# ENVIRONMENTAL VINYL CHLORIDE MONITORING

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Early in 1974 it was reported to OSHA that several deaths due to angiosarcoma, a rare liver cancer, may have been caused by occupational exposure to vinyl chloride (VC). As a result of this an emergency temporary standard was implemented lowering the permissible ceiling concentration to which industrial workers could be exposed from 500 to 50 ppm. Ongoing toxicological research demonstrated that liver cancer could be induced in mice at exposure levels as low as 50 ppm.

A permanent standard was established limiting occupational exposure to one ppm averaged over any eight-hour period and a ceiling of five ppm averaged over not more than 15 minutes. In addition an "action level" of 0.5 ppm was set. The permanent standard requires that all employee exposure levels be determined either by area or personnel sampling. If the exposures of workers are maintained below the action level no routine monitoring is required, if between the action level and the permissible limits, monitoring must be at least quarterly and if above the permissible limits at least monthly.

It is the intent of this discussion to review methods available to conduct monitoring of employee exposures within the workplace. In addition, procedures and techniques for monitoring emissions from industrial operations are presented and discussed.

Obviously, the simplest way to conduct a survey is by using some sort of direct-reading instrument, that is, an instrument which is capable of sampling a volume of air, performing a quantitative analysis and displaying the result. The advantages of using such a system include·

a) immediate estimations of the concentration of the contaminant, permitting on-site evaluations;

b) provision of permanent four-hour records of contaminant concentrations;

c) attachment of alarm system to instruments to warn workers of build-up of hazardous situations;

d) reduction of number of manual tests;

e) reduction of number of laboratory analyses;

f) provision of more convincing evidence for presentation at hearings and litigation proceedings;

g) reduced cost of obtaining individual results.

However, the majority of these systems measure some physical property of the contaminant being studied and consequently are prone to interferences. Before using results obtained with a direct-reading instrument supplementary data should be obtained relating to possible interferences. Calibration of any direct-reading instrument is an absolute necessity - the frequency of the calibration depends on the instrument in question and the degree of accuracy required.

The main application of such instruments is in area monitoring, that is, in monitoring the concentration of VC in a given area at a given instant in time. Personnel monitoring imposes limitations on the sampling procedures and is dealt with later.

There are many principles of operation which have been used in direct-reading instruments for VC. The ones discussed below are those with the highest applicability.

Combustion Conductivity

If vinyl chloride is heated in air at 1000°C it will decompose to $CO_2$ and HCl. By bubbling the HCl into pure water a change in conductivity will be produced which can be measured. The method is very rapid, taking only about thirty seconds.

Interferences are common since any substance which changes the conductivity of the sample solution will interfere. However, if this technique is used in a plant where interferences are known to be low or can be compensated for the method can provide a rapid means of analysis.

In all instruments using conductance as the measured parameter temperature variation becomes a very important consideration and corrections should be made accordingly (2% per degree centigrade).

Flame Ionization Detectors (F.I.D.)

If an organic molecule is burned in a small flame, carbon ions are produced. By applying a potential across the flame and measuring the current produced the concentration of the organic molecules can be measured. This is the principle of operation used in F.I.D.'s. As with the conductivity method above the analysis, while being extremely fast, is only useful for an atmosphere known to contain only VC since any organic compound will produce some response in the detector.

Infrared Analysis

Vinyl chloride absorbs I.R. radiation due to the movement in its chemical bonds, the amount of absorption being dependent upon the concentration of the compound in the sample cell. This method is not entirely specific as interfering substances may

commonly be present. As the spectra are additive the contribution by an unsuspected minor component can be overlooked, leading to incorrect data. Due to design limitations, with the best currently available instrumentation an accuracy of ±10% is the best that can be obtained practically with this method.

In general only about two minutes are required for analysis although additional time may be required to change samples. With a long path length sensitivities of 0.7 ppm can be expected.

Gas Chromatography (G.C.)

This procedure physically separates components of a mixture by passing them through a column containing an inert substance coated with an organic silicone oil. Each component will be absorbed by the stationary liquid and desorbed by the carrier gas stream in a unique manner. Over the length of the column the adsorption-desorption process is repeated many times resulting in a separation of the different components as they are eluted from the column. If the emerging gas stream is made part of the fuel supply for an F.I.D. the compounds can be measured by the response they produce.

The signal produced is amplified and used to produce a peak on a strip chart recorder. The concentration of the compound is proportional to the peak area.

Rugged, battery-operated, portable gas chromatographs have been refined to the point where they may now be considered practical for many field study applications.

These instruments come complete with gas sampling valve, rechargeable batteries, appropriate columns and self-contained

supplies of gases which provide 8 to 20 hours of operation dependent on the flowrates and must be recharged using high pressure gas regulators. The retention times of the compounds of analytical interest must be determined in the laboratory for a given type of column, as is true for the laboratory type chromatographs.

Although interferences can result from other compounds having similar retention times (these can often be removed by changing the column conditions) the primary advantage of the method in the present consideration is its ability to determine vinyl chloride concentrations in the presence of many other compounds. The sensitivity of the method is excellent and extends down into the ppb range. For continuous monitoring the major disadvantage is the time involved in the analysis, which is approximately 30 minutes.

The four above methods are the basis for the majority of direct-reading instruments used for vinyl chloride determinations. As stated earlier results obtained using these techniques are only meaningful when used in conjunction with results obtained using more specific sampling and analysis techniques.

The method of choice for vinyl chloride analysis is gas chromatography. This is relatively fast and provides the accuracy required by the OSHA standard.

The standard VC concentration for the gas chromatograph can be prepared in two ways.

1) By injecting the 5.0 ml of pure vinyl chloride into 10 liters of air in a Tedlar bag. This gives a 500 ppm VC standard.

2) By dissolving 1 ml of vinyl chloride in 10 ml $CS_2$ (conc. = 255.6 μg/ml). Further dilution prepared as necessary, usually a 1:10 series to desired lower level.

Five milliliters or 5 μl respectively of the above standards are injected into a gas chromatograph equipped with a column packed with 10% SE 30 on 80/100 mesh chromosorb (other columns can be used) with a column temperature of about 60°. The limit of detection for each injection is of the order of 100 picograms which gives a detection limit of around 10 ppb in air (5 ml injection volume) which is well below the level specified in the OSHA standard.

Samples for analyses can be collected either by grab or integrated sampling methods. In grab sampling a gas collection device of known volume under measured conditions of temperature and pressure is used. The sample is collected over a period of several seconds up to one or two minutes maximum.

A wide variety of collection devices is used to obtain grab samples. These include vacuum flasks, vacuum bottles, gas- or liquid-displacement type collectors, glass bottles, syringes and plastic bags. The temperature and pressure at the time of sampling must be recorded to permit the reporting of analytical data under standard conditions, typically 25°C and 760 mm of mercury for in-plant samples.

The grab sampling method is useful only for determining instantaneous vinyl chloride levels and is best used for determining VC levels in regions suspected of being out of compliance.

In instances where the atmosphere to be sampled remains relatively constant with time, grab samples will represent the

average air concentrations. However, where the atmospheric concentration varies appreciably in accordance with processing operations and other factors, a sufficient number of samples must be taken to determine the average concentration of the contaminant under each of the relevant processing or ambient conditions. Grab samples have the primary advantage over most other methods of sampling in that the collection efficiency is 100 percent.

Once the sample is collected a portion (usually 5 or 10 ml) can be removed with a gas syringe and injected into the gas chromatograph. By suitable choice of column conditions the vinyl chloride peak can be obtained free of interference effects and the concentrations of vinyl chloride calculated accurately. If other substances are known to be present in the atmosphere, such information should be submitted with the sample as they may cause interferences. For the same reason it is also a good idea if possible to submit a sample of the bulk materials used in the process for the purpose of identifying all atmospheric contaminants which may be collected along with the vinyl chloride.

When sampling atmospheres which have variable concentrations of a contaminant (such as vinyl chloride), for evaluation of personnel exposures and time-weighted average concentration levels, the use of an integrated sampling method is required.

In this method ambient air is drawn over an adsorbing medium (or through an absorbing medium) at a fixed rate for a known period of time. The large volumes sampled by this method lead to increased sensitivity in the overall procedure.

Analysis of the adsorbed vinyl chloride collected by this method produces an estimate of the average concentration of the VC in the sampled air volume.

Basically the integrated sampling method requires the following components:

1) A sampling pump;

2) An adsorptive material capable of trapping all of the VC passed over it during the sampling period.

3) A desorption mechanism to remove quantitatively all the VC from the adsorbant at a later time to permit analysis.

Any pumps used must be calibrated before use to ensure that the air flow measurement is accurate. In addition, if used for personnel sampling, they should be light enough that they are comfortable to wear without interference with the employee's job.

The adsorbing material most commonly used for organic vapor is activated charcoal. The capacity of a charcoal tube at any given flowrate is proportional to the surface area of the charcoal and the affinity of the substance being sampled for the charcoal of a given mesh size.

Commercially produced tubes containing 100 and 50 milligrams of activated charcoal in the front and back-up sections, respectively, have been available for several years. Desorption of the organic vapors adsorbed in these tubes by carbon disulfide followed by gas chromatographic analysis has formed the basis of the NIOSH procedure for organic vapors.

We have found that this method is ineffective in collecting VC at the normal flowrate of 1 lpm. The operational NIOSH procedure for VC presently in general use recommends a sampling rate of 50 ml/minute for a volume of no more than 5.0 liters (giving a detection limit of less than 3 ppb in air).



In order to utilize the 1 lpm sampling rate typically used to sample for organic vapors with charcoal tubes, we have

developed a larger sampling tube. This is an 8-mm (I.D.) glass tube which contains two sections, of 900 mg each, of 20/50 mesh activated coconut charcoal. (Pittsburgh Activated Carbon). Each section has a breakthrough capacity of approximately 170 mg VC compared with 20 mg for the commercially available tube. Five and 50 ppm gas mixtures have been sampled at 1.0 liter/minute for up to two hours with no evidence of breakthrough.

Water can cause an interference to the method by displacing VC from the charcoal. If conditions of high humidity are encountered sampling using the larger capacity tube becomes a necessity.

After sampling is complete both sectinns of the tube are desorbed separately using carbon disulfide. If it is found that the back-up section of the tube contains significant amounts of VC there is a good chance that all the VC sampled has not been adsorbed onto the charcoal.

If possible the desorption and the gas chromatographic analysis should be performed immediately upon completion of sampling. We have found that migration of the VC occurs within the tube leading to high VC values in the backup section. There is also some evidence that polymerization may occur on the activated surface if the samples are left too long after sampling. Both the above phenomena can be avoided by immediately refrigerating the samples upon completion of the sampling. It has been shown that with these precautions a recovery of 95% of the sampled VC can be attained within 48 hours of collection.



Ambient Air Surveillance

The most logical extension of concern for exposure to VC beyond the workplace is in the ambient air quality downwind from

an operation discharging VC to the atmosphere.

The determination of the concentration of a specific pollutant, such as VC, in the ambient air over a given area is a complex problem. Many factors such as local topographical differences, atmospheric chemical reactions, fluctuating emission rates from various sources and variable meteorological conditions cause spatial and temporal influences in air quality. This space-time dependence of air quality must be dealt with on a quantitative basis in order to acquire statistically reliable data of air quality and to meet ambient measurement objectives.

Specific guidelines for ambient VC sampling have been issued recently by the U.S. EPA. Minimum site locations are specified and a sampling schedule is provided. These guidelines are intended for source monitoring only and are to be used in the "interim" until the state-of-the-art of VC sampling is improved.

The EPA guidelines regarding ambient sampling in monitoring VC state that sampling sites should be selected downwind and in the plume of atmospheric emissions from the plant. Samples should be collected only in areas where local residents or neighboring industries would be exposed. They specify that grab samples should be used to the maximum degree possible; however, the shorter the sampling period the larger the variation in concentration values becomes. This leads to poor precision in mean concentration for areas of high variance as the grab sampling data have little quantitative value and can be in no way related to long term exposure.

The basic integrated sampling method dealt with above can be adapted for use in both ambient and stack sampling by enlarging the size of the adsorbent tube (two, 6.5 g charcoal beds). Sampling with these tubes for a minimum of one hour is at present

the most accurate method of determining long term exposures. Optimum sampling rates for these tubes must be determined, generally a maximum rate of 1 lpm is recommended. Background ambient concentrations are obtained by simultaneous sampling upwind of the plant.

Although many of the sources of VC emissions to the atmosphere are fugitive in nature several major sources emit measurable quantities of VC. Measurement of such emissions can be used to document material losses, as an aid for designing and as a means of testing control equipment, as well as determining compliance with regulations. Samples are usually collected in triplicate for each stack condition. The sample time is normally 30 minutes but if the operation is cyclic in nature it should be extended to include at least one complete cycle.

The sampling train normally consists of a probe, adsorption tube, flow meter and pump, however, if stack conditions are such that moisture or other condensate collects in the sampling hose in front of the charcoal tube, a dry trap should be included in the train. Any condensate collected in this trap should be treated as part of the sample and analyzed accordingly.