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Monitoring Exposures to Vinyl Chloride Vapor: Breath Analysis and Continuous Air Sampling

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An environmental survey was conducted to determine the time-weighted average exposure (TWA) of a group of chemical plant workers to vinyl chloride (VCl) vapor. This survey featured continuous multipoint air sampling and analysis using an infrared spectrophotometer. The inhalation exposure data were digitized and recorded on paper tape for subsequent computer analysis and derivation of daily TWA values for each worker. A breath sampling program was conducted concurrently with the environmental survey, and a series of breath decay curves relating postexposure breath concentration to vapor exposure were derived from the data. To validate the breath curves derived from on-the-job data, postexposure breath curves were also constructed from breath data obtained following experimental human exposures to carefully controlled concentrations of VCl vapor. The close agreement between postexposure breath concentrations at the corresponding TWA's obtained by each of the methods suggests that either continuous air monitoring or breath analysis is valid for estimating the worker's individual daily exposure to VCl, and provides further evidence that breath analysis is a useful industrial hygiene technique for evaluating vapor exposure.

Introduction

THE QUESTION THAT MAY ARISE following an environmental survey is whether the chemical vapor concentrations measured are truly representative of the exposure being experienced by the workmen. Evaluation of the ranges of atmospheric concentrations and estimates of time-weighted average concentration (TWA) are all too often based on a few spot samples obtained under conditions which are not representative of all phases of a given operation. A more exact measurement of vapor exposure would have to be based on continuous monitoring of air in the workman's breathing zone during his entire work shift. Obviously this task is made difficult and often impossible by the large number and variety of tasks performed by today's modern chemical plant worker.

Recent improvements in automatic monitoring and data processing equipment have provided a means for a more satisfactory solution. Sequential samplers and automatic analyzers and recorders can now be used to continuously monitor several locations or operations to provide more valid data on which to base estimates of chemical exposure. Computers can be utilized to manage the large volume of data generated by continuous monitoring.[1]

Meanwhile a technique has been under development which more precisely defines the level of individual exposure. The realization that the total body burden of a volatile chemical is directly related to its concentration in expired air led to the development of techniques for collecting and analyzing breath samples useful in estimating the more indi-

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vidualized exposure experience of each workman. Studies by Stewart *et al.* [2-4] have shown that the excretion or "decay" of vapor in the breath can be used to characterize the exposure. Breath decay curves constructed for several chemical solvents have proved clinically useful as an index to chemical exposure.

These breath decay curves, for the most part, were constructed from postexposure breath data obtained from experimental human exposures to carefully controlled and relatively constant vapor concentrations. However, breath decay curves have recently been constructed from breath data collected from workers whose work environment was being continuously monitored.[5]

In this study of human exposure to vinyl chloride (VCl) vapor, breath decay curves constructed from data obtained during experimental exposures to the relatively uniform concentration within an exposure chamber were compared with those derived at the theoretically equal, but broadly fluctuating, concentrations encountered in a chemical plant atmosphere. A measure of the validity of continuous monitoring data and the usefulness of breath analysis in assessing time-weighted average exposure was reflected by a close similarity between the two sets of breath decay curves.

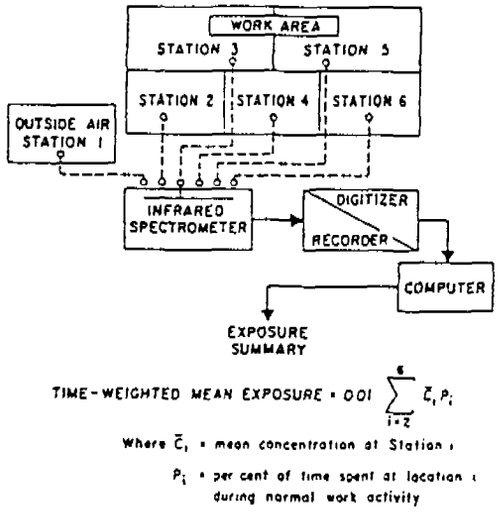

FIGURE 1. Schematic diagram of the infrared continuous monitoring system.

Procedures

Monitoring the Plant Atmosphere

The chemical installation surveyed was a closed structure housing several separate chemical processing operations. First, a job survey was conducted for each of four job classifications to determine the work areas frequented by the workmen and the time they spent in each area. For each job classification, five sampling probes were strategically placed in the work area. A sixth probe was placed outside the building, and charcoal and silica gel filters were placed in the sampling line to assure a clean air reference. The sample probes were 5/16-inch I.D. Saran tubing through which air samples were drawn by a vacuum pump at a rate of 17.5 liters/min to a centrally located infrared spectrophotometer. The spectrophotometer was equipped with a 10-meter path-length gas cell sensitive to 5 ppm of VCl at a wavelength of 10.63 microns. The VCl concentration was linearly related to absorbance up to approximately 1000 ppm.

A schematic diagram of the sampling system is shown in Figure 1. Sampling was executed sequentially with a set of six two-way solenoid valves controlled by a timer which advanced the sampling location every 5 minutes. A visual account of transmittance was recorded on a strip chart recorder. Meanwhile the data were recorded in digital form on paper tape by a tape punch and digitizer-programmed to record three equally spaced transmittances during the last half of each 5-minute sampling period.

The transmittance data furnished by the spectrophotometer was converted to absorbance and reduced to concentration according to Beer's law:

$$A = \mathrm{Log}_{10}\frac{(X_i - X^{\infty})}{(X_i - X^{\infty})}$$

where

A = absorbance
X_1 = base-line response.
X^{∞} = response at total absorption.
X_i = response at location i.
i = 2, 3, 4, 5, 6.

Finally,

$$C = KA$$

where

K = a proportionality constant.
C = concentration

The taped data were processed by a Burroughs 5500 computer at The Dow Chemical Company Computation Research Laboratory. The computer was used to calculate the mean and standard deviation of concentrations at each location for each 8-hour work shift. Finally, time-weighted average concentrations were calculated for each job classification using the time–location data obtained from the job surveys. As described elsewhere,[1] the weighted percentage of time during which concentrations exceeded several prechosen levels was also computed for use in establishing exposure profiles.

Figure 2 describes the exposure profiles (frequency distributions) for the four job classifications studied during this survey. These profiles show the percentage of time that concentrations exceeded the levels shown. They summarize several tens of thousands of individually measured concentrations and reduce them to single curves. Figure 3 shows the corrective trend brought about by actions undertaken to reduce the atmospheric concentration of VCl over the 7-month period during which the study was conducted. Only two job classifications warranted extensive study, but men in all four classifications were asked to participate in the breath sampling program.

On-the-Job Breath Sampling

Three separate breath sampling programs were conducted concurrently with the environmental plant survey, designated by the boxed portions in Figure 3. Each worker collected three breath samples daily—the first on his arrival home from work, the second 5 to 10 hours later, and a final sample before returning to work the following day The samples were collected in pipets constructed from short lengths of 20-mm soft glass tubing to which had been welded at each end the threaded portion af a 2-dram (8-ml) screw-cap glass vial (Figure 4). The overall length of the pipet was about 9 inches, so it could be conveniently and inconspicuously transported to and from work in a lunch bucket.

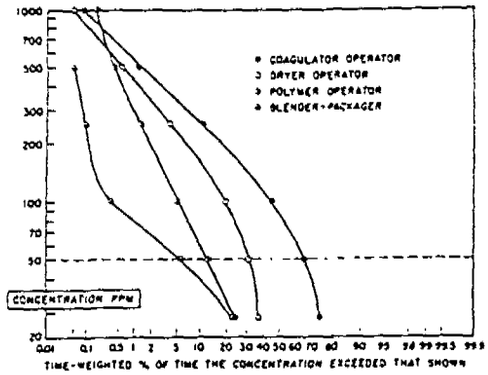

FIGURE 2. Exposure profiles expressed as VCl vapor concentration versus the exposure frequency distribution for the four job classifications.

The plastic caps were lined with six layers of Saran film identical to that used for the construction of Saran air sampling bags. A 3/32-inch hole predrilled through one of the caps provided an access for withdrawing samples. The Saran liners provided an effective gas barrier so that vapor losses were held to less than 10% for a holding period of 3 days.

When collecting a sample the subject was asked to remove the caps, place the pipet to his lips, and breathe normally in through his nose and exhale through the pipet three

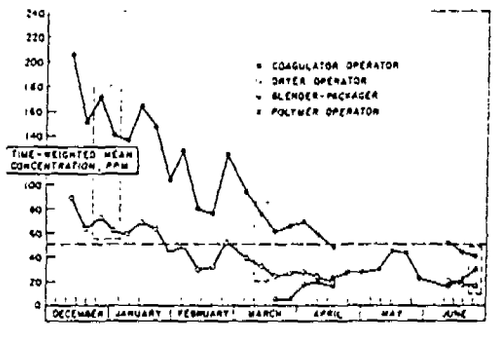

FIGURE 3. Weekly mean vapor exposure concentrations measured during the survey. Periods during which breath sampling was conducted are represented by the boxed-in areas.

FIGURE 4. Glass pipet (50 ml) used for collecting breath samples. One cap has a predrilled hole for gas sampling. Both caps have Saran liners which seal the pipet chamber.

times. After expelling the fourth breath he quickly caps the tube, trapping a portion of alveolar air. The importance of writing the name, date, exact time of sampling, and the workshift most recently completed, on the label attached to each pipet, was stressed.

Aliquots were drawn from the pipets with a 1-ml Hamilton gas-tight syringe and analyzed in an Aerograph A-600B gas chromatograph using N_2 carrier gas and a hydrogen flame detector. Separations were made with a 6-foot, ⅛-inch I.D. stainless-steel column packed with Carbowax 20M alkaline on Chromosorb W 60/80 mesh acid-washed.

Exposure Chamber Operation

Three experimental human exposures to VCl were conducted at nominal vapor concentrations of 50, 250, and 500 ppm. The exposure chamber was a room measuring 41 feet by 6 feet wide by 7.5 feet high. The room had a continuous positive air supply and exhaust system capable of maintaining a slight negative pressure within the chamber. Continuous distribution of the chamber air was achieved by recirculating the air with a squirrel cage fan through a series of inlet and outlet ducts spanning the length of the chamber. The VCl was metered into the duct carrying air exhausted by the squirrel cage fan and entered the room atmosphere via the recirculation system at a rate sufficient to maintain the desired atmospheric concentration. The vapors were introduced from a pressurized storage cylinder through 6 feet of ⅛-inch I.D. stainless-steel tubing into a rotometer prior to entering the circulating air duct. A heating tape wrapped around the stainless-steel tubing prevented condensation of the VCl and stabilized the flow of the vapor.

The concentration of VCl in the chamber was constantly monitored with a Perkin-Elmer infrared spectrophotometer equipped with a 10-meter path-length gas cell. A sampling probe, consisting of 5/16-inch I.D. Saran tubing, was centrally located during the exposure to represent the breathing zone of all subjects within the chamber. The probe was moved about prior to each exposure to detect imbalance of vapor concentrations within the chamber so that necessary corrections in the recirculating system could be made. Air samples collected periodically within the chamber throughout the exposure day were analyzed by gas chromatography for added assurance of analytical accuracy. Both the infrared spectrophotometer and the gas chromatograph were calibrated before each experiment and at intervals throughout the exposure day.

Each 7.5-hour exposure day included a 0.5-hour lunch period in an uncontaminated area outside the exposure chamber. The TWA concentration was calculated on the basis of 7.5 hours of exposure.

Clinical and Laboratory Procedures

Each subject had been under careful medical surveillance by the medical department for a number of years, and each was given a complete medical examination a few days prior to the VCl exposures. Included were a complete urinalysis and 24-hour urine for urobilinogen, complete blood count with sedimentation rate, reticulocyte count, SGOT, SGPT, LDH, alkaline phosphatase, BUN, creatinine, and bilirubin.

Each subject received a repeat physical examination 1 hour before entering the exposure chamber. This examination included measurement of temperature, blood pressure, and pulse rate, a neurological examination, and collection of blood and breath samples. A questionnaire noting the presence of any symptoms of illness (for example, headache, nausea, dry throat) completed the pre-exposure medical evaluation.

After the subject entered the chamber, total expired breath samples were collected every hour by having him breathe out through a Saran tube leading to a Saran plastic collection bag located outside the chamber. Tidal volume and total expiratory capacity

were measured in the morning and again late in the afternoon exposure periods.

Subjective and neurological responses were measured before the subject entered the chamber, 15 minutes after entrance, and at 1-hour intervals thereafter. Flannagan Coordination and Crawford Manual Dexterity Tests were conducted at midmorning and again in the afternoon. Breath sampling began immediately after the subject left the exposure chamber. A 24-hour postexposure urine sample was collected and a blood sample was drawn the following morning for SGPT, LDH, alkaline phosphatase, BUN, creatinine, and bilirubin determinations.

Analysis of Breath Data

The decay curves for the breath vinyl chloride concentrations were constructed by stepwise multiple regression using a digital computer. An empirical relationship of the form Concentration = f (TWA, time) was selected from a choice of several terms, each based on TWA and/or time. The resulting regression equation best represents the ordered relationship between breath vinyl chloride concentration, time-weighted average exposures, and postexposure time.

Each breath decay curve has an associated standard error of regression which can be used to compute the confidence band for any chosen level of significance. The 95% confidence band for the mean of a group of observations was chosen in this case to describe the statistical error associated with the breath data and the regression technique.

Results

Experimental Breath Curves

A total of 13 men participated in the three experimental chamber exposures at nominal concentrations of 50, 250, and 500 ppm producing a total of 160 valid breath data points. Five of the six subjects exposed to 50 ppm were re-exposed at 500 ppm 2 days later. There was no measurable residual vinyl chloride detected on the breaths of the subjects prior to the second exposure. Serial breath sampling was initiated immediately after the subjects left the exposure chamber and continued up to 20 hours following the exposures.

TABLE I
Experimental Human Exposure to Vinyl Chloride

Chamber Concentration (ppm) $\bar{X}$	S.D.	Range (ppm)	TWA[a] (ppm)	Number of Subjects
59	2	63–53	48	6
261	8	289–243	248	4
493	7	518–471	459	4
491	5	525–475	491[b]	7

[a]Time-weighted average concentration based on 7.5 hours including a 0.5-hour lunch period in an uncontaminated area.

[b]Continuous exposure for 3.5 hours.

Table I shows the analyzed concentration to which the subjects were exposed. Calculations of the mean and standard deviation of exposure concentration are based on chart readings from the infrared spectrophotometer taken at 5-minute intervals over the two 3.5-hour exposure periods. The TWA is based on the total 7.5 hours which included a 0.5-hour lunch period in an uncontaminated area.

The final breath decay curves intended for use as an index to VCl exposures were adjusted to TWA concentrations of 50, 250,

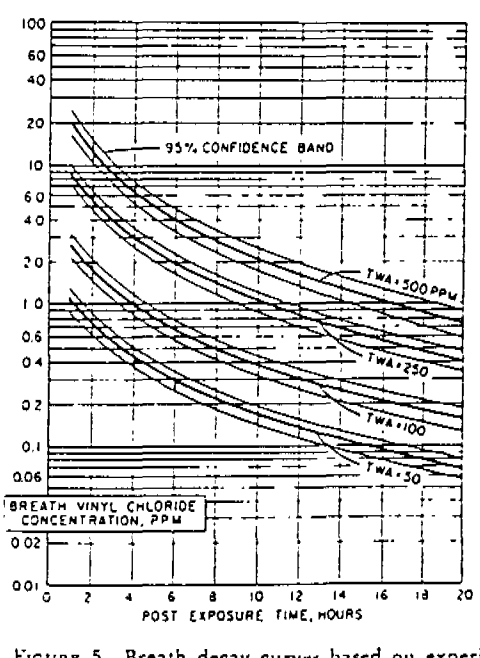

FIGURE 5. Breath decay curves based on experimental human exposures to 50, 250, and 500 ppm of VCl (7.5-hour TWA).

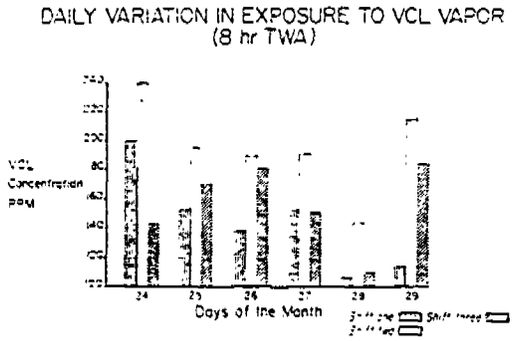

FIGURE 6. Variation in VCl vapor exposure for three shifts.

and 500 ppm (Figure 5). A 100-ppm decay curve was interpolated from the available data using regression analysis. These curves are presented with the calculated 95% confidence bands for the mean of a group of observations.

On-the-Job Breath Curves

Ten workmen participated in the on-the-job breath sampling program, producing a total of 91 usable sets of data. Ten percent of the breath samples collected were discarded because of pipet leakage or poor sampling techniques.

Absolute breath levels ranged from about 20 ppm in one sample taken less than 1 hour after an 8-hour TWA of 250 ppm, to barely detectable levels (<0.05 ppm) in samples taken after exposures at TWA's below 50 ppm.

The extremely broad variation in the TWA's experienced by workmen during one of the periods in which breath sampling was being conducted is demonstrated for three shifts of men bearing the job classification "coagulator operator" (Figure 6). Minute, hourly, and daily fluctuations in the concentration of a contaminant are most descriptively revealed by continuous monitoring. This method of sampling quickly points out the fallacy of judging TWA and peak exposure concentrations on the basis of spot sampling or periodic surveys of brief duration.

The remarkable correlation between breath concentration and corresponding TWA values made it possible to construct the series of breath decay curves shown in Figure 7, with confidence bands only slightly wider than those from controlled human experiments. The close similarity between these curves and those constructed from controlled exposure data are further illustrated in Figure 8.

Human Responses

From a subjective standpoint no significant untoward affects were noted at any of the exposure concentrations. The only complaints were those of two subjects who reported mild headache and some dryness of their eyes and nose during the 500-ppm exposure experiments.

No odor was detected by anyone entering the exposure chamber at 50 ppm. At 250 ppm all four subjects entering the chamber initially reported that they could detect a very slight odor of the chemical. Five of the seven subjects entering the exposure chamber at 500 ppm were able to detect the odor of VCl, but after 5 minutes of exposure those five were unable to detect it even with forced inspiration. Three of the four subjects reentering the chamber after lunch were able

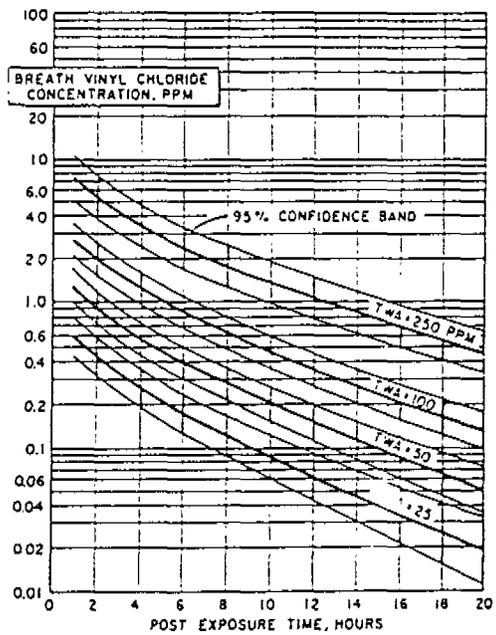

FIGURE 7. Breath decay curves derived from breath data collected from workers following on-the-job exposures to VCl vapor (8-hour TWA).

to detect a faint odor of VCl. One subject could detect a faint odor on deep inspiration for approximately 15 minutes after entering the exposure chamber.

The exposure had no noticeable effect on neurological responses, nor did it produce significant changes in the results of mental, coordination, or manual dexterity tests conducted during the exposure period. All clinical laboratory studies performed in the post-exposure period were normal and not significantly different from pre-exposure values.

Discussion

The object of the environmental health survey is to identify the atmospheric contaminant, determine the exposure level, and relate this to the health hazard it presents. If one is to judge hazard by ambient concentration measurements, then those measurements must accurately describe the exposure on a continuing individual basis. A carefully conducted survey combining continuous analysis of the work room atmosphere with a comprehensive job study will provide data valid for estimating time-weighted average exposure.

On the other hand, breath decay curves constructed from breath data collected during continuous plant monitoring are in close agreement with those obtained from exposure chamber experiments with VCl. These curves should therefore be useful as a second method for assessing exposure to VCl vapor.

The choice of whether one or both methods should be used depends on prevailing circumstances and on the thoroughness desired. For example, data useful in describing peak exposures are obtained from continuous monitoring. Concurrently, exposure trends and concentration gradients may help identify plant operational inefficiencies and equipment malfunctions by revealing specific sources of emission. Correcting these problems not only restores a healthful work environment but often results in bonus savings by reducing losses of raw material and product.

Continuous monitoring, however, is extremely costly both in time and in the equipment required. The scope of data acquired is

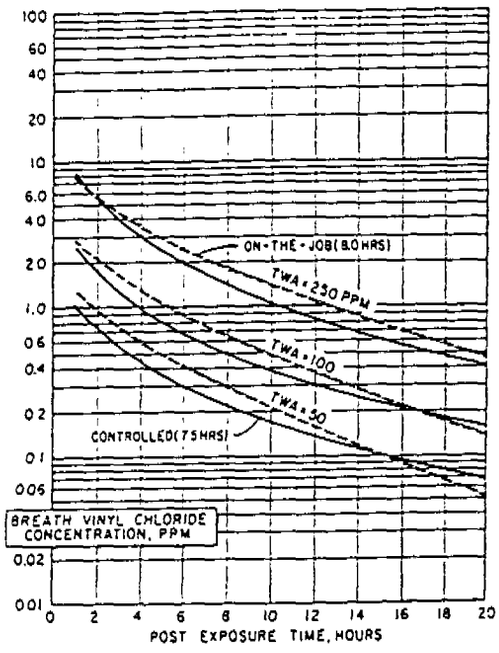

FIGURE 8. Comparison of breath decay curves derived from the on-the-job data and the experimental human exposure data.

limited by the number of sampling probes, and these probes are not always capable of accurately measuring the individual's daily exposure experiences, especially should these involve unusual incidences such as chemical spills or exposures outside the monitored area.

Breath analysis has the advantage of individualizing each worker's integrated daily exposure. Breath decay curves, as an index of exposure, offer a means of estimating the average daily individual exposure on the basis of a few breath samples taken serially in the postexposure period. Consequently breath analysis can be used to diagnose as well as quantitate an exposure which has already occurred. It is a relatively inexpensive and simple method which can be put into operation without extensive and costly preliminary preparations.

However, postexposure breath analysis does not provide information on the daily fluctuations of exposure, and the peak exposure concentrations are not made evident by breath data. Finally, breath analysis is not applica-

ble to all chemicals, and breath decay curves established for one chemical are not useful as an index of exposure to any other chemical.

The decay curves presented here are intended to serve as an index of exposure to vinyl chloride vapor and are based on an exposure duration of 7.5 hours for the experimental exposures, and 8 hours for the on-the-job study. The close agreement between the two sets of curves and the narrow confidence bands obtained in each case demonstrate the usefulness and accuracy of both methods for estimating TWA exposures and indicate the importance of breath analysis and the need for expanding its use in evaluating exposures to other widely used volatile organic chemicals.

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