

IV. ENVIRONMENTAL DATA AND BIOLOGIC EVALUATION

Air Sampling and Analytical Methods

Methods of collection of trichloroethylene in air have included use of evacuated gas sampling flasks, [94] plastic bags, absorptive liquids such as pyridine or toluene [95-97] and silica gel or activated carbon adsorbents. [98-103] Field methods for the estimation of trichloroethylene vapor concentrations have included the use of the Davis Halide Meter and direct reading colorimetric indicator tubes. [104,105]

The analytical methods for determining trichloroethylene fall into three classes: physical methods such as interferometry or gas chromatography; chemical methods which depend on the reaction of trichloroethylene with a chemical reagent; and destructive methods such as the combustion techniques which decompose trichloroethylene and liberate hydrochloric acid. [95]

Adsorption on activated charcoal offers the greatest efficiency and ease of collection. [98,101-103] Use of absorbing liquids is inconvenient for obtaining breathing-zone samples, especially when two or more scrubbers must be connected in series to assure high collection efficiency. [95,96] The use of plastic bags or evacuated containers for collecting air samples may result in a loss of sample due to adsorption on the walls or to permeation through the plastic or around the joints in addition to being inconvenient for transport to the laboratory for analysis. Excessive water vapor tends to displace

the chlorinated hydrocarbons from silica gel when it is used as an adsorbent in a humid atmosphere. [106]

Gas chromatography offers the greatest specificity and sensitivity of the various methods of analysis, and is the method of choice. [101,102,106,107] The other methods including the field methods are subject to interferences from a wide variety of compounds, particularly other chlorinated solvents or other chloride-containing compounds and are useful only if trichloroethylene is the sole contaminant. [97,104] There are direct reading instruments which are not recommended for compliance purposes, but may be useful for emergencies, engineering control studies, and for estimation purposes. The Scott-Davis Halide Meter, and equivalents, have been used to determine trichloroethylene vapors in air. It is a nonspecific method and must be calibrated prior to each use. Detector tubes manufactured by several companies have been used to estimate trichloroethylene atmospheric concentrations. Care should be taken in using these tubes and each batch must be calibrated just prior to use. These are nonspecific as there are numerous interfering chemical contaminants and they are also affected by variations in temperature and humidity. Portable gas chromatographs are highly specific for trichloroethylene; however, they are very costly and can be used only by a well-trained investigator.

Environmental Data

Since 90% of the trichloroethylene produced in the United States is used in vapor degreasing operations, the majority of the limited

available environmental data were obtained from such operations. There are no published reports of environmental levels experienced in manufacture of trichloroethylene. The purpose of this section is to investigate the feasibility of controlling exposures to trichloroethylene to within the recommended standard. The sparse number of surveys and differing methods of analysis limit the discussion to chronological presentation of control methods and their effectiveness. Later in this section are suggestions for improving controls. Specific suggestions are avoided because of the variability of processes, equipment, climate.

In 1943 Morse and Goldberg [108] reported results of a study of chlorinated solvent exposures in different degreasing plants. Three types of controls were encountered: Type I, degreaser tanks equipped with both local exhaust ventilation and condenser coils to condense the vapor; Type II, tanks with condensers but no local exhaust ventilation; and Type III, tanks with no local exhaust ventilation and no condenser. The effectiveness of engineering controls is demonstrated in the following results. The general average for total atmospheric chlorinated solvents was 96 ppm (range 5-393) for Type I, 135 ppm (range 3-900) for Type II, and 221 ppm (range 24-880) for Type III. It was emphasized that perchloroethylene was used with trichloroethylene and sampling was done for total chlorinated solvents, not trichloroethylene exclusively.

Grandjean et al [27] measured trichloroethylene concentrations in workshops using degreasing tanks. All of the tanks studied were

equipped with refrigerated coils and exhaust systems. Atmospheric concentrations near the tanks varied from 20 to 40 ppm. Grandjean reported the operation of cold trichloroethylene vats wholly lacking in safety devices or any ventilation system on two occasions. Concentration of trichloroethylene in the air varied from 67 to 157, averaging 105 ppm.

As part of this study the effectiveness of different types of engineering control was evaluated. Air analyses were made using various methods of ventilation while normal work was performed. The workshop tank under consideration was fitted with a mixed system of mechanical ventilation including both air suction and air blowing. On the upper edge of the trichloroethylene tank there was a fixed lateral exhaust system which was intended to remove the rising trichloroethylene vapor. With no ventilation the average concentration of trichloroethylene in the air was 167 ppm. With the lateral exhaust system at the end of the tank operating, the average concentration was reduced to 112 ppm. The average concentration was lowered further to 53 ppm when general ventilation was used in conjunction with local exhaust. Atmospheric values of trichloroethylene showed a great variation with the degree of ventilation and utilization of the ventilation equipment. Atmospheric trichloroethylene samples were taken with impingers, and measured colorimetrically using the Fujiwara reaction. [27]

Grandjean also studied atmospheric concentrations during the cleaning of tanks and reported the following: "Trichloroethylene

equipment is cleaned once or twice a week. We examined the concentration of trichloroethylene near the tank during one cleaning operation. In the case in question, the workman emptied the tank, rinsed it with water from a powerful hose pipe, then got inside the tank and spent half an hour cleaning with a scrubbing brush. Analyses of the air showed a concentration of 1,120 ppm outside the tank while the hose pipe was in action, with 815 and 395 ppm inside the apparatus during and after the scrubbing respectively."

Skinner [109] reported the use of baffles on windows near degreasers in the plant to control high velocity drafts. Trichloroethylene concentrations of 170 to 230 ppm were reduced to 30 to 40 ppm with this approach to control.

Hargarten et al [110] reported results of tests carried out from 1952 to 1957 around 43 degreaser operations. Ninety-three percent of the operators' breathing zone samples taken during the cleaning cycle of the degreasers were 100 ppm or less. Methods of sampling and analysis were not stated.

In a 1963 report Ahlmark et al [111] found that during the preceding decade, when 570 degreasing plants were inspected in Sweden, the average trichloroethylene concentration exceeded 30 ppm in only 3% of the cases. A more intensive study was then performed on 18 degreasing tanks at 14 works. The breathing zone samples taken with a Davis Halide Meter and with LKB Halogen Detector Tubes are presented in Table X-3 along with relative exposure times for different operations. The mean exposure to trichloroethylene was 50 ppm (range

0-400) for degreasing operations while the highest mean value was 225 ppm (range 10-375) in the cleansing operation.

There are no published environmental data on trichloroethylene concentrations in other industries beyond the descriptions of health hazards associated with the use of this solvent in those industries. Thus, the effectiveness of engineering controls can be demonstrated only for degreasing operations.

Engineering Controls

Industrial or commercial operations that use trichloroethylene have one or more methods available to control the emission of solvent vapors into the general work environment. The strategy of controlling hazardous industrial levels of trichloroethylene includes the following:

1. Substitution of less harmful solvents
2. Proper equipment design
3. Process location
4. Process ventilation
5. Proper operating, maintenance, and waste disposal procedures

1. Substitution

In solvent using industries it is common practice to substitute a solvent with a less toxic one. Full consideration must be given to other solvent properties such as effectiveness, relative volatility, volume of air required to dilute the vapor in the work environment to

a safe level, relative amounts of each solvent required for the task, likelihood of control of the vapor concentrations, and flammability.

2. Equipment design

Hazardous environmental conditions result from solvent escape, resulting from solvent evaporation, carry-out and spills, both those accidental and those incidental to operations, especially in degreasers. It is imperative that the evaporation and condensation of solvents be carefully controlled by balanced heat inputs. Careful and proper design of process operations is still the simplest and most economical method for controlling dangerous vapor emissions.

3. Process location

Process location is one of the most often overlooked and yet most effective methods of minimizing dangerous trichloroethylene vapor levels in the work environment. For example, degreasing operations should be installed in large rooms with good general ventilation wherein the entire work area is constantly flushed with sufficient uncontaminated air to dilute the toxic vapor and thus, in conjunction with local exhaust ventilation render the workroom atmosphere harmless. Areas in the vicinity of doors, windows, or other possible sources of draft conditions should be avoided since excessive air movements in the vicinity of trichloroethylene operations could decrease the effectiveness of local exhaust systems and thus enhance the possibility of vapor escape. Location of trichloroethylene operations in the vicinity of high temperature from high energy sources should be avoided to reduce the possibility of decomposition.

of trichloroethylene into chlorine, hydrogen chloride, or the very toxic gas, phosgene.

4. Process ventilation

Ventilation is by far the most common engineering method for controlling solvent vapors. Vapor recovery systems are sometimes used when a high airflow exhaust system is required for good ventilation.

5. Proper operating, maintenance, and waste disposal procedures

Trichloroethylene losses from industrial operations can be minimized by proper operating procedures and careful supervision. Factors such as the rate of work entering and leaving the vapor zone and the shape of the parts can be critical to the degree of vapor emissions from degreaser operations as indicated in a report by Grandjean et al. [27]

Biologic Evaluation

Biologic monitoring is not part of the recommended standard although such monitoring is used in much of the research dealing with trichloroethylene exposure. Methods used in establishing a diagnosis of exposure to trichloroethylene are based upon the direct analysis of this chlorinated hydrocarbon in the blood or in the breath [17,29,30] or the determination of its metabolites, monochloroacetic acid, trichloroacetic acid or trichloroethanol, in the blood or urine. [18,23, 30,112,113] The determination of trichloroethylene in blood samples is generally not considered to provide a reliable index of exposure because of its rapid conversion to several metabolites. [17,29] The

concentrations of individual metabolites found in blood or urine provide very little correlation with levels of exposure among individual human subjects. [18,30,112]

The measurement of trichloroethylene in the expired air of subjects exposed to different, nonfluctuating vapor concentrations of this solvent in the postexposure period offers promise as a good index of exposure levels. The concentration of trichloroethylene in the breath in the immediate postexposure period represents washout from the lungs and indicates the concentration of the vapor to which the subject was exposed most recently. A breath sample collected approximately three hours after the exposure is considered to provide a concentration of the solvent which is directly related to the time-weighted average vapor exposure. [30] Thus, breath analysis is particularly valuable in the prompt examination of a case of suspected overexposure but it may also prove useful in estimating a time-weighted average exposure when serial analyses of the breath are made on an individual. Since the concentration of trichloroethylene in the breath is influenced further by the duration of the exposure period, concentration-time relationships must be worked out.

V. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1943 the United States Public Health Service [114] published its Manual of Industrial Hygiene and Medical Service in War Industries which listed "maximum allowable concentrations" for several contaminants of the workroom atmosphere. These values were based on cumulative knowledge and collective experience developed in the field of industrial hygiene. Trichloroethylene was given a limit of 200 ppm with the indication that this value was the maximum allowable concentration most widely accepted at that time based on an 8-hour daily exposure.

The list of acceptable concentrations from the same manual was critically reviewed, unified, and extended by Cook [115] in 1945. This list was supplemented by lists of acceptable concentrations supplied by other sources including the California Industrial Accident Commission, the American Standards Association, and the states of Connecticut, Massachusetts, New York, Oregon, and Utah. Each of these sources listed a value of 200 ppm as the maximum acceptable concentration for trichloroethylene. Cook, who also recommended the 200 ppm maximum allowable concentration, cited the works of Seifter [68] and Morse and Goldberg [108] as the bases for his standard.

The Z-37 Committee of the American Standards Association, now the American National Standards Institute, published its standard for trichloroethylene in 1946. The Committee recommended a maximum allowable concentration of trichloroethylene of 200 ppm for an 8-hour

workday. In 1967 this standard was revised by the Z-37 Committee. [116] The revision established 100 ppm as an acceptable time-weighted average concentration for an 8-hour workday. In addition, an acceptable ceiling concentration of 200 ppm, provided that the time-weighted average is kept at or below 100 ppm, was recommended. Furthermore, a concentration of 300 ppm for a duration of not more than 5 minutes was judged acceptable if encountered not more than once in 2 hours during an 8-hour workday. These standards are based on the reports of von Oettingen, [9] Adams et al, [72] Stewart et al, [29] and Kleinfeld and Tabershaw. [36]

The American Conference of Governmental Industrial Hygienists (ACGIH) [117] Threshold Limit Value (TLV) for trichloroethylene was 200 ppm from 1947 to 1961. In 1961 it was lowered to 100 ppm based on the report of Adams et al [72] that there is an extremely small probability of adverse effects on human subjects if the vapor concentrations of trichloroethylene are kept below 100 ppm.

The Hygienic Guides Committee of the American Industrial Hygiene Association [6] has recommended a concentration of 100 ppm of trichloroethylene for a time-weighted average concentration for a normal workday, based on human experience and animal studies, which further indicates that fluctuations of the concentrations should be kept below 200 ppm.

The Occupational Safety and Health Administration, Department of Labor, has adopted a standard for trichloroethylene of 100 ppm for an 8-hour time-weighted average, 200 ppm for an acceptable ceiling

concentration, and 300 ppm for an acceptable maximum peak above the acceptable ceiling provided that it occurs no more often than 5 minutes in any 2 hours. These were developed from and based on the current American National Standards Institute Z-37 limits. [116]

Some European investigators have recommended occupational health standards for trichloroethylene of less than 75 ppm. However, in most cases these recommendations were based on gross estimations of environmental conditions based on extrapolations from the results of biological sampling (analysis of blood or urine for metabolites of trichloroethylene). Where air sampling was conducted the investigators stated that concentrations varied greatly during a normal workday. A summary of the environmental standards, ranging from 2 to 200 ppm, promulgated by foreign countries is presented in Table X-4. [118]

Basis for Recommended Environmental Standard

The number of studies in which comprehensive environmental surveys have been supplemented with a well planned surveillance program for adequate numbers of workers exposed to trichloroethylene are so few that it is difficult to establish an environmental standard based upon unequivocal scientific data. Much of the information correlating exposure and effects have been obtained through experimental studies with human volunteers. [22,29,30,91-93] Such studies are necessarily limited in the total duration of exposure and thus valuable primarily for evaluation of short-term effects, that is

exposure to tolerable concentrations of a substance for relatively short periods of time, up to 5 days.

It is apparent from the literature that exposures to concentrations between 200 and 500 ppm for periods of time less than the normal workday will result in symptoms of "prenarcosis" as well as mild irritation of the upper respiratory tract. This is corroborated by the previously mentioned reports of Stewart et al [29,30] and Stopps and McLaughlin. [92]

The studies with trichloroethylene most relevant directly to the development of an occupational standard are those in which human volunteers were exposed to carefully controlled atmospheric concentrations of the contaminant. The most important observations are the following:

(a) Adverse subjective responses have been reported [29,30] by test subjects exposed to concentrations exceeding 150 ppm. These include mild eye irritation by three of seven subjects exposed to 160 ppm for up to 83 minutes [29] and by one of five subjects exposed to 200 ppm for 7 hours, [30] and feeling of fatigue and sleepiness by all five or by three of five exposed to 200 ppm for 7 hours on the fourth and fifth consecutive days of exposure. [30]

(b) Exposure to 100 ppm for periods of 2-to 3-hours duration did not result in any decrease in psychophysiological performance. [91,92]

(c) Concentrations of approximately 100 ppm trichloroethylene interfered with psychophysiological performance after exposures of 8-hours duration; this was demonstrated by Salvini et al. [93]

(d) Quantitative evaluations of objective and subjective responses of human subjects exposed under controlled conditions to concentrations of less than 100 ppm trichloroethylene have not been reported.

In summary, deaths of several workers from exposure to trichloroethylene have been reported [36,90]; in the best documented case, exposure was at levels estimated to be between 1700 and 3300 ppm for ten minutes. Exposures at 1000 ppm for even short periods of time have resulted in effects on the central nervous system. Subjective complaints by one of 8 male volunteers was reported [91] at exposure levels of 300 ppm for two hours. No adverse effects were noted by psychophysiological testing of the same subjects at 100 ppm. In another paper, [92] results of psychophysiological testing of one subject for 2-1/2 hours indicated no significant effect on psychomotor performance from exposure at 100 ppm, but a slight effect was noted at 200 ppm. Adverse effects were reported by 3 of 7 subjects exposed at 160 ppm for less than 83 minutes. These effects, subjective in nature, included headache, drowsiness and mild eye irritation. [29]

Salvini et al [93] reported a statistically significant decrement in performance without clinical signs or symptoms at 90 to 130 ppm (average exposure level of 110 ppm). He concluded that 100 ppm was very close to the average concentration that would interfere with psychophysiological efficiency. This study included two groups of 6 males each, one of university students and the second of trichloroethylene workers. The same conclusions were drawn from the

results of each study group from which it is inferred that the threshold for psychophysiological effects is not affected by prolonged exposure. There is also evidence that prolonged exposure to trichloroethylene may result in dependency. It is significant that reports of liver damage from trichloroethylene are uncommon. Perhaps the suggestion [21] that liver damage is not caused by trichloroethylene except when it is contaminated by other compounds, especially tetrachloroethane, is the correct explanation.

As discussed above, the study by Salvini et al [93] indicates that exposures of approximately 100 ppm may interfere with the psychophysiological efficiency of the worker. Therefore, a TWA limit of 100 ppm will protect most of the workers but with probably very little margin of safety at this level of exposure.

VI. REFERENCES

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