IV. ENVIRONMENTAL DATA AND ENGINEERING CONTROLS

Sampling and Analytical Methods

Most of the sampling methods for tetrachloroethane are dependent on its effective and reproducible uptake by various collection media. Collected air samples are usually transported to a laboratory, then desorbed or chemically treated, and finally analyzed quantitatively.

Elkins et al [58] used amyl acetate in a sampling train to collect tetrachloroethane from sampled air. Midget impingers containing m-xylene have been used for collection in conjunction with gas chromatographic analysis [59]. Bubbler bottles containing pyridine have been used for collection of tetrachloroethane in conjunction with colorimetric analysis [52]. The use of liquid in impingers and bubblers poses problems in field measurements because breathing-zone samples are difficult to collect and to transport without liquid spillage.

Williams and Umstead [60] reported the use of porous polymer beads as a collection medium. With this method, the same column was used for sample collection and gas chromatographic analysis. The advantage of this method is that it consolidates collection and analysis into one operation. However, only one analysis can be performed on each sample, and the method has not been adapted to field use.

Silica gel has been widely used as a collection medium for organic vapors [61-64]. Silica gel is a polar adsorbent and shows pronounced selectivity in adsorbing polar molecules, particularly water. Hence, during sampling of large volumes, atmospheric moisture may compete for the adsorption sites and displace tetrachloroethane [61,65].

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Activated charcoal is another popular solid adsorbent for organic vapors [62], and its use in conjunction with gas chromatography has been well documented [66-68]. Activated charcoal is nonpolar and will generally adsorb organic vapors in preference to water vapor; this results in less interference from atmospheric moisture than is the case with silica gel [65]. Activated charcoal has been specifically shown to be an effective adsorbent for tetrachloroethane [69].

When a solid collection medium is used, it is necessary to desorb the tetrachloroethane from the medium prior to analysis. The choice of desorbing agent depends on its desorption efficiency for tetrachloroethane and, if gas chromatography is the chosen analytic method, on the comparative retention times for the desorber and for tetrachloroethane. Carbon disulfide has been shown to be a highly efficient desorber of numerous organic solvents from activated charcoal [66,70]. In a report [69] on tetrachloroethane sampling and analysis, it was shown that carbon disulfide efficiently desorbed tetrachloroethane from activated charcoal and did not interfere with tetrachloroethane in gas chromatographic analysis. Petroleum-based charcoal was preferred over coconut-based charcoal in this study [69] because tetrachloroethane was more efficiently desorbed from the petroleum-based charcoal. Adsorption and desorption efficiencies may vary with different batches of charcoal. It is, therefore, necessary to determine the desorption efficiency for each batch of charcoal. The recommended air sampling method using activated charcoal tubes and the recommended desorption method using carbon disulfide, as well as an equation for the desorption efficiency calculation, are presented in Appendices I and II.

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Other sampling methods have included grab samples taken directly from tetrachloroethane-contaminated atmospheres with a variety of containers ranging from plastic bags to hypodermic syringes [66,71,72]. Although no specific data have been found on collection of tetrachloroethane in plastic bags, several types have been shown to have good retention times for other chlorinated hydrocarbon solvents such as dichloromethane (greater than 98% after 120 hours) [71] and trichloroethylene (90% after 90 hours) [72]. The advantages of using plastic sampling bags are that they are resistant to chemicals and that it is possible to collect unknown gaseous contaminant mixtures for subsequent quantitative and qualitative analysis. Also, the samples can be injected directly from the bag into a gas chromatograph. A disadvantage is that the shorter sampling duration and smaller sample volume available with this method would not accurately represent the atmosphere in a plant location during a work shift.

The numerous analytical methods for quantifying tetrachloroethane in air samples can be divided into two broad categories: methods based on chemical reactions and methods based on physical and chemical properties and analytical instrumentation.

The three most extensively used chemical methods are dechlorination with strong alkali followed by gravimetric or volumetric chloride determinations; colorimetric measurement of the reaction products of tetrachloroethane and pyridine heated in alkali solution (Fujiwara reaction [52]); and direct-reading with colorimetric indicators.

The dechlorination method requires collection of the tetra-chloroethane-contaminated air by a suitable collection medium such as silica gel [30] followed by alkaline hydrolysis in isopropyl alcohol. The

liberated chloride may be determined gravimetrically when silver nitrate is added to the solution (which has been slightly acidified with nitric acid) to produce silver chloride, a curdy, white precipitate. The precipitate is washed, carefully dried, and weighed [73]. The chloride ion may be determined volumetrically by the Volhard method [27], by the Mohr method [35], or with adsorption indicators [74,75]. Each of these involves the direct or indirect titration of the liberated chloride with silver nitrate. The chloride ion has also been measured by potentiometric methods [76]. Two disadvantages of the alkaline hydrolysis method are that the dechlorination step is nonquantitative, ie, the amount of chloride liberated depends on the reaction duration, and that the method is not specific for tetrachloroethane in the presence of other halogenated compounds.

In the colorimetric analytical method based on the Fujiwara reaction, a stream of air containing tetrachloroethane is passed through a wash bottle containing pyridine [52]. Then methylethyl ketone (MEK) and NaOH are added to an aliquot of the sample solution in pyridine, and this mixture, together with an aliquot of the MEK and NaOH solution (blank), is heated in a boiling water bath and cooled for a specific time period. The sample and blank absorption coefficients are then determined with a suitable spectrophotometer. This method requires less time than the dechlorination method, but the problem of specificity with mixtures of chlorinated hydrocarbons remains.

The third chemical method utilizes direct-reading detector tubes [77]. Glass tubes are packed with solid chemicals that change color when a measured and controlled flow of air containing tetrachloroethane is passed

through the packed material. The test vapor may be drawn directly through the tube and compared with a calibration chart, or it may be drawn into a pyrolyzer and then through the packed tube [77]. In either case, the method is not specific for tetrachloroethane since the stain to be read is produced by the liberated halogen ion, and any halogen or halogenated compound will interfere. Although widely used for other chlorinated hydrocarbons, detector tubes have not been recommended for measuring tetrachloroethane because of their lack of sensitivity in the critical, low-ppm range necessary for tetrachloroethane (5-ppm TLV).

The analytical methods based on the physical and chemical properties of tetrachloroethane include those using infrared spectrometry [78], photodetector analyzers (halide meters) [79], and gas chromatography [66].

An infrared spectrophotometer in conjunction with a suitable recorder can be used to indicate concentrations instantaneously. With this method, concentrations are measured directly, and it is not necessary to collect individual samples and transport them to a laboratory for analysis. Infrared has been used for continuous monitoring of industrial operations for chlorinated hydrocarbons [78]; however, complicated instrumentation is necessary to draw the samples and continuously record the data. It is also important that the atmosphere of relevant working stations is sampled and that such samples correspond to the breathing zones of workers at their assigned stations [78]. Infrared analysis is subject to interferences from other air contaminants. Substantial knowledge of infrared spectrophotometry is needed if one is to easily detect and resolve such interferences with assurance.

Halide meters detect the increased brightness of an a-c arc (metal electrode) when it is enveloped by an atmosphere contaminated with halogenated hydrocarbons [79]. These instruments are sensitive to all halogens and halogenated compounds, and consequently they are not specific for tetrachloroethane. Halide meters seem suitable for continuous monitoring if tetrachloroethane is known to be the only halogenated air contaminant.

Gas chromatography provides a specific quantitative analytical method for tetrachloroethane when appropriate column conditions are provided [80]. The sensitivity of the flame ionization detector is more than adequate to allow quantitation of tetrachloroethane in the low-ppm range. However, the possibility exists that several compounds found in an occupational environment may have similar column retention times. Resolution of interferences can be overcome by changing the stationary phase of the gas chromatography column or by changing the column temperature or other chromatographic conditions. Two separatory columns with different stationary phases can be used for more positive identification of compounds.

Also, mass spectrometry can be used with gas chromatography to identify more positively the substances present. Cooper et al [81] reported the use of a capillary charcoal tube to trap and transfer the material associated with a gas chromatogram peak to a mass spectrometer for qualitative identification. There are gas chromatography-mass spectrometry instruments available that do not require the intermediate transfer step [82].

Of the analytical methods reviewed, gas chromatography is recommended as the method of analysis for samples of tetrachloroethane collected from the workplace environment in tubes containing activated charcoal. Carbon disulfide is the preferred desorbent. The recommended sampling method has the advantage of using a small, portable collecting device which requires no liquid; this is convenient for sampling employees' breathing zones. The gas chromatograph possesses adequate sensitivity, and it is capable of separating and quantitating organic compounds in a mixture. Gas chromatographic procedures which are specific for tetrachloroethane are available [69]. The recommended sampling and analytical methods are described in detail in Appendices I and II.

Environmental Levels

In 1957, airborne concentrations of tetrachloroethane ranging from 1.5 to 247 ppm were reported by Jeney et al [28] from 170 area samples taken in a penicillin-manufacturing plant in Czechoslovakia. Air samples were collected in bubblers containing amyl alcohol and analyzed according to the method described by Lehmann and Hasegawa [34]. This involved the addition of sodium to the sample solution, refluxing for 8 hours, and titration of the liberated chloride with silver nitrate. Tetrachloroethane was used to extract the penicillin from the fermentation liquid. Because of the nature of the process, "separators," which were used to break the emulsions, had to be routinely dismantled and cleaned by rinsing the parts. The extraction and especially the cleaning processes introduced airborne tetrachloroethane into the 900-cu m workroom. During the course of the 3-year study, the ventilation system was improved once at the original plant,

and then the whole extraction process was moved to another building, where initially the ventilation was worse but was greatly improved later. Airborne levels of tetrachloroethane during the three different ventilation conditions are shown in Table III-1. The greatest reduction in airborne tetrachloroethane levels occurred in the sludging process (part of the cleaning process) where maximum concentrations were reduced from 247 to 36.4 ppm. Jeney et al [28] stated that, at the new plant, airborne tetrachloroethane concentrations during normal operations were about 15 ppm and increased to no more than 36.4 ppm during the cleaning operations. The extent of dermal contact with tetrachloroethane by the workers, if any, was not mentioned.

In 1963, Lobo-Mendonca [29] reported concentrations of tetrachloroethane in air ranging from 9 to 98 ppm in India's bangle-manufacturing industry. Tetrachloroethane, an efficient solvent for cellulose acetate, was used during several manufacturing stages, including the initial cylinder making (precut bangles) and the polishing of the individual bracelets. Breathing-zone air samples were taken at one to three worksites at seven different factories. Tetrachloroethane was collected on silica gel, extracted with alcohol, hydrolyzed with potassium hydroxide, and the chloride was titrated against silver nitrate [30]. The reported concentrations of tetrachloroethane in the air at the different worksites within the seven factories are given in Table IV-1. In a written communication (LR Lobo-Mendonca, September 1976), it was stated that these were averages, but the number of determinations made for each value was not reported.

TABLE IV-1

TETRACHLOROETHANE IN AIR CONCENTRATIONS AT SEVEN BANGLE FACTORIES

Factory Number	Sampling Site	Concentration (ppm)	Remarks
1	Near cylinder making; at breathing zone of 2 workers	39.3	Cylinder makers on platform between door and windows
	"	74.1	Poorly ventilated platform between 2 windows
2	Packing, near cylinder making	9.1	Well ventilated room with several windows and doors
	Cylinder making	17.4	"
3	Heating; between workers	10.59	25 ft from polishing; shed with 3 walls, 1 side open
	Cylinder cutting	14.00	15 ft from polishing; shed with walls on 2 sides
4	Cylinder making	98.00	Platform in small room with 1 window; no ventilation
	"	65.00	Center of large room
5	"	29.00	Open shed
6	"	60.56	Corner of room
	Polishing; at breathing zone	40.58	Workers squatting on floor near doors
7	Polishing	61.48	Workers beside table
	Near polishing; at floor level	50.00	3 ft from polishing table
	Near polishing; at breathing zone	20.49	Amylacetate area 10 ft from polishing table

Derived from Lobo-Mendonca [29]

Horiguchi et al [31] measured concentrations of tetrachloroethane in the air at three Japanese artificial pearl factories where individual beads were strung on racks and immersed in tanks of tetrachloroethane to produce a clear surface membrane. Two surveys were conducted 16 months apart in 1960 and 1961. The first survey revealed concentrations of tetrachloroethane in air ranging from 70 to 224 ppm in the three factories. By the time of the second survey, two of the factories had replaced tetrachloroethane in their processes and had no detectable airborne tetrachloroethane. The third factory had instituted local ventilation, and the second survey showed that the tetrachloroethane had been reduced to 20 ppm there. No details about the type of local ventilation were given. Horiguchi et al [31] also did not describe their sampling schedule, sampling locations, or analytical methods. The reported values of the two surveys are given in Table IV-2.

In 1968, Gobbato and Bobbio [32] reported the results of a survey of tetrachloroethane concentrations present during normal operations, as well as during maintenance periods, in a plant manufacturing tetrachloroethane in Italy. The process involved the chlorination of acetylene. The tetrachloroethane produced was converted to trichloroethylene and tetrachloroethylene. The proximity of the areas where these two operations were performed was not clearly stated in the report, but they were designated as being at separate locations. Samples of airborne tetrachloroethane were taken at five different manufacturing plant locations. Except for the laboratory and staff room, the sampling sites were outdoors. Bubblers containing absolute ethanol were used to collect tetrachloroethane, and a modification of the Fujiwara reaction [33] was

TABLE IV-2

TETRACHLOROETHANE IN AIR CONCENTRATIONS AT
THREE ARTIFICIAL PEARL FACTORIES*

Factory	Tetrachloroethane (ppm)	
	July 1960	Nov 1961
A	139.8	0
	86.8	
B	111.9	19.8
	88.5	
	74.6	
C	223.7	0
	113.7	0
	70.0	

*Work areas not specified

Derived from Horiguchi et al [31]

used for analysis. The disadvantage of this method was that it is not specific for tetrachloroethane, and interference by other chlorinated compounds was possible. All values were therefore based on the assumption that tetrachloroethane was the predominant chlorinated compound being sampled. Six determinations were made at each of the five worksites. Table IV-3 shows the mean as well as the maximum and minimum values found at each location. The location with the highest mean concentration of tetrachloroethane in air, 1.33 ppm, was the product-recovery zone. Higher concentrations were reported during maintenance periods: 5-15 ppm in the staff room and the reaction zone, and 40 ppm in the actual zone of maintenance work. These unspecified maintenance activities usually lasted

TABLE IV-3

TETRACHLOROETHANE IN AIR CONCENTRATIONS
AT A TETRACHLOROETHANE PRODUCTION PLANT

| | Tetrachloroethane (ppm) | | |
Work Area	Mean	Maximum	Minimum
Staff room	0.37	0.51	0.00
Tower reaction zone	1.12	3.10	0.46
Product recovery zone	1.33	3.20	0.31
Water tank ejector zone	0.94	1.65	0.50
Laboratory	0.79	2.00	0.30

Derived from Gobbato and Bobbio [32]

less than 30 minutes. At tank and tank-truck loading openings, tetrachloroethane concentrations between 10 and 20 ppm were measured; however, these operations were of very short duration.

Engineering Controls

Engineering design for working safely with tetrachloroethane should be such as to reduce the concentration of airborne tetrachloroethane. Closed systems under negative pressure, properly operated and maintained, should be used in all cases where practicable. Frequent tests must be conducted for leaks in closed systems. Where closed systems are not feasible, well-designed local exhaust ventilation systems must be provided.

Guidance for design can be found in Industrial Ventilation--A Manual of Recommended Practice [83], or more recent revisions, and in Fundamentals Governing the Design and Operation of Local Exhaust Systems, ANSI Z9.2-1971 [84]. In operations where tetrachloroethane is transferred, charged, or discharged into otherwise normally closed systems, continuous local exhaust should be provided at the transfer point. Sufficient ventilation with clean air should be maintained in the area to prevent recirculation of contaminated air into the workplace.

Respiratory protective equipment is not an acceptable substitute for proper engineering controls, but it should be available in emergencies and for nonroutine maintenance and repair work.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

Regulation of the industrial use of tetrachloroethane occurred during World War I when the toxicity of this solvent became apparent in the aircraft industries of Europe and the United States. In November 1915 [85], toxic jaundice, caused by tetrachloroethane in a factory or workshop, was added to the list of diseases in section 73 of England's Factory and Workshop Act of 1901. This Act stipulated that such cases be reported by the employer or medical practitioner to the Chief Inspector of Factories and Workshops. Before the end of World War I, Germany, France, Holland, and England banned the use of tetrachloroethane in their airplane industries [5] because of its high toxicity.

In the United States, Bowditch et al [86] recommended a "maximum concentration" of 10 ppm for tetrachloroethane in their 1940 "Code for Safe Concentrations of Certain Common Toxic Substances Used in Industry." They stated that this exposure limit did not guarantee prevention of ill health, nor did it mean that medical controls could be neglected. They did not report the bases for the recommended levels.

A list of maximum allowable concentrations (MAC's) of industrial atmospheric contaminants compiled by Cook [87] in 1945 included the tetrachloroethane standards set by the federal government and five states. A 10-ppm MAC was recommended by the US Public Health Service and by the following state agencies: California Industrial Accident Commission, New York State Department of Labor, Oregon State Board of Health, and Utah

Department of Health. The Massachusetts Department of Labor and Industries

recommended a 5-ppm MAC. These concentrations were specified generally as

allowable for prolonged exposures, presuming a 40-hour workweek [87].

Cook [87] also stated that 10 ppm was a tentatively acceptable

concentration for tetrachloroethane. In deriving this level he considered

the severe poisonings in industry, many of them fatal, together with animal

experiments that indicated tetrachloroethane was more potent than carbon

tetrachloride in inducing anesthesia. Cook [87] cited specific human case

studies reported by Hamilton [10] and Coyer [57]. In addition, he urged

that workers who were exposed under industrial conditions to

tetrachloroethane at known concentrations be observed to verify this

tentative MAC.

The American Conference of Governmental Industrial Hygienists (ACGIH)

adopted a list entitled "Maximum Allowable Concentrations of Air

Contaminants for 1946" which was prepared by its Subcommittee on Threshold

Limits [88] and included the 10-ppm MAC for tetrachloroethane recommended

by Cook [87].

The ACGIH [89] recommended an MAC of 5 ppm for tetrachloroethane in

1947; no justification for the reduction was reported at that time. In

1948, the designation of the limit was changed from "MAC" to "Threshold

Limit Value (TLV)," but the level remained at 5 ppm. In 1953, the ACGIH

[90] defined threshold limit values (TLV's) as the "maximum average

atmospheric concentration of contaminants to which workers may be exposed

for an 8-hour working day without injury to health." In 1958, the preface

of the TLV list [91] included the statement that TLV's "represent

conditions under which it is believed that nearly all workers may be

repeatedly exposed, day after day, without adverse effect." In 1962, the ACGIH [92] added the "Skin" notation to the tetrachloroethane TLV and thus indicated that there was a potential for exposure to airborne and liquid tetrachloroethane.

The 1971 ACGIH Documentation of TLV's [93] gave the basis for the recommended TLV of 5 ppm for tetrachloroethane. It contained references to Von Oettingen [94], Coyer [57], and Wilson and Brumley [95] who had detailed fatal poisonings attributed to tetrachloroethane, as well as the neurologic and gastrointestinal symptoms and the liver injuries associated with these poisonings. A report by Lobo-Mendonca [29] describing the general, neurologic, and gastrointestinal effects noted from occupational exposure to airborne tetrachloroethane at concentrations between 9 and 98 ppm, mostly between 20 and 65 ppm, was cited. There was also a reference to Elkins [62] who cited unpublished information from an unavailable personal communication indicating that adverse human effects had occurred at levels below 10 ppm. The 5-ppm TLV was recommended by the ACGIH [93] with the statement that it would probably prevent serious health effects and minimize, if not totally eliminate, the neurologic and gastrointestinal symptoms.

In addition to the existing TLV-TWA, in 1976, the ACGIH [96] proposed a Threshold Limit Value-Short Term Exposure Level (TLV-STEL) for tetrachloroethane of 10 ppm. They defined this as the "maximal concentration to which workers can be exposed for a period up to 15 minutes continuously without suffering from 1) intolerable irritation, 2) chronic or irreversible tissue change, or 3) narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce work

efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA also is not exceeded."

According to a 1968 joint report of the International Labour Office and the World Health Organization [97], tetrachloroethane standards, each as an "MAC," for six countries were as follows: Finland, 5 ppm; Germany (Federal Republic), 1 ppm; Japan, 5 ppm; Rumania, 1.5 ppm; USSR, 0.7 ppm; and Yugoslavia, 1 ppm. The USSR standard is an absolute limit never to be exceeded. According to the publication, it was set at a concentration expected to produce neither disease nor other detectable deviations from normal in any exposed person.

The current federal standard for worker exposure to tetrachloroethane is 5 ppm (35 mg/cu m) as a TWA concentration limit with a "Skin" notation (29 CFR 1910.1000). This was based on the 1968 ACGIH recommendation for a TLV, which was documented in 1971 [93].

Basis for the Recommended Standard

Effects on the nervous system, the gastrointestinal tract, and the liver from occupational exposures to tetrachloroethane have been documented in numerous reports [5,7,8,10-13,28,29,98] since the beginning of World War I. The reduction in industrial use of tetrachloroethane and in poisonings resulting from it since 1945 may account for the paucity of recent industrial exposure data that can be used in arriving at an environmental limit. Therefore, much of the information correlating exposure and effect has been obtained through experiments on humans [26] and animals [26,40,47-51].

The early case studies did show that two different groups of symptoms, sometimes overlapping in part, were produced by chronic tetrachloroethane exposure. The more common clinical picture was characterized by gastrointestinal and hepatic symptoms [5,7,8,10,12,28,98]. These symptoms included anorexia, exhaustion, nausea, and vomiting followed by jaundice and sometimes liver enlargement. Jaundice increased with the progression of the disease and was often accompanied by delirium, convulsions, coma, and finally death. Autopsies generally revealed fatty degeneration and cirrhosis of the liver.

Other cases [11,13] were characterized by signs and symptoms of the nervous system. Usually the first signs and symptoms were numbness of the toes and fingers, paresthesia, hand tremors, and plantar pain. Although fatalities were rare, the advanced effects were incapacitating and persisted for long periods, even in the absence of continued exposure.

Some early reports suggested that tetrachloroethane affected the kidneys [8,12,98], the cardiovascular system [8,12,98], and the lungs [98]. However, when found, these less common effects always occurred in conjunction with severe hepatic injury.

In one of the few studies providing occupational exposure data, Lobo-Mendonca [29] reported hand tremors in a high percentage (14%) of a transient working population at a factory where average airborne tetrachloroethane concentrations of 9 and 17 ppm were measured. The author stated that only those workers present at the time of the survey, and not those who had left work because of illness, were included. Because this factory had a very limited sampling schedule and several processes involved dermal contact, the reported airborne concentrations of tetrachloroethane

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are viewed only as approximations of the actual worker exposure.

Occupational exposure to airborne tetrachloroethane at concentrations ranging from 1.5 to 247 ppm was shown by Jeney et al [28] to produce signs of liver damage, such as enlarged liver, urobilinogenuria, and increased serum bilirubin, in factory workers. These signs were still reported after improved ventilation in the work area had decreased the concentration of tetrachloroethane in the air to 15 ppm during normal operations and to no more than 36.4 ppm during the cleaning process. Screening examinations of workers in alternate months helped to prevent serious liver disease at this factory; those workers showing signs and symptoms of incipient liver dysfunction were transferred to other work areas.

Until recently, most of the studies of the hepatotoxicity of tetrachloroethane in animals consisted of short-term exposures at high concentrations. These experiments showed fatty degeneration of the liver in rabbits, guinea pigs, rats, and mice [43-45]. Since 1969, five reports [47-51] of effects in animals exposed to tetrachloroethane at lower concentrations have confirmed a direct dose-effect relationship. Increased hepatic triglycerides with decreased serum triglycerides in mice exposed at 800 ppm for 6 hours were reported by Tomokuni [49], who also observed increased hepatic triglycerides in mice exposed at 600 ppm for 6 hours [48]. The activity of SGOT, a cellular enzyme released when cells are damaged, is measured as an index of liver cell destruction. Deguchi [47] reported increased SGOT activity in rats 24 hours after a 6-hour exposure at 100 ppm; in rats exposed for 6 hours at 10 ppm, increased SGOT activity, which peaked 72 hours postexposure, was noted. Navrotskiy et al [50] reported morphologic changes in the liver and kidneys of rabbits exposed

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repeatedly to tetrachloroethane vapor at 14.6 ppm. Several changes associated with suppression of the immunoresponse system of the rabbits were also noted at this concentration. Evidently this important homeostatic process was altered at this exposure concentration. Increased total fat content of the liver was reported by Schmidt et al [51] after 265 days in rats chronically exposed to tetrachloroethane at 1.94 ppm for 4 hours/day. They also reported decreased body weights, increased white blood cell counts, and increased pituitary ACTH in rats at different times during the experiment. Navrotskiy et al [50] reported minimal effects in blood studies and no morphologic changes in rabbits repeatedly exposed to tetrachloroethane at 1.46 ppm; no effects were seen at 0.3 ppm.

A comparison of available data suggests that hepatotoxic effects from inhalation exposure to other chlorinated hydrocarbons are produced at similar concentrations in animals and in humans. Carbon tetrachloride has been shown to cause adverse liver effects, such as increased liver weights in guinea pigs exposed at 5 ppm for 7 hours/day, 5 days/week, for 184 days [99] and enlarged livers with liver fatty infiltration in monkeys, rats, guinea pigs, and rabbits exposed continuously at 10 ppm for 90 days [100]. Available occupational data show that carbon tetrachloride at concentrations in air of 6.3-9.5 ppm caused liver effects, including increased serum iron and serum glutamic dehydrogenase, in workers exposed 2 or 3 times/year, 14 workdays each time, for 5 years [101]. At 100-200 ppm, tetrachloroethylene has been shown to cause increased liver weights and fatty liver degeneration in guinea pigs exposed for 7 hours/day, 5 days/week, for 132 exposures [102]. Workers exposed to tetrachloroethylene

at concentrations of 232-385 ppm for 8 hours, twice a week, for at least 2 years had increased BSP retention, liver cirrhosis, and urobilinogen in the urine [103]. One worker exposed at 50-250 ppm for 4 months died; liver cell necrosis was observed during autopsy [104]. No such information on other chlorinated hydrocarbon solvents was found, so similar comparisons cannot be made for them. However, the data indicate that hepatic effects from exposure to carbon tetrachloride and tetrachloroethylene were produced at similar air concentrations in humans and in animals.

The major concern in occupational exposure to tetrachloroethane is the hepatotoxic effect. In a factory where the air concentrations of tetrachloroethane had been reduced to 15-35 ppm, adverse liver effects were still seen in the workers [28]. No other data were found that would indicate exposure levels at which tetrachloroethane initiates liver damage in humans. Tetrachloroethane at an exposure concentration of 15 ppm administered repeatedly by inhalation to rabbits caused liver morphologic changes [50]. This concentration is within the range that caused liver effects in humans [28]. In view of the comparison showing similar liver effect levels in humans and animals from exposure to carbon tetrachloride, tetrachlorethylene, and tetrachloroethane, the animal data on tetrachloroethane cannot be ignored in recommending an environmental limit that will protect the health and safety of exposed workers. Consistent with these observations, the data showing biochemical indications of liver effects in rats at tetrachloroethane concentrations as low as 2 ppm [51] suggest that the current TLV of 5 ppm is too high to protect employees chronically exposed to tetrachloroethane for up to 10 hours/day, 40 hours/week, over a working lifetime. NIOSH therefore recommends that the

current federal standard of 5 ppm for tetrachloroethane be reduced to a TWA exposure limit not to exceed 1 ppm.

In addition, because tetrachloroethane is structurally similar to other hepatotoxic chlorinated hydrocarbons, some of which NIOSH has recognized as potential human carcinogens, the possibility for tetrachloroethane to have similar carcinogenic potential can not be disregarded. This lends further support for recommending a low exposure limit. Tetrachloroethane is currently being tested by the National Cancer Institute in its Carcinogenesis Bioassay Program.

It has been shown that hepatic and neurologic effects are of primary concern in occupational exposure to tetrachloroethane. Thus, a medical surveillance program should include preplacement and periodic medical examinations that give attention to liver function tests, such as serum transaminase determinations, and screening tests for neurologic function. The preplacment examination may identify workers that are susceptible to tetrachloroethane exposure at concentrations below the recommended environmental limit and will provide baseline data that can be used to evaluate the health of workers after varying lengths of exposure. The annual examination will provide the opportunity for early detection of effects on the health of the workers, as well as provide information for evaluating the effectiveness of the recommended environmental limit.

For the medical program to be effective, it is important that workers recognize the signs and symptoms of overexposure and the hazards of working with tetrachloroethane. A physician should be consulted immediately if specific symptoms attributable to exposure occur. Thus, NIOSH recommends that employees be informed of health hazards and that warning signs be

posted in appropriate locations in plants where tetrachloroethane is manufactured, used, or stored. Further information should be transmitted through a continuing education program instituted by the employer.

Absorption of liquid tetrachloroethane through the skin has been shown in rabbits [36], and one human fatality was attributed primarily to skin absorption [57]. Because of this, care must be exercised to ensure adequate protection against contact with tetrachloroethane. Personal protective clothing and respiratory protective equipment should be available and worn where indicated. Work practices that prevent skin and eye contact must be followed. Showers and eye wash fountains must be available for immediate use if accidental contact occurs.

Engineering controls must be used whenever feasible to control concentrations of airborne tetrachloroethane within the recommended limit. When tetrachloroethane is present, a closed system of control should be used. During the time required to install adequate controls and equipment, to make process changes, to perform routine maintenance operations, or to make repairs, overexposure to tetrachloroethane can be prevented by the use of respirators and protective clothing.

Medical and other pertinent records, which are important in assessing an employee's exposure, must be maintained for the duration of employment plus 30 years. This will allow enough time for future detection of chronic sequelae which may be related to the employee's known occupational exposure.

It is recommended that airborne tetrachloroethane be collected with charcoal tubes, desorbed with carbon disulfide, and analyzed by gas chromatography [69]. The basis for this recommendation is discussed in

Chapter IV and in Appendices I and II. These methods have been chosen because of their specificity, the availability of the necessary components, and their relative convenience.

Concern for worker health requires that protective measures be instituted below the enforceable environmental limit to ensure that exposures stay below that limit. An action level is set as a TWA concentration of one-half the environmental limit. It has been chosen on the basis of professional judgment rather than on the basis of any quantitative data that delineate nonhazardous areas from areas in which hazards may exist. However, in the case of tetrachloroethane it is also recognized that employees work with the liquid form of the substance in situations where there may be skin contact with it, resulting in dermal or systemic effects. Consequently, appropriate work practices, training, and other protective measures should be required regardless of concentrations of tetrachloroethane in air. Therefore, occupational exposure to tetrachloroethane has been defined as work in an area where tetrachloroethane is stored, produced, or otherwise used. Under these conditions, all provisions of this recommended standard except environmental monitoring and associated recordkeeping should be complied with; in work areas where the action level is exceeded, this latter requirement (Section 8) should also be complied with.