAC in Czechoslovakia [208] presented the table shown in Table XII-8. The basis for the Czechoslovak MAC can be stated as

follows: in formaldehyde, the irritating effect predominates. This is the primary reason for establishing of a maximum allowable concentration (MAC). The mean MAC should therefore lie below the limit of irritation, and the peak concentration below the limit of damage or of severe irritation. The conclusion of the Czechoslovak Committee was that the concentration of formaldehyde in industrial environments then accepted as the MAC in the USSR of 1 mg/cu m was too strict and could be adhered to by Czechoslovak plants only with difficulty. Accordingly, a ceiling concentration of 2 ppm with a short-term peak concentration of 5 ppm was established.

Writing in support of the Italian standard for the Clinica del Lavoro, Vigliani and Zurlo [209] suggested 5 mg/cu m formaldehyde and noted the problem of setting standards for accustomed and nonaccustomed employees. However, they do not say for which group their standard applies and do not offer any supporting argument for the limit selected.

In 1967, Zaeva et al [51] submitted to the Ministry of Public Health of the USSR a recommendation that the maximum permissible concentration of formaldehyde in air of factories be decreased from 1 mg/cu m to 0.5 mg/cu m. This recommendation was based largely on published reports of disturbed sleep and irritation of the eyes and throat after exposures to formaldehyde at 1-1.9 mg/cu m [50], of irritation of the membranes of the orbit and upper airway at 1-9.6 mg/cu m [50], of chronic rhinitis and illness in workers exposed to formaldehyde at 0.6-36.3 mg/cu m [51], and of irritation of the membranes of the upper airway and orbit, respiratory disorders, changes in autonomic nervous system function, and altered alpha-rhythm of the EEG in some degree after exposure to formaldehyde at 1 mg/cu m [A.K. Sgibneyeu, quoted in 51]. In addition, the recommendation was based on a finding by the Ivanosk Institute of Labor Protection [quoted in 51] that

most workers complained of upper airway irritation on exposure to formaldehyde at 2-3 mg/cu m in air. This recommendation by Zaeva et al [51] was apparently accepted, as the MAC listed for the USSR in 1968 [210] was that recommended by Zaeva et al [51].

Basis for the Recommended Standard

The recommended workplace environmental standard will protect all but the sensitized worker from the adverse health effects associated with exposure to formaldehyde, ie, monomeric formaldehyde, HCHO, and its aqueous solutions. Formaldehyde gas may be generated from a variety of materials, which include, but are not limited to, trioxane, paraformaldehyde, polyoxymethylene, and hexamethylenetetramine. The latter materials are included in this standard to the extent that they act as sources of formaldehyde (FM) exposure.

The odor of formaldehyde is perceptible to previously unexposed individuals at concentrations varying from one individual to another but generally at or below 1 ppm [42,57,58,92-94]. The lowest concentration at which formaldehyde was perceived by odor was 0.06 ppm [57]. Although perception does not necessarily signify an adverse health effect, studies defining the odor threshold serve as indications of environmental concentrations which are below the threshold of irritation, whereas an annoyance may occur at any concentration at or above the odor threshold.

When inhaled, formaldehyde at massive concentrations has caused pulmonary edema [27,48] and death [27], while at concentrations of 1-11 ppm [43,47,51,52,54,98] it has caused upper respiratory tract irritation. Formaldehyde may be irritating or annoying to some individuals at airborne

concentrations of 1-2 ppm. In addition, several investigators [52,54,58] have indicated that, despite the fact that the ability to perceive the odor of formaldehyde is blunted within 1-2 hours of exposure, this ability returns when the exposure is interrupted by lunch or upon returning to the workplace the next day.

Inhalation experiments with guinea pigs have shown transient alterations of airway resistance which vanished within 1 hour after exposure to formaldehyde at 11 ppm but persisted for over an hour after exposure at 49 ppm [113,114]. Immediately reversible airway resistance changes were noted following the exposure of guinea pigs to formaldehyde at as little as 0.31 ppm for 1 hour [113,114]. Such resistance changes were observed with 1-hour exposures to formaldehyde at as little as 0.11 ppm in the presence of an aerosol of NaCl solution acting as a carrier [126]. Considering the mass medium diameter of 0.04 μm and the particularly large proclivity of guinea pigs to undergo bronchioconstriction, the data are roughly in keeping with the correlation of airborne formaldehyde concentrations and reported upper respiratory tract irritation in humans. In cats, exposure to formaldehyde at as little as 0.8 ppm has caused slight microscopic alterations in lung tissue [93].

Inhalation of formaldehyde has caused allergic dermatitis in hypersensitive humans at concentrations of 10.5 ppm for a brief period, or when the skin contacted formaldehyde solutions as dilute as 1:5,000,000. Such findings demonstrate that it is undesirable for sensitized individuals to work in any area where formaldehyde is likely to be present. In addition to allergic dermatitis, primary irritation of the skin has been caused by solutions as dilute as 4% formaldehyde [65,66]. Based on reports of irritation, objectionable odor, and disturbed sleep for a few employees

on exposure to formaldehyde at 0.3 ppm and of more general complaints at concentrations exceeding 1 ppm (Table III-1), a ceiling value of 1 ppm (1.2 mg/cu m) for formaldehyde (FM,FS) in air is proposed as the workplace environmental limit. Any other substance that readily decomposes to react as formaldehyde with chromotropic acid under the recommended conditions of sampling and analysis is also regarded as contributing to formaldehyde exposure. Individuals sensitized to formaldehyde should not be assigned to work in any area where formaldehyde, paraformaldehyde, or any other substance capable of releasing formaldehyde is likely to be present.

Many employees may be exposed to small amounts of formaldehyde or may work in situations where, regardless of the amount generated, there is only negligible exposure. In such situations, compliance with the provisions of this recommended standard which are intended to protect the health and provide for the safety of employees under more hazardous circumstances would not be necessary. However, to ensure that exposures remain at or below the ceiling limit, protective measures must be instituted when significant exposures begin to occur. Occupational exposure has been defined as exposure to formaldehyde at concentrations exceeding 0.6 mg/cu m (0.5 ppm), thereby delineating those exposure situations which require increased monitoring of the environment, medical surveillance of employees, and associated maintenance of records.

VI. WORK PRACTICES

The effectiveness of good work practices is entirely dependent on the knowledge and the cooperation of employers and employees. The employer must take all necessary steps to ensure that [6]:

(1) each employee receives adequate instruction and training in safe work procedures, the proper use of all operational equipment, the correct use of protective devices and practices, and all emergency procedures;

(2) each employee periodically receives refresher sessions and drills to maintain a high level of competence in safe work practices and emergency procedures;

(3) each employee is provided with proper tools, equipment, and personal protective clothing or devices; and

(4) each employee is given adequate, responsible supervision to assure that all safety requirements and practices are followed.

Only properly trained individuals should be permitted access to areas in which exposures to formaldehyde, paraformaldehyde, or formaldehyde-generating substances are likely. All such areas should be clearly identified by appropriate posted warnings (Chap I, Sect 3).

For the prevention of injuries from contact by formaldehyde solutions and/or formaldehyde-yielding substances with the eyes, skin or other sensitive tissues, good work practices include, but are not limited to, the wearing of personal protective garments and equipment as recommended or required in Chapter I, Section 4. Work practices, procedures, and protective equipment and devices should be developed and utilized so that

the likelihood of employees suffering injurious contact with these chemicals is minimal. The wearing of personal protective garments and equipment is necessary for additional, positive protection in those activities and accidental situations where exposures are likely in spite of other precautions [6,49,97,198,200].

Each employee potentially exposed to gaseous formaldehyde or likely to come in contact with formaldehyde in solutions or solids must be provided with, and required to wear, adequate protective clothing and equipment for the tasks and area of work. Adequate supervision must be exercised to ensure that the protective clothing and equipment are regularly and properly worn. The garments and equipment must be inspected and maintained on a regular basis. Items damaged by wear or abuse to the extent that the effectiveness of protection is impaired or doubtful must be repaired or replaced. All personal protective devices must be washed thoroughly after each wearing and before being reused. If any such item becomes contaminated with formaldehyde during the work shift, it should be immediately flushed with large amounts of water; when such flushing makes the item unsuitable for continued wear, it must be removed and replaced by a clean one.

Eye protection is of particular importance because of the irritant effects of formaldehyde. Well-fitted chemical safety goggles must be worn as protection from irritating concentrations of formaldehyde gas or formaldehyde-yielding substances and as protection from mists, splashes, and spills of formaldehyde solution. Full-face respirators provide the necessary eye protection. Full-length, plastic face shields also should be worn to protect the face from splashes and spills, but the chemical safety

goggles are still necessary to protect the eyes from vapor, mists, and splashes which may enter behind the edge of the shield [6].

In emergencies and in routine operational situations where engineering and administrative controls are not capable of reducing the amount of exposure at or below the recommended limit, the wearing of approved respiratory protection (see Chap I, Sect 4) is necessary. The use of cartridge or air-supplied half-mask respirators is limited to relatively low concentrations of formaldehyde [198], because such respirators do not afford eye protection and because the combination of half mask respirators with chemical goggles is neither well tolerated by employees nor as effective as a full face mask respirator.

Cartridge and canister respirators with full facepiece are rated to provide protection for limited periods in concentrations up to 20,000 ppm [211] and can be used for evacuation or escape purposes (Chap I, Sect 4, Table I-1).

At formaldehyde concentrations of 100 ppm or greater, breathing becomes very difficult or impossible [6,41]. A self-contained breathing apparatus with positive pressure in a full facepiece or a full facepiece supplied-air respirator of the pressure-demand type with auxiliary self-contained air supply is necessary, therefore, for working in such concentrations.

When employees are required to enter any room, equipment, or other confined space suspected of, or possibly subject to, contamination by formaldehyde, tests should be made to determine the safety of the atmosphere before entering. The irritant effects should provide adequate warning of dangerously high concentrations but not necessarily of the degree of respiratory protection required (Chap I, Sect 4).

The hazards of contact with formaldehyde solutions and gas or with formaldehyde-yielding substances are best controlled (when enclosure is not possible or practical) by a combination of good work practices to eliminate or minimize splashes, spills, and other causes of contact (Chap I, Sect 6) and the wearing of proper protective garments and equipment (Chap I, Sect 4). The use of automated and remote control methods can reduce the number of situations presenting the hazard of possible contact.

Formaldehyde gas is a flammable vapor having explosive limits of 7.0-73% by volume [6]. Paraformaldehyde solid is combustible and airborne dust of paraformaldehyde is explosive at concentrations of or in excess of, 32 mg/liter with more than 8.6% oxygen (v/v) [198]. At elevated temperatures, paraformaldehyde (PF) will yield the more flammable formaldehyde gas (FM). In storage areas and in any process or handling system, appropriate measures are necessary to ensure that concentrations do not exceed the lower flammable limit, that electrical and mechanical systems are well grounded and explosion-proof, and that fire and explosion safety systems and equipment are provided. [6,198,199]

Respiratory protective devices approved for escape or evacuation from areas of excessive exposure to formaldehyde should be provided for each employee in any area of potential emergency or should be readily available at prominently and clearly identified locations throughout the area. The equipment should be available in numbers sufficient for use by all employees likely to be present in the area.

The program for respiratory protective equipment shall meet the requirements and standards as provided in 28 CFR 1910:134 and ANSI Z88.2-1969 Standard Practice for Respiratory Protection [211]. This program

provides for the routine regular cleaning, inspection, servicing, and maintenance of respirators for effective and safe usage.

Each plant must establish an emergency plan and program to meet any emergency which can reasonably be anticipated. The employees and emergency teams must be thoroughly informed and trained in their responsibilities and actions for emergencies. Stations equipped with first-aid supplies and equipment, approved respiratory protective devices, protective garments, and other special equipment as needed should be established and maintained in readiness at easily accessible locations adjacent to areas of likely emergencies.

Eye-flushing stations and safety showers should be available in plant areas where splashes or spills of formaldehyde solutions are possible. Immediately on any contact with formaldehyde, the individual should flush the eye or skin areas with a copious flow of water [198,199].

To prevent and limit contact dermatitis from formaldehyde the employees should practice good personal hygiene. Showers, washing facilities, lockers, and change rooms should be provided. Facilities for flushing the eyes and skin with large amounts of water should be provided and readily available from areas where splashes or other contact hazards are likely to occur. These facilities should be clearly marked as to location and should have emergency and first-aid instruction posted nearby.

Employees should exercise care not to transfer formaldehyde from contaminated gloves or other protective garments to unprotected eye or skin surfaces. Such contact with formaldehyde has been a reported cause of some eye injuries and dermatitis [49].

Administrative control through selective assignment of employees may be necessary to protect hypersensitive or sensitized individuals [79].

Sensitive individuals may experience adverse reactions to low formaldehyde concentrations tolerated by most other employees.

The following work practices and procedures should be observed by all employees:

(1) Enclosed process machinery and containers of formaldehyde solutions should be kept closed or covered, except when operations require otherwise.

(2) Respirators and protective clothing and equipment should be worn in accordance with recommendations and requirements (Chap I, Sect 4).

(3) Containers of formaldehyde should be securely closed during transport of such containers.

(4) Large containers (carboys, drums, etc) should be moved and handled by mechanical equipment of design applicable to the procedure.

(5) Carboys or other breakable containers should be handled with care. Specially designed inclinators should be used for pouring from carboys.

(6) Transfer of formaldehyde solutions from a container should be done with care to minimize any splashing and to prevent spills. Transfer by pumping through hermetically sealed systems or lines is preferred.

(7) Transfer of formaldehyde solutions from tank cars or tank trucks must be done only by specially trained employees under responsible supervision.

(8) Tanks, machines, pumps, valves, and lines must be drained and flushed thoroughly with water before doing maintenance or repair work on them. Care must be exercised to avoid contact with the drained or flushed fluids.

(9) No individual may enter any tank or equipment until it has been flushed free of formaldehyde, the atmosphere therein has been determined to be safe, and a permit has been issued by a responsible supervisor.

(10) No individual may enter any tank or confined space whose entrance is not large enough to admit an individual fitted with safety harness, lifeline, and an emergency respiratory protective device.

(11) An individual may work in a tank or confined space only with another person outside in constant contact and having rescue equipment and assistance available.

(12) Pipelines and hoses, if any, shall be blanked off or disconnected to prevent inadvertent entry of formaldehyde into a confined space wherein an individual is working.

(13) Containers and lines shall be purged of formaldehyde before doing any external welding, grinding, or other operation which might offer a source of ignition for flammable vapors.

(14) Spills and leaks of formaldehyde solution shall be immediately flushed away with an abundant flow of water. Employees shall wear respiratory protection and protective garments during the clean-up of spills.

(15) Eyes and skin surfaces coming into contact with formaldehyde shall be immediately flushed with large amounts of water. In the case of contact with the eyes, a physician should be consulted as soon as possible.

(16) Employees shall properly utilize ventilation, enclosures, remote controls, and other engineering or administrative controls provided.

(17) Employees must wear protective clothing and respiratory protection during such operations.

VII. OCCUPATIONAL RESEARCH PRIORITIES FOR FORMALDEHYDE

(1) Effects of Repeated Exposures in Man

More information is needed on effects produced by prolonged repeated exposures to low airborne concentrations of formaldehyde. Information on effects produced at the recommended environmental ceiling limit of 1.2 mg/cu m based on a 30-minute sampling period would be particularly useful. Research on the development of hypersensitivity produced by formaldehyde reaction with skin proteins could provide an understanding of possible immune mechanisms involved and allow identification of individuals at higher risk of exposure. Epidemiologic investigations of various occupational groups exposed to formaldehyde with data on airborne concentrations associated with clinical findings, if any, would allow refinement of the recommended standard.

(2) Formaldehyde Chemistry

The chemistry of formaldehyde is complex, and reactions of formaldehyde in air or solutions, including polymerization, degradation, and combinations with other substances, require continued investigation. Numerous substances may act as sources of FM or FS, producing adverse effects. Development of an analytical and sampling technique suitable for personal monitoring and rapid analysis in the field would be particularly useful. Such a technique should allow specific identification and quantitative determination of formaldehyde and substances acting as sources of formaldehyde. The reaction of monomeric formaldehyde in either gas or liquid phase with Lewis acids in the presence of halogens requires

additional study. Monitoring of occupational environments for chloroethers would be appropriate.

(3) Metabolism

Additional information on the metabolic fate of formaldehyde could provide an understanding of the underlying toxic effects, leading to a more definitive medical treatment for intoxication and prevention of adverse physiologic effects, both acute and chronic.