*Pittsburgh PCB 12x30 activated carbon is found to be the most suitable of the commercially available carbons tested for personnel sampling of vinyl chloride, vinylidene chloride, and methyl chloride. The carbon is desorbed with $CS_2$ at dry ice temperature or with a thermal desorption technique.*

# Monitoring personnel exposure to vinyl chloride, vinylidene chloride and methyl chloride in an industrial work environment

L. W. SEVERS and L. K. SKORY
Dow Chemical U.S.A., Midland, Michigan 48640

### *Introduction*

Late in 1973, information became available linking angiosarcoma of the liver (a rare form of cancer) with occupational exposures to high levels of vinyl chloride. Reacting to this, OSHA issued an Emergency Temporary Standard for vinyl chloride exposures limiting them a a maximum of 50 ppm. Subsequently, a reduction of this standard was proposed and became effective whereby the permissible eight hour time-weighted average exposure may not exceed 1 ppm, with a ceiling of 5 ppm averaged over no more than a 15 minute sampling period.[1] A study was undertaken to develop a reliable method for long and short term personnel sampling and analysis of vinyl chloride. Methyl chloride and vinylidene chloride were also included in this investigation because of their chemical similarity to vinyl chloride.

### Breakthrough Studies

Field use of commercially available adsorbent carbon tubes gave significantly differing results than sophisticated chlorohydrocarbon analyzers thus indicating that existing adsorbents were not adequate to quantitatively define vinyl chloride exposures to workers.

Available carbons were obtained and studied for breakthrough time by passing 200 ppm (parts per million by volume in air) vinyl chloride through a 30 ml bed of carbon at a flowrate of approximately 2 lpm (liters per minute) representing typical conditions that existed a year ago. Comparison of the parts per million breakthrough versus time is shown in Table I.[2,3] Dow Experimental Carbon (XF-4175L), Pittsburgh MSC-V 14X40 mesh and Columbia Carbon showed the best breakthrough characteristics; however, the Dow Experimental Carbon and the MSC-V are not commercially available at this time.

Replicate samples of Columbia Carbon TS-570 were tested against those of Pittsburgh

Loren W. Severs, received a B.A. in chemistry from the University of California, Irvine in 1972. Joined The Dow Chemical Company, Analytical Laboratories, Midland, Michigan, after graduation. Worked on analysis of trace contaminants in water and air. Recently served as consultant to the Industrial Hygiene Laboratory to develop methods of collection and analysis of organic vapors in air.

Lyman K. Skory graduated from Michigan State University in 1949 with a B.S. degree in Chemistry and from Pennsylvania State University with an M.S. degree in Organic Chemistry and joined The Dow Chemical Company, Midland, Michigan, in 1951. He is currently a Group Leader in the Dow Industrial Hygiene Laboratory, Midland. He works closely with OSHA and NIOSH in health standards programs and with Product Stewardship for Dow customers.



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TABLE I
Comparison in Parts per Million of Commercial Carbons;
30 ML Bed Volume, 200 ppm Vinyl Chloride, 1.97 lpm Flowrate

| TIME (HOURS) | WESTVACO NUCHAR WVH 8x30 MESH | FISHER-SCIENTIFIC COCOANUT CARBON 6x14 MESH | COLUMBIA CARBON SMALL MESH | PITTSBURGH BPL 4x10 MESH | DARCO 4x12 MESH | PITTSBURGH MSC-V 14x40 MESH | WITCO GRADE 360 10x20 MESH | DOW EXPERIMENTAL CARBON XF-4175L |
|---|---|---|---|---|---|---|---|---|
| 0.5 | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.02 | < 0.1 | < 2 | < 0.1 |
| 1.0 | < 0.05 | < 0.05 | < 0.05 | 0.24 | < 0.02 | < 0.1 | 2 | < 0.1 |
| 1.5 | 0.08 | < 0.05 | < 0.05 | 0.86 | 0.02 | < 0.1 | 4 | < 0.1 |
| 2.0 | 0.53 | 0.21 | < 0.05 | 1.77 | 0.12 | < 0.1 | 4 | < 0.1 |
| 2.5 | 5.22 | 0.95 | < 0.05 | — | 0.51 | < 0.1 | 12 | < 0.1 |
| 3.0 | 26.30 | 5.45 | 0.05 | 3.15 | 11.80 | < 0.1 | 40 | < 0.1 |

PCB 12X30 Activated Carbon. The bed size was reduced to 1 gram of carbon contained in a stainless steel tube (14 cm x 0.25" O.D. x 0.028" wall) fitted with Swagelok caps. The test concentrations was reduced to 50 ppm vinyl chloride and the pump flowrate was reduced to 0.2 lpm. Table II shows the Pittsburgh PCB carbon to be the most suitable for eight hour time-weighted average personnel sampling. The 1 gram slugs of PCB carbon were also tested at 25 ppm with flowrates of 0.5 and 1.0 lpm. Table III gives the results of those tests. Based on these data, the following sampling conditions were recommended for the 1 gram slug of Pittsburgh PCB 12X30 Activated Carbon: (1) 0.2 lpm for 8 hours, (2) 0.5 lpm for 10 to 60 minutes, and (3) 1.0 lpm for 10 minutes.

Further breakthrough testing was conducted with different sized tubes for short time periods. The NIOSH method for vinyl chloride in air[4] uses a 150 mg divided charcoal tube. This charcoal tube was tested with 1 ppm and 5 ppm vinyl chloride at a flowrate of 1 lpm. Figure 1 shows breakthrough within the first minute and approximately 12% breakthrough after 10 minutes. The flowrate for this size tube was reduced to 0.2 lpm and the experiment repeated at the 5 ppm level.

Figure 2 shows that the breakthrough under these conditions is nearly 3% after 15 minutes. The NIOSH method also states that 5 liters of 200 ppm vinyl chloride can be collected at 0.05 lpm without significant amounts of vinyl chloride being found on the back section. Duplicate test runs under these conditions showed that substantial breakthrough occurs well before 5 liters of sample has been collected (Figure 2).

A direct comparison of the carbon in the NIOSH recommended tubes and PCB 12X30 was made by repacking the NIOSH tube with 150 mg of PCB carbon and repeating the experiment. Figure 1 shows that the two carbons have similar breakthrough characteristics under these conditions. However, this may be due to carbon bed size than type of carbon. The tubes could be used in a 5 ppm atmosphere at 0.05 lpm for 15 minute sampling; however, only 0.75 liter is collected. Even with a GC sensitivity of 1 $\mu$g/sample, a less than value of 0.52 ppm is obtained, which is above the action level (0.5 ppm) and much higher than the desired 0.1 ppm sensitivity. We, therefore, concluded that the 150 mg NIOSH recommended tube was inadequate for vinyl chloride sampling.

Two larger tubes of carbon were tested under similar conditions. A 600 mg charcoal

TABLE II
Percent Breakthrough for Columbia and Pittsburgh PCB Activated Carbons at 50 ppm Vinyl Chloride and 0.2 lpm Flowrate

| TIME (HOURS) | COLUMBIA CARBON TS-570 | PITTSBURGH PCB 12x30 |
|---|---|---|
| 5.0 | 1.0 | < 0.3 |
| 5.5 | 2.5 | < 0.3 |
| 6.0 | 12.0 | < 0.3 |
| 6.5 | 24.0 | < 0.3 |
| 7.0 | 46.0 | < 0.3 |
| 7.5 | — | < 0.3 |

TABLE III
Percent Breakthrough for One Gram of Pittsburgh PCB 12x30 at 25 ppm Vinyl Chloride With 0.5 and 1 lpm Flowrates

| TIME (HOURS) | 0.5 LPM | 1.0 LPM |
|---|---|---|
| 1.0 | < 0.06 | — |
| 1.25 | — | — |
| 1.7 | — | 0.4 |
| 1.8 | < 0.06 | 0.8 |
| 2.5 | < 0.06 | — |
| 2.9 | 0.30 | — |
| 3.3 | 2.60 | — |
| 3.8 | 13.00 | — |

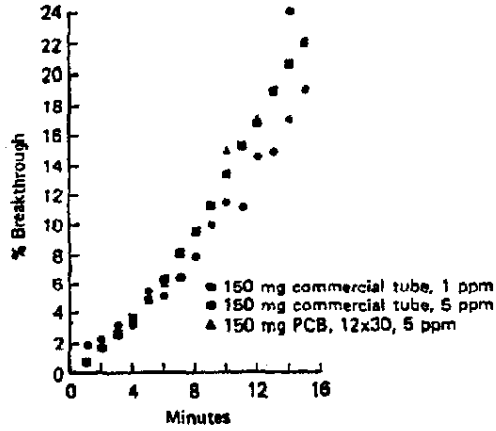


*Figure 1–Vinyl chloride breakthrough, 150 mg tube at 1 lpm.*

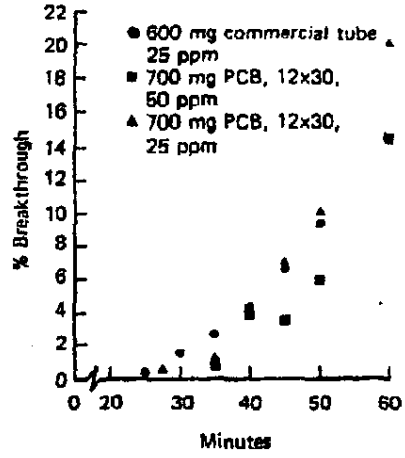


*Figure 3–Vinyl chloride breakthrough, 600 and 700 mg tubes at 1 lpm.*

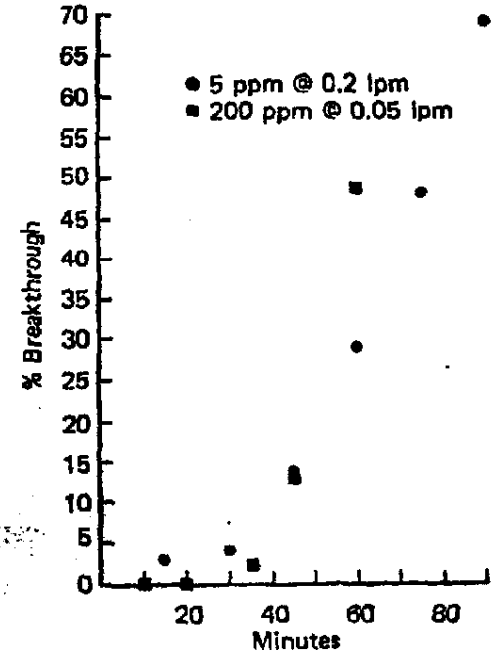


*Figure 2–Vinyl chloride breakthrough, 150 mg tube at reduced flowrates.*

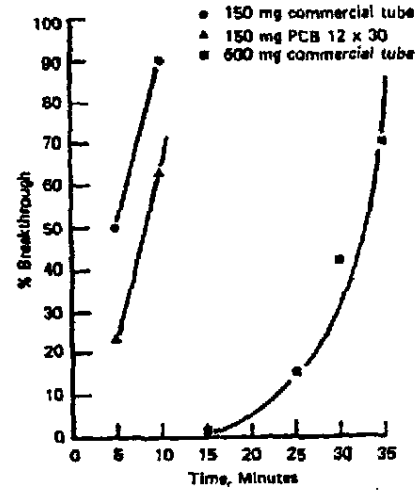


*Figure 4–Methyl chloride breakthrough, 100 ppm at 0.2 lpm for 150 and 600 mg tubes.*

tube is manufactured by the makers of the 150 mg NIOSH tube. A tube was also made from a disposable glass transfer pipette containing approximately 700 mg of the Pittsburgh PCB 12X30 Activated Carbon. Figure 3 shows the results for testing these tubes at 25 and 50 ppm vinyl chloride at 1 lpm. Either tube could be used for the 15 minute sampling and at

reduced flowrates (0.2 or 0.1 1pm) for extended periods of time (7-8 hours) at these levels.

Two items of interest are evident from Figures 1 and 3: (1) the breakthrough time and percentages are not directly proportional to those seen for the 150 mg tube, indicating additional factors in adsorption (possibly tube dimension and/or a change of carbon), and (2) the breakthrough curves for 25 and 50 ppm are almost identical, as are those for 1 and 5 ppm on the 150 mg tube. These data indicate that the percentage breakthrough for a given flowrate and tube size is independent of the concentration for at least the 1-50 ppm range.

Similar breakthrough testing was performed for methyl chloride and vinylidene chloride. Methyl chloride was tested at 100 ppm (TLV) for various flowrates and tube sizes. Figure 4 shows 150 mg tubes are not suitable for methyl chloride sampling at the current allowable levels, although the PCB carbon appears to have better retention capabilities. The 600 mg size tube might be used for short term samples. Reducing the flowrate below 0.2 1pm would increase the time of sampling. However, by using the 1 gram slug of PCB 12X30 and reducing the flowrate to 0.1 1pm, sampling times of up to 80-90 minutes are feasible (Figure 5).

This figure also shows the increase in sampling time possible by decreasing the flowrate from 0.5 to 0.2 to 0.1 1pm. A sample test of 200 ppm at 0.2 1pm flowrate is also known for comparison. If methyl chloride and vinyl chloride are to be sampled in the same area, the methyl chloride will be the limiting factor in choosing a sampling period and flowrate. Only by increasing the amount of carbon and/or greatly reducing the flowrate can eight hour sampling be attempted.

(Methyl chloride breakthrough was also determined on the 1 gram slug of PCB 12X30 at the 50 ppm level. The breakthrough curves are the same as those shown in Figure 5 for 100 ppm. This further demonstrates that percentage breakthrough for a given flowrate and tube size is independent of concentration.)

The breakthrough characteristics for vinylidene chloride are much less severe than for methyl chloride and vinyl chloride throughout testing. Figure 6 shows that the 150 mg size tube may be used for short term samples (10-15 minutes) at 1 1pm. However, the PCB 12X30 carbon begins to show definite advantages over the carbon used in the commercial tube. Reducing the flowrate will, of course, allow for longer sample times, but not long enough for eight hour samples. The 600 mg size tube has very good retention capability for vinylidene chloride. A test of 31 ppm vinylidene chloride samples at 1 lpm showed less than 0.08% breakthrough after 75 minutes.

Thus, with a reduction in flowrate to 0.1 or 0.2 1pm, eight hour sampling is quite possible. (These data suggest that the type of carbon has been changed in this size tube because a similiar test run a year ago showed substantial breakthrough after 60 minutes. The 150 mg and 600 mg tubes were SKC Lot 104 and Lot 105, respectively. SKC has confirmed a change of carbon between the two lots. This change in carbon was recommended to the supplier after NIOSH had received our recommendations.) One gram of the PCB 12X30 carbon in a stainless steel slug has been run under these conditions for eight hours with no detectable breakthrough.

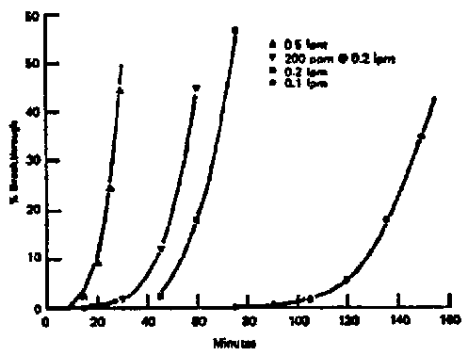


*Figure 5—Methyl chloride breakthrough, 100 ppm at various flows for 1 gram Pittsburgh PCB 12X30 activated carbon.*

**Carbon Disulfide Desorption**

A desorption technique for vinyl chloride was devised that would ensure the integrity of the sample. An experiment in one of our laboratories indicated a 98% recovery was obtained when the carbon was slowly added to the $CS_2$ cooled in a dry ice, acetone slurry.[2] The following procedure has since proven to be satisfactory: (1) cool 10 ml of $CS_2$ to dry ice temperature; (2) slowly add the carbon to the cold $CS_2$; (3) agitate for 30 minutes, keeping cold; (4)

refrigerate until analysis, analyzing from a wet ice bath. It was found that by thus minimizing the heat generation during desorption, replicate samples have given a recovery range of 93-101%.

This same desorption technique has been applied to samples of methyl chloride. Over a period of time, 25 known samples have shown a recovery range of 70-97% with an average of 83% ±8% (one standard deviation). The wide range of recovery values has not yet been accounted for.

Desorption of vinylidene chloride samples is accomplished by the same procedure. A wet ice bath can be used, unless one or more of the low boiling gases are to be determined also.

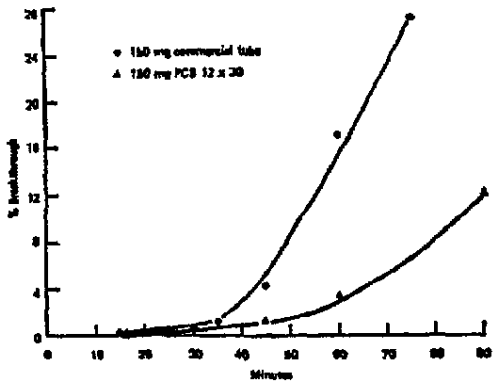


*Figure 6–Vinylidene chloride breakthrough, 20 ppm at 1 lpm for 150 mg tube.*

Recoveries for vinylidene chloride in $CS_2$ have a range of 95-100%.

### Standard Preparation

A technique was adapted from a procedure used at Dow for many years.[3] Vinyl chloride gas is condensed in a tared, narrow neck ampule in dry ice. The ampule is flame sealed and reweighed to constant weight. A small Swagelok nut is carefully placed over the neck of the ampule and the whole assembly gently lowered into a measured volume of $CS_2$. The ampule is then broken by shaking the bottle. No bubbles of gas are seen during this operation, indicating that the vinyl chloride is completely dissolving in $CS_2$.

Methyl chloride standards can be made by following the same procedure.

Standards of vinylidene chloride are routinely prepared by injecting a measured volume of vinylidene chloride into a known volume of $CS_2$ with a microliter syringe.

There was some question about standards made by injecting a known volume of gas into a known volume of $CS_2$ in a sealed serum vial at room temperature and wet ice temperature so the above technique was utilized. Condensing the vinyl chloride in dry ice and using a 10 ml glass syringe cooled to dry ice temperature to prepare a standard proved difficult to duplicate.

### Sample Storage

The flood of inquiries from industrial hygienists, both from industry and government regarding personnel samples taken at one location and forwarding to a laboratory at another location for analysis, set the priority for determining sample storage characteristics. The backlog of samples taken in our own company and limitations of available manpower and instrumentation further substantiated the need to know how much absorbed vapor was being lost during storage or shipment of carbon tubes.

Sample of 10 liters of vinyl chloride at 1 ppm on the PCB 12X30 activated carbon were stored in polyethylene tubing for one to three weeks; 10 to 20% loss was noted with increased storage time. The effects of four weeks storage at room temperature were checked with both the stainless steel and glass tubes, and no apparent sample degradation was observed.

However, it was found that if samples were removed from their tubes and placed in small vials sealed with Polyseal caps, up to 40% of the initially loaded vinyl chloride was lost after one week of storage in the freezer. Samples, therefore, should be kept sealed in the original sample tubes until desorbed.

The storage effects on vinylidene chloride in glass tubes proved to be within the error (±5%) of the analytical method. Effects on methyl chloride samples have not yet been determined.

### Thermal Desorption

Thermal desorption was investigated as an alternate to $CS_2$ desorption. Thermal desorption, if perfected, offers several advtanges over carbon desorption, such as reduced health hazards.

The experimental apparatus consist of gas source, a dry test meter for measuring gas volumes, a muffle furnace and a Saran* film bag to collect the expelled vapors. The inlet and outlet tubes are of stainless steel as are the sample tubes. Prepurified nitrogen at a flow rate of 500-800 ml/minute is used as the purge gas. The oven temperature was initially set at 225°C, however, the low and erratic recoveries obtained were eliminated by raising the temperature to 430°C.

The desorption procedure is as follows. Place a 10 liter Saran film bag at the exit end of the outlet tube; connect the sample tube in the line and start the nitrogen flow. Purge the system with approximately 1 liter of nitrogen before placing the tube in the furnace. After placing the tube in the furnace, collect the expelled vapors until the desired volume is obtained. Divert the nitrogen flow from the collection bag and remove the bag for analysis.

For samples of approximately 100 liters of 50 ppm vinyl chloride, 4 liters of nitrogen were sufficient to obtain recoveries of 97% ±4%. The same was true for 100 liters of 10 ppm. However, for short term samples, *e.g.*, 10 liters collected at 1 lpm, it was found that more nitrogen was needed. At 25 ppm, 4 liters of nitrogen gave 90% recovery. At the 10 ppm level, 10 liters of nitrogen had to be used to obtain 93% recovery and at 1 ppm, 12 liters of nitrogen were needed to obtain this recovery. Fifteen replicate samples of 1 ppm vinyl chloride were analyzed by this method. The average recovery was 92% ±3.5% (one standard deviation). Subsequent series of tests have shown a recovery factor of 80% ±5%. Attempts were made to find the cause of the decrease. Neither the use of glass tubing nor deactivated and conditioned stainless steel tubing increased the recovery factor to its original value. Replacement of the inlet/outlet tubing and the nitrogen supply has had the same negative effect. Although this new factor is lower than what was originally found, it has been reproducible and could, therefore, be effectively used as the recovery factor for this technique.

The recoveries of methyl chloride and vinylidene chloride have also been determined by this technique. A recovery of 75% ±5% is obtained (one standard deviation) for 6 liters of both 50 and 100 ppm methyl chloride desorbed with 10 liters of nitrogen. Replicate samples of 10 ppm vinylidene chloride gave a recovery of 88% ±5% (one standard deviation) when desorbed with 10 liters of nitrogen.

**Analytical Conditions**

Analysis is performed by gas chromatography/flame ionization detection. No one column or set of conditions can cover all situations involving analysis for vinyl chloride. A variety of columns have been used depending upon the situation. Figures 7-11 show some of the columns that can be used under varying circumstances.

Breakthrough was determined by periodically injecting air samples drawn from a glass tee placed behind the carbon tube. The following GC conditions were employed.

| | |
|---|---|
| Column: | 6' x ⅛" stainless steel 20% DC 200 on Chromosorb W, 80/100 Mesh |
| Column Temperature: | 80°C |
| Carrier Flow: | 30 ml/min $N_2$ |
| Hydrogen Flow: | 30 ml/min<br>240 ml/min |
| Detector Temperature: | 250°C |
| Sample Size: | 0.5 cc with GSV, or 1.0 ml Pressure-Lok Syringe |

Sample analysis was originally performed on this same column at 40°C. Both vinyl chloride and vinylidene chloride can be determined (Figure 7); however, light hydrocarbons may interfere with the vinyl chloride determination. Such interferences were eliminated by employing the following conditions (Figures 8 and 9).

| | |
|---|---|
| Column: | 20' x ⅛" stainless steel Carbowax 4000 on Supelcoport 80/100 Mesh |
| Column Temperature: | 80°C |
| Injection Port: | Unheated, on-column injection |
| Sample Size: | 2 microliters |

Other parameters were the same as previously stated. Temperature and carrier flow are quite critical because the vinylidene chloride is not completely separate from the $CS_2$;

*Saran is a trademark of The Dow Chemical Company abroad.

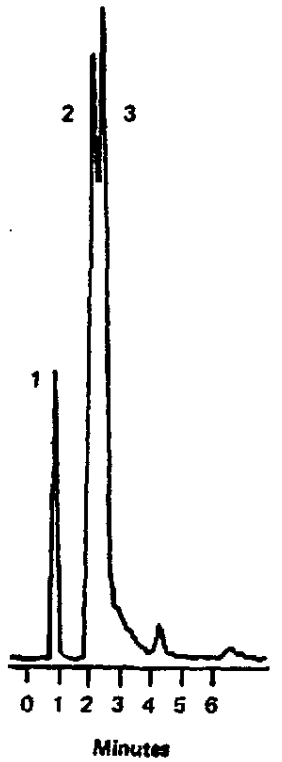


*Figure 7 – Chromatogram of components on DC 200 column; (1) vinyl chloride, (2) vinylidene chloride, (3) $CS_2$*

small changes in either of these parameters results in loss of resolution.

These conditions have proved satisfactory except for samples containing methyl chloride, dichlorodifluoromethane and/or dimethyl ether in addition to vinyl chloride. For these situations satisfactory separations have been achieved under the following conditions (Figures 10 and 11).

| | |
|---|---|
| Column: | 5′ x ⅛″ stainless steel Porapak QS, 80/100 Mesh |
| Carrier Flow: | 40 ml/min $N_2$ |
| Column Temperature: | 70°C (methyl chloride, dichlorodifluoromethane, vinyl chloride)<br>115°C (methyl chloride, dimethyl ether, vinyl chloride) |

**Conclusions**

When the vinyl chloride situation arose it was found that existing techniques for personnel sampling and analysis of vinyl chloride exposures were found to be inadequate because vinyl chloride vapor was easily lost from the sample at several different stages in the collection and analysis.

This study evaluated numerous adsorbing media and found that one specific cocoanut carbon, Pittsburgh PCB 12X30 Activated Carbon, is the most suitable of the commercially available carbons tested for personnel sampling of vinyl chloride and related compounds. One gram of this carbon packed in a stainless steel tube (14 cm x 0.25″ O.D. x 0.028″ wall) can be used satisfactorily to collect vinyl chloride, vinylidene chloride and methyl chloride according to the sampling conditions developed herein. The study developed improved techniques of desorbing the carbon using $CS_2$ at dry ice temperature. Thermal desorption was also investigated as an alternative to $CS_2$ desorption.

**Acknowledgement**

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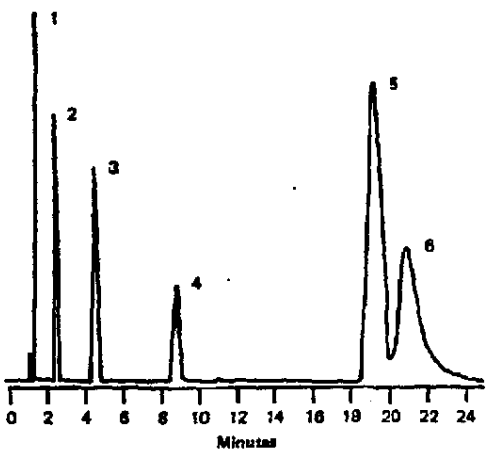


*Figure 8 – Chromatograms of components in air on Carbowax 4000 column; (1) isobutane, (2) vinyl chloride, (3) vinylidene chloride, (4) trans-1, 2-dichloroethylene, (5) methacrylonitrile, (6) acrylonitrile.*

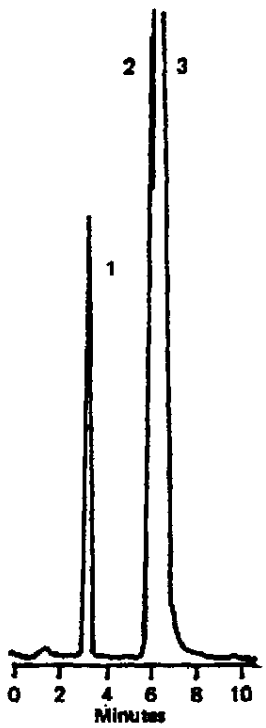


*Figure 9—Chromatogram of components in $CS_2$ on Carbowax 4000 column; (1) vinyl chloride, (3) $CS_2$.*

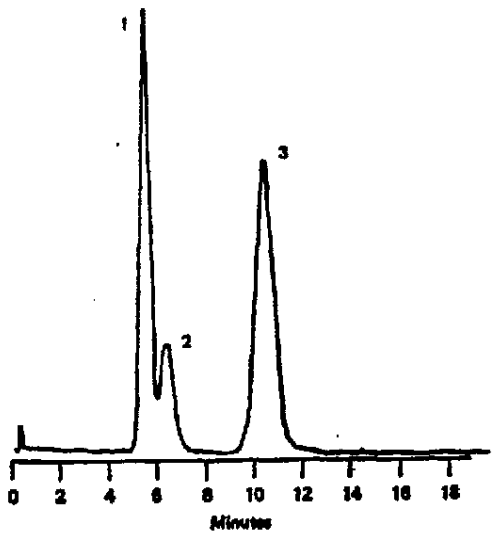


*Figure 10—Chromatogram of methyl chloride and vinyl chloride in the presence of Freon-12 on Porapak QS column; (1) methyl chloride, (2) Freon-12, (3) vinyl chloride.*

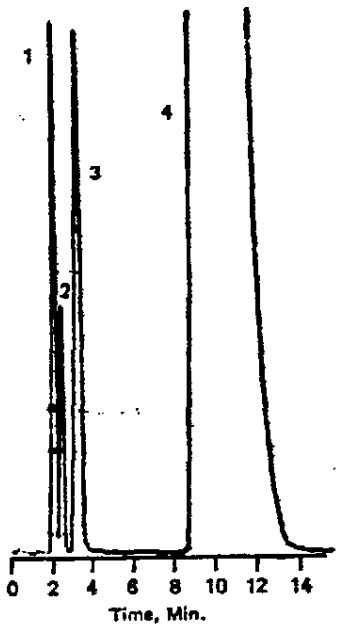


*Figure 11—Chromatogram of methyl chloride and vinyl chloride in presence of dimethyl ether on Porapak QS columns; (1) methyl chloride, (2) dimethyl ether, (3) vinyl chloride.*

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