IV. ENVIRONMENTAL DATA AND BIOLOGIC EVALUATION OF EXPOSURE

Environmental Concentrations and Engineering Controls

Smyth and Smyth [97] in 1935 studied concentrations of tetrachloroethylene at which workers were exposed in two drycleaning plants. Samples were collected in 35 and 77 minutes in the two plants, respectively. In the first plant, the average concentration found was 47 ppm with a peak of 2,960 ppm. In the other plant, an average concentration of 280 ppm was found with a peak of 4,636 ppm. Closed drycleaning machines were used in both plants. The concentrations were determined with a 50-cm portable interference refractometer as close as possible to the workmen's noses.

An extensive study of tetrachloroethylene concentrations in drycleaning plants was made in southwestern Ohio and southeastern Indiana in 1971 by Kerr. [98] Twelve commercial plants that daily cleaned 100-1,000 lbs of clothing and four coin-operated plants were studied. Six of the commercial plants were studied on only one occasion; the others were studied two or three times. The mean concentration of the 30 field studies conducted was 104 ppm. Nineteen of the 30 studies conducted in comercial package plants resulted in a mean concentration of 92 ppm ranging from 31 to 270 ppm. Most measurements were obtained with a halide meter, but some use was made of colorimetric indicator tubes. Average concentrations are summarized in Tables XII-6 and XII-7. The proportion of the sampling time that concentrations exceeded 200 and 300 ppm is summarized in Tables XII-8 to XII-11. Peak concentrations near 1,000 ppm were found in some plants. [98]

Kerr [98] reported that the greatest single factor to influence tetrachloroethylene vapor concentrations in the drycleaning operations studied was ventilation. In one of the drycleaning plants he found that a mean concentration of 100 ppm was accompanied by an air movement of 125 to 205 feet/minute while a 270 ppm mean concentration was observed when no air movement was recorded.

In evaluating the results of the study Kerr observed that the design of the solvent recovery systems in many of the plants surveyed was based on invalid concepts regarding the behavior of tetrachloroethylene vapor in the air. While tetrachloroethylene has a pure vapor density of 5.22-5.83 g/l, the low vapor pressure limits the amount of vapor that can exist in air without condensation to about 3% at 77 F. The density of this "saturated" (3%) air is considered to be 1.11 compared to air at 1.0. Such a vapor and air mixture would certainly not sink to the floor but would immediately disperse.

A study of 96 professional drycleaning institutions in the Denver area was made by the Department of Health and Hospitals in 1974-75. Halide meters were used to determine concentrations of tetrachloroethylene representative of the workers' breathing zones in machine service areas, such as loading, unloading, and maintenence of machines. Sampling times varied from 10 to 30 minutes. The levels of tetrachloroethylene found ranged from 5 to 125 ppm and averaged 41 ppm. Of 96 professional drycleaners, 68 had concentrations of tetrachloroethylene in worker breathing zones of 50 ppm or less. In most of these cases the air velocity at the face of the washer was greater than 100 feet/minute. (T Bullock, written communication, July 1975).

Coler and Rossmiller [51] used a halide meter to measure tetrachloroethylene concentrations in the breathing zone of an operator in a degreasing operation. Concentrations of 232-385 ppm were found.

Morse and Goldberg in 1943 [99] studied 108 degreasing units of the condensing and noncondensing types. A portable micro-furnace, which they developed and described, was used to make the atmospheric determinations. Tanks employing either trichloroethylene or tetrachloroethylene were included in the study. The data were summarized in ppm of solvent without distinguishing between the two solvents. Average concentrations were 96 ppm total solvent for the ventilated tank of the condensing type, and 221 ppm total solvent for the nonventilated, noncondensing units. Tetrachloroethylene is usually used with noncondensing units. The results of 402 determinations are presented in Table XII-12. [96]

In degreasing operations, equipping solvent vapor type degreasers with a "vapor level control" should serve to control the concentration of tetrachloroethylene in air. This device is a sensitive bulb-type thermostat with the sensitive bulb set at a temperature 10 F to 15 F below the vapor temperature (BP) of the solvent in use. The device is activated by an increase in vapor height of 3 to 4 inches above normal. Another means of reducing emissions is the use of a free board buffer which is basically a pair of refrigerated coils installed in the free board area of a degreaser. The cooling effect of these coils and the establishment of a cold air blanket above the solvent vapors results in reducing solvent emissions in the range of 35 to 50%. (TJ Kearney, written communication, April 1975)

The use of appropriate local exhaust systems is recommended for drycleaning and degreasing operations. Local exhaust systems should be designed and operated in conformance with American National Standard, Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971. [100]

Environmental Sampling and Analytical Methods

(a) Sampling Methods

Most analytical methods are dependent on the effectiveness and reproducibility of the uptake of tetrachloroethylene by different collection media. Air samples are usually collected and transported to a laboratory, desorbed or chemically treated, and analyzed quantitatively.

Silica gel, which has been used as a collection medium, [101,102] is a polar adsorbent and shows pronounced selectivity in adsorbing polar molecules, particularly water. [103] A laboratory study indicated that water vapor could displace tetrachloroethylene when sampling more than three liters of air through 1-inch diameter silica gel tubes. [103]

Activated charcoal has been used as a collection medium in conjunction with gas chromatography. [104] It is nonpolar and will generally adsorb organic vapors in preference to water vapor, resulting in less interference from atmospheric moisture than with silica gel. [103]

Williams and Umstead [105] reported the use of porous polymer beads as a collection medium. With this method, the same column is used for sample collection and gas chromatographic analysis. This method consolidates collection and analysis into one operation, but only one analysis can be made on each sample. This method has not been developed for field use.

Liquids have been used to collect chlorinated hydrocarbons from contaminated atmospheres. Midget impingers containing m-xylene have been used for collection with gas chromatographic analysis. [106] Bubble bottles containing a pyridine solution have been used for collection in conjunction with colorimetric analysis. [107] Success in the use of impingers and bubble bottles for collection of breathing zone samples requires careful handling of glassware during collection and shipment of samples to the laboratory.

Other investigators have collected grab samples of contaminated atmospheres directly in a variety of containers ranging from plastic bags to hypodermic syringes. [108]

(b) Desorption Methods

When solid collection media are used it is necessary to desorb the collected contaminant from the medium. Desorption from charcoal was studied by Otterson and Guy. [108] They recommended the use of different desorbing agents depending on the comparative gas chromatograph retention times for the desorber and the contaminant. The investigators determined carbon disulfide to be the best desorbent for tetrachloroethylene collected in charcoal tubes.

(c) Analysis

Several methods have been used to quantify tetrachloroethylene in air samples. The analytical methods can be divided into two broad categories: (1) methods based on tetrachloroethylene chemical reactions, and (2) methods based on its physicochemical characteristics.

(1) Chemical Methods

The three chemical methods that have been used extensively are: (A) dechlorination of collected vapor samples with strong alkalis followed by titration of the chloride ion (alkaline hydrolysis) [109]; (B) colorimetric measurement of the reaction products of tetrachloroethylene and pyridine heated in alkali solution (Fujiwara reaction) [110]: and (C) direct reading colorimetric indicators. [111]

(A) The dechlorination method (alkaline hydrolysis) requires collection of the tetrachloroethylene contaminated atmosphere by a suitable collection medium followed by alkaline hydrolysis in isopropyl alcohol, and titration of the liberated chloride with silver nitrate. [109] The percent of chlorine hydrolyzed is determined by comparison between samples and known controls. A disadvantage of this method is the difficulty of achieving hydrolysis and the inconsistent hydrolysis of the compound. Another disadvantage is that it is not specific for tetrachloroethylene.

(B) In the colorimetric analytical method based on the Fujiwara reaction, a stream of air containing tetrachloroethylene is passed through a bottle containing pyridine. [110] Potassium hydroxide (KOH) is then added to a portion of the sample, which is heated in a boiling water bath and cooled during a fixed time period. After coloring with a benzidene solution, absorption coefficients are determined with a spectrophotometer. This method requires less time than the dechlorination method, but the problem of specificity with mixtures of chlorinated hydrocarbons remains.

(C) The third chemical method utilizes direct reading detector tubes. [111] These are glass tubes packed with solid chemicals that change color when a measured and controlled flow of air containing tetrachloroethylene passes through the packed material. Depending on the type of detector tube, the air can be drawn directly through the tube and compared with a calibration chart, or the air may be drawn into a pyrolyzer accessory prior to the detection tube. [111] In either case, the analysis is not specific for tetrachloroethylene since liberated halogen ions produce the stain and any halogen or halogenated compounds will interfere. Regulations on detector tubes (42 CFR 84.50) provide that measurements with colorimetric indicator tubes shall be correct within ±25% of the values read. Tubes that meet these specifications have been evaluated and are available. [112]

(2) Physicochemical Methods

Photodetection (halide meters) [113], infrared spectrometry, [114] and gas chromatography [115] are among the analytical methods based on the physicochemical properties of tetrachloroethylene.

(A) Halide meters are made to detect the increased brightness of an arc across metal electrodes when they are enveloped by an atmosphere contaminated with halogenated hydrocarbons. These instruments are sensitive to all halogens and halogenated compounds and consequently they are not specific for tetrachloroethylene. Halide meters are suitable for continuous monitoring if tetrachloroethylene is the only halogenated contaminant present in the sampled air. [113]

(B) An infrared spectrophotometer in conjunction with a suitable recorder can be used to measure instantaneous concentrations or to record continuously. With this method, concentrations are measured directly and it is not necessary to collect individual samples or to transport them to a laboratory for analysis. Infrared spectrophotometry has been used for continuous monitoring of industrial operations for chlorinated hydrocarbons. [114] The atmosphere of relevant work stations must be sampled, and such samples must correspond to the breathing zone of the workers at the work stations. Infrared analysis is subject to interferences from other air contaminants and these interferences are not easily detected or resolved without substantial knowledge of infrared spectrophotometry.

(C) Gas chromatography provides a quantitative analytical method which can be specific for different chlorinated hydrocarbons. [104] Every compound has a specific retention time in a given chromatograph column, but several compounds in a mixture may have similar retention times. This problem can be overcome by altering the stationary phase of the chromatograph column or by changing the column temperature or other analytical parameters. Altering conditions will usually change the retention times and separate the components.

A mass spectrometer can be used subsequent to gas chromatography to identify the substance present in a gas chromatographic peak more positively. Linked gas chromatograph-mass spectrometer instruments perform this identification automatically. A charcoal capillary tube has been used to trap and transfer the material associated with a gas chromatographic peak to a mass spectrometer for qualitative identification when only unlinked units are available. [116]

(d) Conclusions and Recommendations

(1) Compliance Method

Based on review of air sampling and analytical methods, it is recommended that tetrachloroethylene in air samples be collected with activated coconut shell charcoal, desorbed with carbon disulfide, and analyzed by gas chromatography. Although the indirect system of measurement requiring collection and desorption prior to analysis is a disadvantage, this sampling and analytical method has the following attributes:

(A) Charcoal tubes are easy to prepare, ship, and store.

(B) Estimation of exposure with personal samplers is easily achieved.

(C) Desorption with carbon disulfide is effective and reproducible. However, carbon disulfide is a hazardous substance and should be handled in a chemical hood without sources of heat.

(D) Tetrachloroethylene can be identified in combination with many other compounds.

(E) At the sample volumes recommended, interference by moisture is minimal.

(F) Sampling tubes and personal pumps are commercially available.

(2) Monitoring Methods

Exposure to tetrachloroethylene associated with its continuous and constant use can be monitored by infrared spectrophotometry, or if it is the only halogenated hydrocarbon in the workroom air, halide meters can be used. Air from representative work sites can be drawn directly into the infrared spectrophotometer or halide meter by a multiprobe sampling apparatus. A time-location study of the workroom at the different probe locations can be used to estimate TWA exposures to tetrachloroethylene.

Direct reading colorimetric tubes (gas detection tubes) can be used as an inexpensive way to monitor tetrachloroethylene concentrations. The tubes must be used as instructed by the manufacturer. They are not suitable for determining compliance with the standard, but may be useful for determining exposure areas.

Biologic Evaluation of Exposure

Evaluation of some types of exposure to tetrachloroethylene, using breath analysis data, is feasible because nearly all the material is excreted through the lungs. [41,68,87,88] Data have been gathered from experiments where concentration and duration of exposure have been set at a variety of levels. The resultant alveolar concentrations were plotted according to time during and after exposure. From these data a map of breath concentrations resulting from an array of exposure conditions could be constructed to allow reasonable estimation of past exposures, provided the end point of the last exposure was known.

The alveolar concentration of tetrachloroethylene has been shown to be proportional to the concentration in the inspired air, and does not increase in proportion to the length of exposure. [68] Where the environmental conditions are such that the inspiration concentrations are fairly constant, breath analysis would be applicable for evaluation of exposure.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

There was little information on which to base early standards for occupational exposure to tetrachloroethylene. Hamilton, [117] in 1934, had only to say that it was a new solvent about which little was known. The first report found in the literature of an attempt to set a standard was from the Commonwealth of Massachusetts. [118]

The Subcommittee on Fumes of the Massachusetts Dust and Fume Code Committee prepared a list of proposed maximum allowable concentrations of industrial fumes in 1937. [118] No basis was given for the proposed value for tetrachloroethylene of 200 ppm.

The Subcommittee on Threshold Limits of the National Conference of Governmental Industrial Hygienists (NCGIH) published a list in 1942 entitled "Maximum Permissible Concentrations of Atmospheric Contaminants as Recommended by Various State Industrial Hygiene Units." [119] Eight states were listed as recommending 200 ppm for tetrachloroethylene, and Michigan was listed as recommending 100 ppm. The material was presented without comment other than that the tabulated values were not to be construed as recommended safe concentrations.

A list of maximum allowable concentrations of atmospheric industrial contaminants was compiled by Cook [120] in 1945 from the following governmental agencies: California Industrial Accident Commission, Connecticut Bureau of Industrial Hygiene, Massachusetts Department of Labor and Industries, New York State Department of Labor, Oregon State Board of Health, Utah Department of Health, and the United States Public Health Service.

All of these agencies recommended 200 ppm which was considered allowable for prolonged exposures, usually assuming a 40-hour workweek. [120]

Cook [120] also presented a list of accepted and tentative values based on industrial experience, animal experimentation, sensory responses of persons, or a combination of these. In this tabulation, he listed 200 ppm for tetrachloroethylene and cited the animal experiments of Carpenter. [37] Cook suggested that until more evidence was available on human exposures under industrial conditions, workers exposed at concentrations in the vicinity of the suggested allowable limit of 200 ppm should be under medical observation. [120]

The American Conference of Governmental Industrial Hygienists (ACGIH), formerly the National Conference of Governmental Industrial Hygienists, adopted a list of "Maximum Allowable Concentrations of Air Contaminants for 1946" which was prepared by the Subcommittee on Threshold Limits. [121] The selected value of 200 ppm for tetrachloroethylene was based on the recommendation of Cook [120] and the values tabulated by the NCGIH Subcommittee on Threshold Limits in 1942. [119]

The ACGIH Committee on Threshold Limits recommended, and the ACGIH adopted, a threshold limit value (TLV) of 100 ppm for tetrachloroethylene in 1947. [122,123] No basis for this change was given. The 1947 TLV for tetrachloroethylene was restored to 200 ppm in 1953. [124] The basis given for the change was information received from conference members that was not elaborated upon.

A preface to future tables of threshold limits proposed by the TLV Committee and adopted by the ACGIH in 1953 defined the values as "maximum average atmospheric concentration of contaminants to which workers may be exposed for an 8-hour working day without injury to health." [124] The preface was modified in 1958, and included the statement that "They [Threshold Limit Values] represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect." [125]

The first Hygienic Guide for tetrachloroethylene, published in 1960, gave 200 ppm as the recommended maximum atmospheric concentration for 8 hours. [126] This was believed to be a maximum which should not be exceeded in repeated daily exposure. It was not to be used as an integrated average concentration, and it was suggested that 100 ppm would be better for this purpose. The basis of the recommendation was given as human experience and the report of Rowe et al. [38]

The Committee on Threshold Limits proposed, and the ACGIH adopted, a TLV of 100 ppm for tetrachloroethylene in 1961. [127] This value, recommended on the basis of prevention of minimal narcotic effects in man, was supported by the reports of Carpenter, [37] Stewart et al, [39] Rowe et al, [38] and Smyth [128] in the first "Documentation of Threshold Limit Values" published in 1962. [129]

A standard of 4.4 ppm (0.03 mg/1) was proposed in 1965 as the maximum permissible concentration of tetrachloroethylene in air of industrial premises in Russia by Dmitrieva. [73] This recommendation was based on EEG and ECG changes in rats from chronic exposure at 15 ppm (0.1 mg/1). Similar changes were not found when the exposure concentration was 1.5 ppm (0.01 mg/1). [73,74]

The Hygienic Guide for tetrachloroethylene was revised in 1965. [130] The recommended maximum atmospheric concentration for 8 hours of 100 ppm was based on ACGIH recommendations.

American National Standard Acceptable Concentrations of Tetrachloroethylene (ANSI Z37.22-1967) [131] published in 1967 gave an acceptable time-weighted average for protection of health, assuming an 8-hour workday, of 100 ppm, an acceptable ceiling concentration of 200 ppm if the time-weighted average was below 100 ppm, and a maximum peak above the ceiling of 300 ppm for not more than 5 minutes of every 3 hours. This standard was based on the reviews by von Oettingen, [132] and Irish, [5] and the reports of Rowe et al, [38] Stewart et al, [60] and Stewart et al. [39]

Tables of "Permissible Levels of Toxic Substances in the Working Environment" for many countries were published by the International Labour Office in 1970. [133] The USSR values are absolute values never to be exceeded. They are set at a value believed not to produce, in any of the persons exposed, any deviation from normal, or any disease. Standards for several other countries are listed in Table V-1.

The most recent documentation of the threshold limit values was published by the ACGIH in 1971. [134] The reports of Carpenter, [37] Rowe et al, [38] Stewart et al, [60] Stewart et al, [39] Stewart et al, [40] Coler and Rossmiller, [51] Meckler and Phelps, [53] Dumortier et al, [59] and Lob, [43] were used to support the TLV of 100 ppm adopted in 1961. It was believed by the TLV Committee that 100 ppm would prevent serious narcotic effects, and that chronic intoxication involving hepatic or central nervous system effects would be unlikely if concentrations were maintained below this level. [134]

TABLE V-1

STANDARDS FOR SEVERAL COUNTRIES

Country	Standard		Qualifications
	mg/cu m	ppm	
Bulgaria	50	7.5	Ceiling
Finland	670	100	8 hours continuous exposure
Hungary	50	7.5	8-hour average
Hungary	250	37	30 minutes
Japan	670	100	None stated
Poland	200	29	None stated
UAR and SAR	67	10	None stated
USSR	10	1.5	Ceiling
Yugoslavia	670	100	None stated

Adapted from reference [133]

The Occupational Safety and Health Administration, US Department of Labor, adopted ANSI standard Z37.22-1967 [131] as the federal standard for tetrachloroethylene (29 CFR 1910.1000). This standard is 100 ppm for an 8-hour TWA exposure, with an acceptable ceiling exposure concentration of 200 ppm, and an acceptable maximum peak above the acceptable ceiling concentration for an 8-hour shift of 300 ppm for 5 minutes in any 4 hours.

Basis for Recommended Standard

(a) Environmental limits

Exposure to tetrachloroethylene has resulted in effects on the central nervous system, mucous membranes, eyes, lungs, liver, kidneys, heart, and skin. [31,33,36-38,41-44,46,50,55,56]

The most frequent effects have been on the nervous system. Tetrachloroethylene is a central nervous system depressant. Unconsciousness, dizziness, headache, vertigo or light narcosis has occurred after many occupational exposures. [43,44,49,63,72]

Experimental exposures to tetrachloroethylene at concentrations greater than 2,000 ppm have resulted in unconsciousness in humans after acute exposures. [37] At lower concentrations, such as those reported in the study of German drycleaners by Munzer and Heder, workers exposed at concentrations between 25 and 400 ppm showed signs of effects on the autonomic nervous system as indicated by hyperhidrosis, dermographism, and tremor of the fingers and eyelids. [63] The average environmental concentrations were not reported so it is difficult to determine at what concentrations these workers were exposed.

Similar signs and symptoms were reported by Franke and Eggeling [72] in their survey of 46 drycleaning plants in Germany. They reported concentrations resulting from 326 samples taken at random and 16 measurements taken at 15-minute intervals. Seventy-five percent of the measurements were less than 100 ppm. The maximum reported concentration was 400 ppm. Various subjective complaints among 113 workers were reported, including headaches, 35%: insominia, 34%: dizziness, 29%: and unspecified heart complaints, 30%. Tremors, hyperhidrosis, and dermographism were found in 40% of the surveyed workers.

In the studies by Munzer and Heder [63] and by Franke and Eggeling [72] concentrations reportedly ranged to 400 ppm. Workers surveyed or examined showed no irreversible neurologic effects of chronic tetrachloroethylene exposure. Irreversible neurologic effects have been reported in other studies but in most cases the concentrations were not known. [43,45,46, and E Baginsky, written communication, March 1975]

In nine cases of chronic exposure to tetrachloroethylene, symptomatology included vertigo, headache, nausea, vomiting, anorexia, insomnia, and eye and throat irritation. [43] In two of the cases involving 2-4 years of employment in an environment where tetrachloroethylene was used, severe neurological disorders were observed. In the case of one man working for 4 years in a poorly ventilated environment, loss of memory, blindness in the left eye, pronounced dermographism and vestibular dysfunction were observed upon examination. These disorders persisted even after the exposure had been discontinued.

Mild central nervous disorders were found in another man 2 months after he began using tetrachloroethylene in his work. However, 6 months prior to his work with tetrachloroethylene, he had degreased metal parts with trichloroethylene. He worked with tetrachloroethylene for 9 months, enduring the symptoms until they progressed to include numbness of the fingers, difficulty walking, trembling, exaggerated dermographism, and general weakness. Slight but positive reactions for urinary urobilinogen were also found. [43]

Gold [46] reported that a man who worked for 3 years in a drycleaning operation presented symptoms of increasing fatigue, dizziness, muscle cramps, memory difficulties, and restlessness. Neurological examination revealed an absence of olfactory sensitivity, deviation of the septum, and conjunctivitis, all on the right side. Most signs and symptoms persisted during the follow up year after exposure had ceased.

Peripheral neuropathies have also been reported resulting from tetrachloroethylene exposures (E Baginsky, written communication, March 1975).

The failure to find irreversible neurologic changes in the two studies of German drycleaning plants where concentrations ranged to 400 ppm was consistent with studies by Rowe et al [38] of four animal species. Rats, rabbits, monkeys and guinea pigs were exposed at up to 400 ppm for 7 hours/day, 5 days/week for up to 6 months. No neurologic changes were observed.

There is little information on the effects of chronic exposures to tetrachloroethylene at 0-200 ppm. Studies of acute exposures show effects consistent with the action of a central nervous system depressant.

Rowe [38] found that four subjects exposed at 216 ppm tetrachloroethylene for 2 hours required mental effort to maintain motor coordination. Similarly, in studies by Stewart et al in 1961, [39] and 1970, [40] at concentrations of 210-244 ppm for 30 minutes and 101 ppm for 3 hours, respectively, subjects experienced difficulty in maintaining a normal Romberg test.

Stewart et al [40] also found that of 15 subjects exposed for 7 hours at 101 ppm tetrachloroethylene, 25% reported mild frontal headaches, 60% complained of mild eye, nose and throat irritation developing within the first 2 hours, 25% experienced some difficulty speaking, and 40% felt slightly sleepy. No control group was provided.

Stewart et al [41] reported that results from the Flanagan coordination test indicated impaired motor coordination after 7.5 hours of exposure to tetrachloroethylene at 150 ppm. [41] Clinical evidence of central nervous system depression has not been reported with exposure concentrations below 150 ppm, [38,41] but there is preliminary evidence in EEG tracings of subclinical central nervous system response to repeated 7.5-hour daily exposures of humans at 100 ppm. [41] There is also evidence that these changes were maintained for at least 3 days after four 5-day weeks of 7.5-hours/day exposures at average concentrations of 20-150 ppm. [41] Data were not presented nor discussed for the results of EEG tracings during the week of exposure at 20 ppm of tetrachloroethylene. [41] The EEG tracings obtained with 100 ppm exposures indicated that the preliminary signs of narcosis were present in most subjects exposed at 100 ppm for 7.5 hours/day. [41]

The alteration of EEG tracings (increased delta wave activity), and subjective responses such as headaches, reported by Stewart et al, [40,41] after exposures at 100 ppm for 7.5 hours/day, were the only effects found at this concentration. While these alterations may be a preliminary subclinical response to tetrachloroethylene exposure, their appearance can result from various other factors unrelated to exposure. Stewart et al [41] reported no EEG alterations for subjects exposed at 20 ppm.

The data on human exposures at less than 100 ppm is sparse. Tuttle et al [50] reported neurologic and behavioral examinations of 22 workers in drycleaning operations with a mean of 7.47 years of exposure to tetrachloroethylene. The average TWA exposure for machine operators was 37.2 ± 24.96 ppm with an average ceiling of 214.90 ± 179.44 ppm. The investigators could identify no behavioral effects in workers exposed to tetrachloroethylene compared to an unexposed group. Differences in the neurologic examinations existed between the exposed and unexposed workers in proximal motor latency of the peroneal nerve, electrodiagnostic rating score, neurologic rating score and total neurologic score. The significance of these findings is in doubt because of the mean age of the exposed workers was 43.45 years and of the controls it was 34.44 years. The results of this study could easily have been confounded with the differences due to age.

Neurologic effects were not found in humans either from exposures at 20 ppm for 1 week, 7 hours/day by Stewart et al, [41] or at 55 ppm for 6 hours in the metabolism studies of Bolanowska and Golacka. [65] Studies of acute and chronic exposure at or near 100 ppm indicated that slight signs and symptoms of central nervous system depression may result. These effects are reversible and have been not shown to be painful or dysfunctional. There is very little evidence to indicate that exposures at less than 100 ppm will result in effects on humans.

Tetrachloroethylene is slowly eliminated from the body. [39,41,67] With repeated daily exposures it builds up in the blood and tissues, especially adipose tissues. [41,67] It is slowly metabolized. [58,69,70] All aspects of the metabolism are not known. Various metabolites have been found with tetrachloroethylene exposure. Trichloroacetic acid has been frequently determined in the urine. [69-71] Other metabolites of lesser urinary concentrations include trichloroethanol, oxalic acid, dichloracetic acid and ethylene glycol. [65,69-71,74,87,88]

It is recommended that the environmental limit for tetrachloroethylene be a time-weighted average concentration of 50 ppm. This limit should prevent neurologic effects as well as eye and respiratory tract irritation. No evidence of liver damage at or near the recommended limit has been reported.

Human exposures at concentrations between 100 and 300 ppm have resulted in neurologic effects such as difficulty maintaining a normal Romberg test and impaired motor coordination on the Flanagan test. To protect against temporary neurologic dysfunction, it is recommended that ceiling exposures be limited to 100 ppm as determined by sampling periods of 15 minutes.

It is recognized that many workers handle small amounts of tetrachloroethylene or work in situations where, regardless of the amounts used, there is only negligible contact with the substance. Under these conditions, it should not be necessary to comply with all of the provisions of this recommended standard. However, concern for worker health requires that protective measures be instituted below the enforceable limit to ensure that exposures stay below that limit. Therefore, environmental monitoring and recordkeeping is recommended for those work situations which involve exposure above one-half the recommended limit, to delineate work areas that do not require the expenditure of health resources for control of inhalation hazards. One-half the environmental limit has been chosen on the basis of professional judgment rather than on quantitative data that delineate nonhazardous areas from those in which a hazard definitely exists.

Tetrachloroethylene has caused abnormalities in fetal animals. [84] These included an increased incidence of subcutaneous edema, delayed ossification of skull bones, and split sternebrae in fetal mice. There was also an increased incidence of fetal resorptions in rats. In both species, exposures occurred on days 6 through 15 of gestation for 7 hours a day at 300 ppm. The significance of these findings and their applicability to human workers is still in question. However, since the effects observed in the animals studied reflect in part maternal effects that the recommended environmental limits are expected to prevent, it is not recommended that additional considerations for exposure be given to females of child bearing age. Further investigations are warranted and discussed in Chapter VII. Additional considerations for protecting women of child bearing age will be recommended if indicated by results of additional research.

Other information which may affect the recommended environmental limit are the results of the National Cancer Institute study of carcinogenesis which is currently in progress. When this information is made available it will be evaluated and the recommended standard will be revised if necessary.

(b) Medical Monitoring

It is recommended that all workers be given preplacement and annual medical examinations. The preplacement examinations may identify workers that might be susceptible, due to predisposing conditions, to exposure to tetrachloroethylene below the recommended environmental limit. Examinations given prior to employment will provide data for evaluating workers after various lengths of exposure. The annual medical examination has been recommended to supplement the environmental monitoring which is not continuous. These examinations should provide additional evaluation of the effectiveness of the recommended environmental limit. The medical examinations should be general with emphasis on the hepatic and nervous systems, which have been reported to be the most effected systems. [38,43,55] Since information on the effects of tetrachloroethylene on pregnant women and offspring is inconclusive it is recommended that physicians report any spontaneous abortions or fetal abnormalities that might result from exposure to tetrachloroethylene. The annual schedule for the examinations will provide the opportunity for early detection of effects on the health of the workers.

(c) Sampling and Analytical Methods

It is recommended that tetrachloroethylene in air samples be collected with activated coconut charcoal, desorbed with carbon disulfide, and analyzed by gas chromatography. [104] The basis for this is discussed in Chapter IV and Appendices I and II. These methods have been chosen because of the availability of components, specificity of the method, and relative ease of use.

Since tetrachloroethylene is used in many small scale operations, such as drycleaning, it is recommended that direct reading colorimetric detector tubes be used to supplement the primary method of sampling and analysis for tetrachloroethylene. [111,112]

(d) Work Practices

Exposure to tetrachloroethylene will be minimized by adherence to the work practices recommended in Chapter I and discussed in Chapter VI. The basis of these practices is the avoidance of tetrachloroethylene by confinement of the material, and by personal protection of the worker.

Tetrachloroethylene is confined by various storage containers, tanks, pipes and valves. These are maintained by periodic inspection. Tetrachloroethylene can linger in confined spaces and concentrations may build up. For this reason, entry into confined spaces shall not occur until the appropriate ventilation procedures and respiratory protective measures recommended in Chapter I are instituted. Table I-1 shows the concentrations for which various types of respirators are effective. These should be used in confined spaces under conditions specified in Chapter I.

Eyes and skin are vulnerable to tetrachloroethylene. [38,40,44,46,61,63,64] It is recommended that goggles be worn in activities where splashing is possible.

VI. WORK PRACTICES

The manufacture of tetrachloroethylene requires large amounts of chlorine. [1,9] Information on safe handling of chlorine is available. [135] Other chlorohydrocarbons may be used as starting materials or may be formed as coproducts. Caution must be taken to avoid exposure to these substances as well as any hydrocarbons which may be used as starting materials.

Further information concerning specific work practices for tetrachloroethylene can be found in the Manufacturing Chemists Association Safety Data Sheet SD-24, and in various other publications. [6,136,138]

(a) Transport, Handling, and Use

Tetrachloroethylene may be stored in mild steel, cast iron or galvanized iron containers. Commercial grades are stabilized to prevent decomposition in air or light up to 140 C (284 F). It is nonflammable, but since it can be decomposed to toxic and corrosive compounds such as phosgene and hydrochloric acid by contact with open flame or red-hot surfaces, it should be appropriately stored and handled to prevent such contacts. [1,6,9] Damaged drums or other storage or transporting containers should not be welded until thoroughly purged with steam, flushed with water, and air dried. [139]

All piping and valves at the loading or unloading station should be of tetrachloroethylene-resistant material and should be carefully inspected prior to connection to the transport vehicle and periodically during the operation. Personal protective clothing must be provided during both inspection and connection. Eye wash and safety shower installations should be readily available in the immediate area. Signs indicating the location of safety showers and eye wash facilities should be prominently displayed throughout the work area. Unloading areas must be posted "Danger: loading or unloading tetrachloroethylene."

Tetrachloroethylene has been found to cause effects on the skin. Prolonged or repeated exposure of skin to tetrachloroethylene should be avoided to prevent cutaneous effects.

Due to the toxicity of tetrachloroethylene, processes in which it is used in large quantities should be carried out in closed systems. Well designed hoods and ventilation systems should be used to maintain exposures at or below concentrations specified by this standard. Further protective measures include the use of personal protective equipment and clothing and purging of equipment prior to and during servicing and maintenance.

Tetrachloroethylene is a component of some insecticidal fumigants and conventional work practice guidelines are inappropriate to protect agricultural workers from the hazards of exposure. For these uses, fumigants containing tetrachloroethylene must be used in a manner consistent with their labeling requirements. These usually specify allowable time limits before a fumigated area or space may be reentered, and safe practices for the application of the particular pesticide. Consideration must be given to the wearing of personal protective equipment including a long-sleeved shirt, long-legged pants (or suitable coveralls), a hat, shoes, socks, and solvent-resistant gloves. Specific requirements of worker protection standards for agricultural pesticides may be found in 40 CFR 170.

Where a fumigant is applied to a crop in confined storage, hazardous concentrations may be encountered and entry to such areas must not be made without proper personal protective equipment including a self-contained breathing apparatus.

Safety showers and eye wash facilities are necessary in areas where tetrachloroethylene is handled. In locations where such facilities are not available, a container of water for emergency use must be kept with the first aid supplies.

(b) Equipment Maintenance

All equipment used for handling tetrachloroethylene must be emptied and purged prior to entry or disassembly. Steaming followed by washing with water is recommended for purging tanks and other containers which have held tetrachloroethylene. [6] Pipe lines should be disconnected and capped. Under conditions where it is necessary to enter or otherwise work with tetrachloroethylene contaminated equipment, maintenance personnel must use either a self-contained breathing apparatus of the pressure-demand mode, with an impervious protective suit, or a combination supplied-air suit with auxiliary self-contained air supply. Ventilation should still be continued during this time by blowing or drawing fresh air through the system. Safety precautions for emergency rescue require that all maintenance personnel be informed of the toxic properties of tetrachloroethylene and be instructed on the necessity of wearing personal protective equipment. [6] Constant observation of anyone entering a tank should be maintained in case rescue work is necessary.

(c) Emergencies

Spills must be anticipated. Storage tanks should be diked to contain the contents of the tank. Drum storage areas must also be diked to contain the tetrachloroethylene in the drums, preventing release to other areas. Areas where major spills are likely to occur should be constructed so that they may be closed until properly protected personnel can ventilate, enter, and clear the area. Warning signs must be posted so that unauthorized personnel will not enter the area. Normal work should not be continued until the concentration of tetrachloroethylene has been reduced to that prescribed by this standard. Any high temperature operations must be stopped until the spill is cleared. Disposal of tetrachloroethylene must be done in compliance with local, state, and federal waste disposal regulations. Consideration should be given to pumping the diked spill to another tank. In addition, it is advisable to have facilities for transfer of the contents of a leaking tank to another suitable tank.

Areas in which spills have occurred should be evacuated and well ventilated. Small, portable exhaust fans may be used in confined areas where local exhaust ventilation is not feasible. Workers should not return to any work area if the odor of tetrachloroethylene is still perceptible without first determining the concentration.

(d) Respiratory Protection

For adequate respiratory protection against the multiplicity of conditions which may be encountered in individual operations, many types of respirators have been developed and approved. Each have particular applications and limitations from the viewpoint of protection, as well as advantages and disadvantages from the viewpoint of operational procedures and maintenance. Detailed information on the selection and use of respirators can be obtained from the respiratory protection devices manual [140] published by the AIHA and the ACGIH in 1963. The American National Standards Practices for Respiratory Protection, ANSI Z88.2-1969, [141] also classifies, describes, and gives the limitations of respirators.

There are three categories of respirators: atmosphere-supplying respirators, air-purifying respirators, and combination atmosphere-supplying and air-purifying respirators.

One factor that affects the overall performance of demand-type (negative pressure) respirators is the variability of the face seal. Facepiece leakage is the major limitation of half-mask and quarter-mask facepieces operated with a negative pressure.

For purposes of uniform regulations covering the many face sizes and shapes of the US population, NIOSH recommends that the half-mask or quarter-mask facepieces operated with a negative pressure not be used for protection above 10 times the TWA limit, although the majority of wearers can obtain protection in atmospheres of higher tetrachloroethylene concentrations. On the same basis, NIOSH recommends that the full facepiece, operated with negative pressure, may be used up to 50 times the TWA limit.

These maximum use concentration guides do not take into account the service life of the filters and/or absorbent canisters which also affect the performance of air-purifying respirators. The approval tests (30 CFR 11) for these two devices specify only carbon tetrachloride for the service life test. Based on recent tests by Nelson and Harder, [142] who tested standard respirator cartridges against many types of industrial organic solvents, it is now possible to estimate the service life of approved organic vapor canisters or cartridges against tetrachloroethylene. With a test concentration of 1,000 ppm of tetrachloroethylene, they reported that the standard organic vapor cartridge has a service life of 129 minutes before a breakthrough of 100 ppm of tetrachloroethylene. Under the same test conditions, a service life of 90 minutes for carbon tetrachloride was obtained. The standard industrial size gas mask canister is tested against 20,000 ppm of carbon tetrachloride and it must have a service life of 12 minutes before a breakthrough of 5 ppm. Since it has been shown that charcoal can adsorb 0.7 times as much carbon tetrachloride as tetrachloroethylene, it can be estimated that the service life for an industrial size canister is 340 minutes in an atmosphere of 1,000 ppm tetrachloroethylene.

NIOSH periodically issues a list of approved or certified respiratory protective devices. All devices approved by the Bureau of Mines are listed in Information Circular 8559 and supplements. All types of devices certified by the Testing and Certification Laboratory of NIOSH are listed in a separate publication. These are available from the Testing and Certification Laboratory, NIOSH, Morgantown, West Virginia, 26505.