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Industrial hygiene, as we think of it today, began in The Dow Chemical Company in the late 1930's. The technology we used in the beginning was crude by today's standards, but nevertheless the efforts were useful in helping to assess the degree of exposure of workmen. These data were used very early to correlate with medical findings and subjective responses of the people.

In the early days, samples were taken by drawing known volumes of workroom air through absorbers containing an appropriate solvent or if particulates were involved, an impinger was used. Most of the equipment we used was handmade except for air pumps and wet test meters. Analyses were by wet chemical methods that left a lot to be desired, both from the qualitative as well as the quantitative points of view.

As the years have passed, analytical specificity and sensitivity have gradually increased.

At the present time, four methods generally are available for environmental monitoring of air for the presence of vinyl chloride. They are:

1. Gas chromatography,
2. Total hydrocarbon analyzer with flame ionization detector,
3. Combustion-conductivity, and
4. Infrared spectrophotometry.

The most desirable method will depend upon individual plant conditions, particularly interfering substances.

Gas chromatography is very specific, but requires about 20 min/sample. Flame ionization detectors have no specificity; they respond to all carbon-carbon or carbon-hydrogen bonds. However, they are portable and the measurement is instantaneous. The combustion-conductivity method responds to any material which burns to produce ions or any material which produces ions when dissolved in water. It responds rapidly. Infrared analyzers are very specific, respond quickly, and are portable. All of these techniques have adequate sensitivity, detecting concentrations of 1 ppm. The sensitivity achievable through the use of gas chromatography, in particular, can easily be extended to parts per billion.

Personnel monitoring is achieved through use of absorption tubes filled with activated carbon. The absorbed chlorinated hydrocarbons are determined by gas chromatography after thermal release or extraction by carbon disulfide. A word of caution is in order here. Activated carbon from different sources and different batches from the same source vary in their capacity to absorb vinyl chloride and to release it. This makes it imperative that one check each batch before use.

Another method[1] that has not been much used for personnel monitoring involves breath analysis. This method was researched some years ago and the data obtained show that there is a direct relationship between the total exposure and the concentration in the expired air at the end of the workday. This method can be very specific and if workmen will cooperate, it can be a very useful tool.

At Dow, most of our environmental monitoring has been with combustion-conductivity analyzers.[3] We have used these analyzers for continuous monitoring since 1959 with excellent results. More recently, however, we have begun to employ continuous gas chromatography units, as well as portable instruments based on infrared spectrophotometry, because in certain locations there are too many materials which will interfere with the combustion-conductivity method.

Recently, we have successfully connected our combustion-conductivity analyzers to the computer and from this we get a daily printout of the data in two forms.[3] One printout gives, for each probe, the number of readings taken during the shift, the 8-hr average at that location, the maximum concentration that occurred, and the time at which it occurred. In our present polymer plant there are 12 probe locations and another unit of six is to be added. These analyzers can be set to give a general warning if concentrations in the excess of specified levels occur. The other printout is based on a computer program which considers the amount of time the man on a described job is in different locations and then calculates the percentage of his time he would be exposed to a level of 0–5 ppm, 5–10 ppm, 10–25 ppm, 25–50 ppm, 50–100 ppm, 100–200 ppm, and above 200 ppm. A time-weighted average for that particular job and shift is then calculated and printed. Printouts on both bases are posted each day for anyone to see.

In the early days of Dow experience with vinyl chloride, from 1946–1959, relatively few samples of the workroom air were taken because no one was particularly concerned about the toxicity of the material. Those that were taken show the time-weighted averages for some jobs ranging from 5–10 ppm, others from 15–150, and a few ranging from 100–385 ppm. These were all 10–20-min samples and analysis was for total halogen; thus, they represented maximums for any halogenated material present. For example, if hydrogen chloride were present, it would have been calculated as vinyl chloride. In 1959, when the results of our toxicological studies on animals caused us to be more concerned for both vinyl and vinylidene chloride exposure, continuous monitors were installed in our polymer plants and a rather dramatic reduction in workroom air concentration was achieved. This was brought about by setting a goal that a time-weighted average exposure for an 8-h, 5-day week should not exceed 50 ppm for vinyl chloride and 25 ppm for vinylidene chloride.

Although in the ensuing years between 1960 and 1967 we were generally successful in reaching these goals, there were a few jobs in which we achieved improvement but not total success. Nevertheless we did identify our so-called "hot spots" or areas where exposures could be above our guidelines.

During the period between 1967 and 1972, continuous monitoring of our polymer plants was routine. The charts were observed and discarded. If the readings were within limits, there was no concern; high readings were a cue to supervision that the situation needed correcting.

In the late 1960's, after discovery of acroosteolysis in workers in polyvinyl chloride operations abroad and in the United States, our workers were examined and no such disease was found. Consequently, we felt that our operations were generally acceptable. However, after Viola and co-workers[4] disclosed that they had induced tumors in rats exposed to high concentrations of vinyl chloride monomer, we decided to take a closer look at all of our operations. In addition to extensive medical surveillance programs, extensive industrial hygiene surveys were undertaken to assess in more detail the extent of our worker exposure to vinyl chloride. These studies are continuing with much attention being given to correcting those situations where the greatest potential for exposure existed or exists.

In our oldest monomer plant we found time-weighted averages to be generally less than 2 ppm but there was one job that showed 45 ppm and another job that showed 14 ppm. Personnel monitoring during 1973 revealed that all time-weighted average values were below 10 ppm except for the laboratory employees who worked in an area where the average concentration was, at times, as high as 30 ppm. This situation is being corrected.

In our second oldest monomer plant, which began operation in 1958, concentrations were found by personnel monitoring in 1973 to be well controlled, the highest time-weighted average exposure of 10–15 ppm again was associated with laboratory workers; all others were less than 5 ppm.

In the newest monomer plant which began operation in 1969, time-weighted average values ranged from ≤ 1–10.4 ppm.

In the only polymer plant now operating, time-weighted average values have been markedly decreased, the levels during 1973 generally were well below 25 ppm, most of them being in the 1–5 ppm range. One job, however, is not under adequate control and respiratory protection is required because concentrations in that area sometimes average from 100–150 ppm. Obviously, some major changes are needed to correct this situation.

I must emphasize that there is some variation in time-weighted average values from day to day for a given type of operation. For example, operators involved in pumping reactors showed values ranging from 1–34 ppm. Similarly, three operators involved in loading operations had time-weighted values ranging from 8–31 ppm. We encourage recognition that such variation will occur in normal day-to-day operations involving transfer of monomer. Furthermore, short-spot samples may reveal sudden short excursions to concentrations in the 1000–4000 ppm range. Such conditions may not show on a long sample which averages the concentration over the sampling time but will show in a 10-min sample taken at the right time.

During the first quarter of 1974, emphasis has been placed upon obtaining samples from individuals on most of the jobs involving vinyl chloride. These samples have been very informative for they have enabled us to pinpoint particular parts of jobs where there are excessive concentrations for short periods of time even though the time-weighted average is low. By identifying such operations we hope to be able to reduce further overall exposure. Personnel sampling has also confirmed the need for personal respiratory protection in certain jobs and parts of jobs. In such operations, protection is required and will be required until appropriate changes can be made in the equipment or procedures which will reduce environmental concentrations to acceptable levels.

With the thought in mind that some things we have considered important might be of value to others who are concerned with controlling industrial exposures, the following points are offered.

A. For toxic and hazardous materials:

1. Establishment of safe, practical allowable environmental levels.
2. Implementing appropriate engineering and operating procedures to achieve or better these levels.
3. Provide analytical monitoring capability to ensure the environment is maintained below the established levels and to detect excursions above such levels.
4. Initiate appropriate corrective action when breakdowns occur and guidelines for environmental levels are exceeded.

5. Develop and support an appropriate medical surveillance program.

B. With respect to vinyl chloride, we are implementing the following design and engineering principles:

1. Processing systems are closed with no open vessel operation.

2. Current buildings where vinyl chloride is manufactured or polymerized are open to the atmosphere or have ventilation to minimize concentration buildups.

3. Engineering design emphasizes reasonable process automation and reasonable remote operation in order to minimize personnel exposure.

4. Vent exhaust systems are selectively located to minimize the possibility of personnel exposure.

5. The number and quantity of samples for control analyses are minimized.

6. Employees are familiarized with emergency procedures and signals; for example, wind directional signals, horn emergency calls, and evacuation routes.

7. Collection of analytical samples of vinyl chloride from storage tanks involves a closed loop sampling system in order to return vinyl chloride to the process rather than venting vapor in the workplace environment. Laboratory samples of vinyl chloride are handled in hoods and sample cylinders are grounded when discharged, and unused samples are vented back into the process. On-line gas chromatography is being used extensively to monitor product purity and process operation; this has reduced markedly the number of manual sample collections required.

8. Specially designed vapor equalizing lines connected back to the storage tank are employed in the loading of tank cars.

9. Environmental monitoring of air is being conducted by a number of techniques. Gas detector alarms are located throughout the plant at a number of strategic locations to warn of any flammable concentrations. Portable detector instruments are available for checking plant areas or process equipment prior to nonroutine operations and procedures. Continuous analyzer systems have been or will be installed where needed.

10. In our polymerization operations, we have not had problems of worker illness from the cleaning of polymerization vessels. We utilize high pressure water jets after each polymerization reaction to prevent polymer build-up. Our emulsion polymerization kettles require manual clean-out every 2 or 3 months. After water cleaning of the vessel, all lines are blanked to prevent any material from entering the vessel; the atmosphere is tested for oxygen supply, and a continuous vinyl chloride monitoring probe is put into the vessel. For a number of years, operating procedure required that the concentration be below 50 ppm prior to vessel entry. Air purge is maintained on the vessel during the cleaning operation.

In summary, I have tried to give you some idea of the methodology we have used in our industrial hygiene efforts. I hope it will be helpful to you in your considerations of environmental control and personnel protection.

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