

# Artifact Interference in Vinyl Chloride Analysis by Thermal Desorption Gas Chromatography

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## Abstract

A thermal desorption gas chromatographic method is applied to the sampling and analysis of airborne vinyl chloride in the workplace. Vinyl chloride is sampled to the solid adsorbent. The adsorbed compound is then thermally desorbed to a gas chromatograph for analysis. This method is safe, sensitive, convenient, and reliable. There is, however, interference from the artifact caused by water vapor adsorbed in the solid adsorbent. This interference causes problems in compound identification and analyte concentration calculation. This artifact can be eliminated entirely by the combination of water removal and a thermal focusing procedure prior to analysis.

## Introduction

Vinyl chloride is a known carcinogen (1). The major route of exposure is through the respiratory system. The standard method used for sampling and analysis of vinyl chloride in workplace air is National Institute of Occupational Safety and Health method 1007 (2). This traditional solvent extraction method uses a flammable and toxic solvent, carbon disulfide, to extract vinyl chloride from activated charcoal for analysis. The method is less sensitive because only a few microliters are taken from the solvent extract for analysis. Thus, a thermal desorption gas chromatographic (GC) method was developed for vinyl chloride monitoring of air in a polyvinyl chloride production plant (3) because this method eliminates the problems mentioned above in the analysis using the traditional solvent extraction method. In addition, this thermal desorption method requires no sample pretreatment because the compound is thermally desorbed directly to a gas chromatograph for analysis. The linear correlation (0.9991) of the calibration curve was more than acceptable. The precision of analysis was within 3.0% (10 replicates). The desorption efficiency of the compound was 100%. The recovery efficiency of the target compound after 15 days of storage was 99.8% at 4°C and 94.8%

at room temperature. Thus, this method is not only reliable, but also proves to be safer, more sensitive, and more convenient than the traditional method of analysis.

However, the effect of water vapor on the analysis of airborne vinyl chloride was observed during a series of studies using thermal desorption GC. This effect showed up as a vinyl chloride double peak in the chromatogram. The artifact causes problems in compound identification. It might also lead to a miscalculation resulting in a lower concentration if both peaks are not included in the calculation of vinyl chloride concentration. These problems were not reported in a study on the effect of water vapor on Carbotrap adsorbent (4). A very similar effect was also observed in the application of thermal desorption GC-mass spectrometry (GC-MS) on volatile organic compound (VOC) analyses (5). Supelco used a combination of Carboxen and Carbotrap adsorbent to reduce the water content of a sample by dry-purging the adsorbent prior to

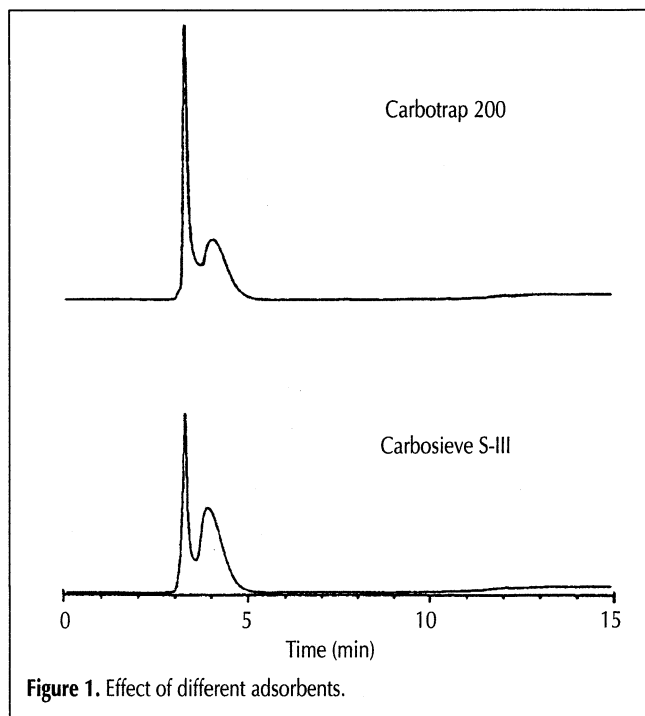


Figure 1. Effect of different adsorbents.

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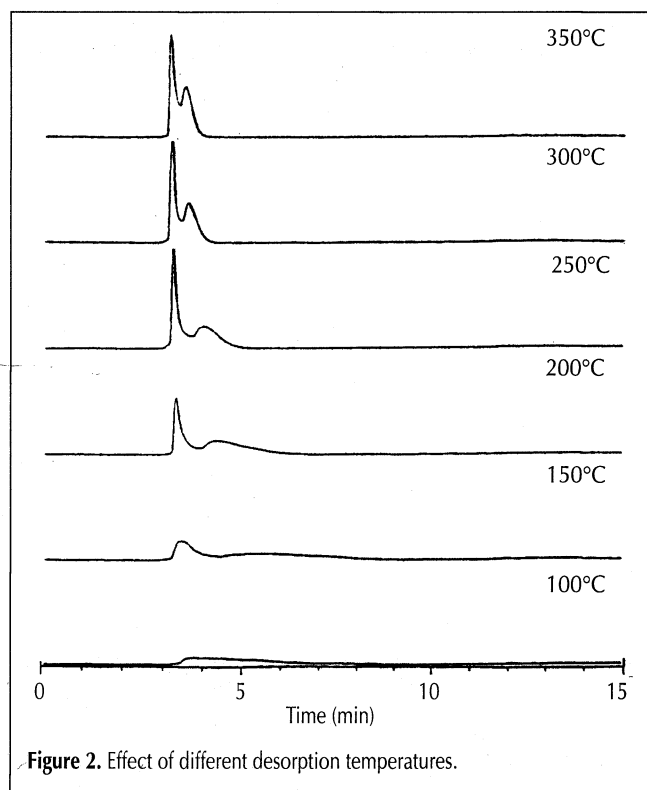
analysis (6). The effect of water vapor was eliminated using solid multisorbent packings in VOC accumulation and by drying the sample before analysis (7). In this paper, we reported findings from studies of water vapor effects on vinyl chloride analysis.

## Experimental

### Materials and Instruments

Vinyl chloride–nitrogen (1964 ppm by volume, blended using gravimetric master gas against National Institute of Standards and Technology [NIST] certified weight), prepared by Scott Specialty Gases (San Bernardino, CA), was used to prepare the gas standards. Carbosieve S-III adsorbent, Carbotrap 200 thermal desorption tubing (6-mm o.d., 4-mm i.d., 11.5-cm length, containing 80 mg 70/80 glass beads, 170 mg 20/40 Carbotrap B, and 350 mg 60/80 Carbosieve S-III), and Carbotrap 201 focusing tubing (6-mm o.d., 1-mm i.d., 11.5-cm length, containing 11.5 mg 60/80 Carbotrap B and 12.5 mg 60/80 Carboxen-1000) purchased from Supelco (Bellefonte, PA) were used for air samplings.

A dual-mode low-flow air sampler (model LFS-113) was obtained from Gilian Instruments (West Caldwell, NJ). A thermal desorption unit (2-2895) was obtained from Supelco. A Hewlett-Packard (Wilmington, DE) model 5890 series II GC equipped with a flame ionization detector (FID) was employed for sample analyses. Signal processing and integrated areas of the chromatograms were handled using the software (Chem-Lab version 3.0) from Scientific Information Service Corporation (Taipei, Taiwan). A Hewlett-Packard model 5988A GC-MS was used for compound identification.



### Preparation of gas standards and samples

Vinyl chloride gas standards were prepared using a dynamic flow system (8). A standard gas generation system was maintained at 30°C with adjustable relative humidity for the preparation of vinyl chloride standards. The relative standard deviation (RSD) of 1.2 and 1.6% for temperature and humidity measurements, respectively, were maintained during the preparation of samples. The flow rate of air used for instrument zeroing was set at 100 mL/min, and the certified vinyl chloride was set at 1 mL/min. The concentration of vinyl chloride was 19.6 ppm after 10 min of equilibrium in the system. Different concentrations of the vinyl chloride gas standard were prepared by varying the flow rate of zero air.

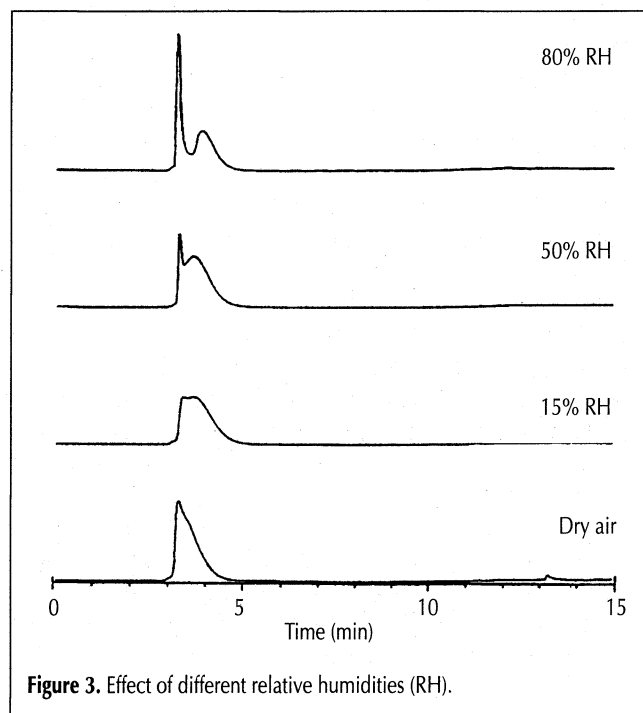
Airborne vinyl chloride samples were obtained by sampling workplace air into a thermal desorption tube containing solid adsorbent by a personal sampling pump running at a flow rate of 50 mL/min for 20 min. The thermal desorption tube was then analyzed directly by the thermal desorption GC method.

### Thermal desorption unit

The temperature of the desorption chamber was maintained at 250°C for a total of 5 min to desorb the vinyl chloride from the adsorbent. The thermal desorption unit used in this study did not have a preheat feature, so none was used. A temperature of 240°C was kept for the valve compartment and the transfer line. The total flow in the transfer line was fixed at 10 mL/min. The split ratio was set at 6:4 (column:vent) to provide a flow of 6 mL/min for the GC capillary column.

### GC

The column used for analysis was a Supelcowax 10 glass capillary column (30 m × 0.75-mm i.d.), 1.0- $\mu$ m film thickness (Supelco). The flow rate of nitrogen gas in the column was 6 mL/min, and the flow rate of makeup gas (nitrogen) was 30 mL/min. The column was programmed with an initial



temperature of 35°C for 5 min, then the temperature was increased 30°C/min until it reached 240°C, and this final temperature was held for another 5 min. The temperature of the GC injector and the FID were set at 200 and 250°C, respectively. The flow rate of air was 430 mL/min, and the flow rate of the hydrogen was 30 mL/min for the FID.

#### GC-MS

Samples were analyzed using a Hewlett-Packard 5988A GC-MS system. The GC was fitted with a 30-m  $\times$  0.53-mm-i.d. (1.0- $\mu$ m film thickness) Supelcowax 10 fused-silica capillary column. The column oven was maintained initially at 35°C for 5 min, then with a temperature program of 25°C/min to 200°C, and then held for 4 min. The capillary column was installed directly into the ion source without using a split adapter, and the temperature of the ion source was maintained at 250°C. The carrier gas was helium at a flow rate of 3.5 mL/min. The MS system was operated in the electron impact mode at 70 eV. The

scanning operation covered the range of 50–350 amu. Vinyl chloride was identified by a Hewlett-Packard 59970 MS Chem-Station with a NIST library database (NBS49K.L).

#### Results and Discussion

A vinyl chloride standard of 20 ppm concentration was prepared at 30°C and 80% relative humidity. This standard gas was sampled to one thermal desorption tube that contained Carbotrap 200 and another that contained Carbosieve S-III adsorbent. These two samples were analyzed by the thermal desorption GC method. Chromatograms of these vinyl chloride standards are shown in Figure 1. These chromatograms are very similar because Carbotrap 200 tube also contains 350 mg Carbosieve S-III in addition to 80 mg glass beads and 170 mg Carbotrap B. Both chromatograms have a double peak; the first one is sharper, and the second one is broader. This result was puzzling because only one peak is normally observed for each compound in GC analysis. However, it was clear at this stage of analysis that the presence of a double peak in the chromatogram was not caused by multisorbent packing of the desorption tube.

Chromatograms of vinyl chloride standards prepared at 30°C and 80% relative humidity and analyzed at different desorption temperatures are shown in Figure 2. A double peak appeared in all chromatograms. These peaks were more distinguishable and better resolved at higher desorption temperatures. The integrated area of the double peak increased with the increase in desorption temperature. The desorption temperature for later analyses was fixed at 250°C to avoid the possible degradation of adsorbent or chemical reactions within the adsorbent at higher temperatures.

Vinyl chloride standards prepared at four different relative humidities were analyzed, and the chromatograms are shown in Figure 3. The chromatogram of the dry air sample shows a merged broad peak, and chromatograms of humid air samples show a resolved double peak. Thus, a double peak appears only in chromatograms from the analysis of samples that were prepared in humid atmospheres. The resolution of this double peak was more distinct when the humidity was higher. The integrated area of vinyl chloride calculated from both peaks of this double peak is given in Table I. The average integrated area from four different humidities had a very small RSD of 2.8%. Apparently, the concentration of vinyl chloride calculated by including two peaks of this double peak was not affected by the variation of water content in the adsorbent up to 80% relative humidity.

All vinyl chloride standards prepared in a humid atmosphere were characterized by a vinyl chloride double peak in the chromatograms. This phenomenon was also observed in chromatograms from field samples taken in humid workplace air. Because this double

Relative humidity (%)	Integrated area	Average integrated area	RSD (%)
0	38913156		
15	36416628	37550215	2.8
50	37579292		
80	37291784		

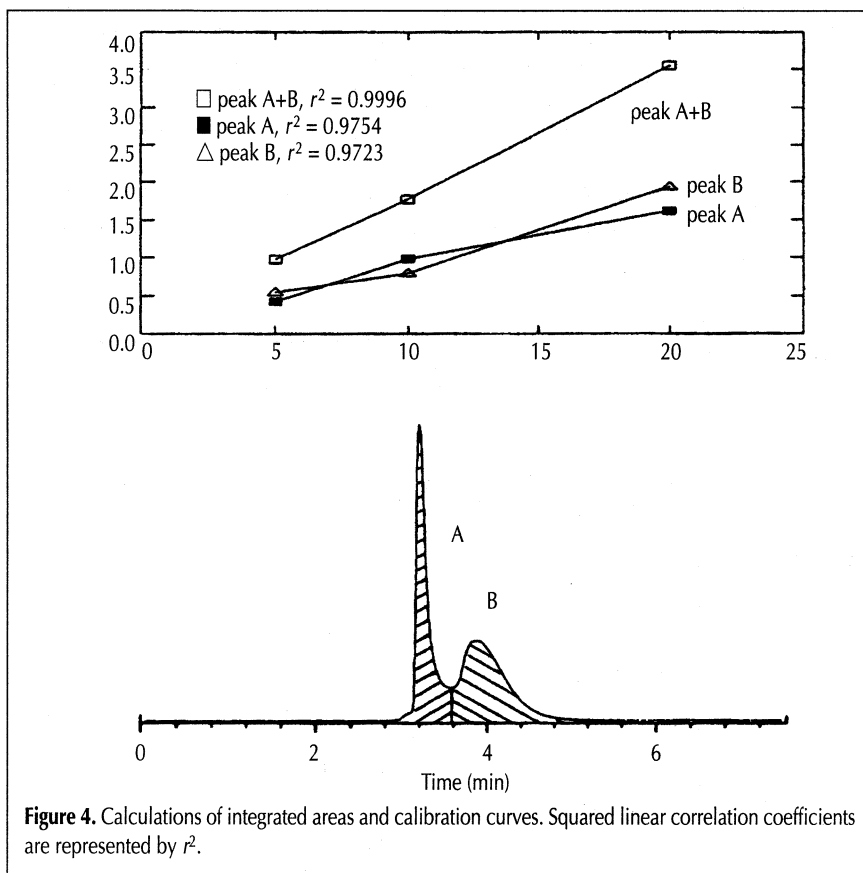


Figure 4. Calculations of integrated areas and calibration curves. Squared linear correlation coefficients are represented by  $r^2$ .

peak from vinyl chloride was not observed in the analysis of air sampled directly from a gas cylinder (dry), the appearance of a double peak was therefore attributed to the presence of water in the adsorbent. The above analyses demonstrate that a vinyl chloride double peak in the chromatogram is a general phenomenon present in samples prepared in humid atmosphere, regardless of whether there is a difference in adsorbent, desorption temperature, or water content in this study.

This effect raises two questions in GC analysis. First, which peak should the analyst use for the identification of vinyl chloride? Second, should one use the integrated area of a single peak or a double peak to calculate the actual concentration of vinyl chloride? In Figure 4, a typical chromatogram of vinyl chloride standard is shown with a double peak. The calibration curve from analyzing three different concentrations of vinyl chloride standard is plotted above to show the linear correlation. The respective correlation coefficients are 0.9996, 0.9754, and 0.9723 for the calibration curve obtained by calculating the sum of integrated areas A and B, only integrated area A, and only integrated area B. The calibration curve plotted by including both peaks has a better linear correlation (0.9996). Neither integrated area A nor B alone gives a better linear correlation for the cali-

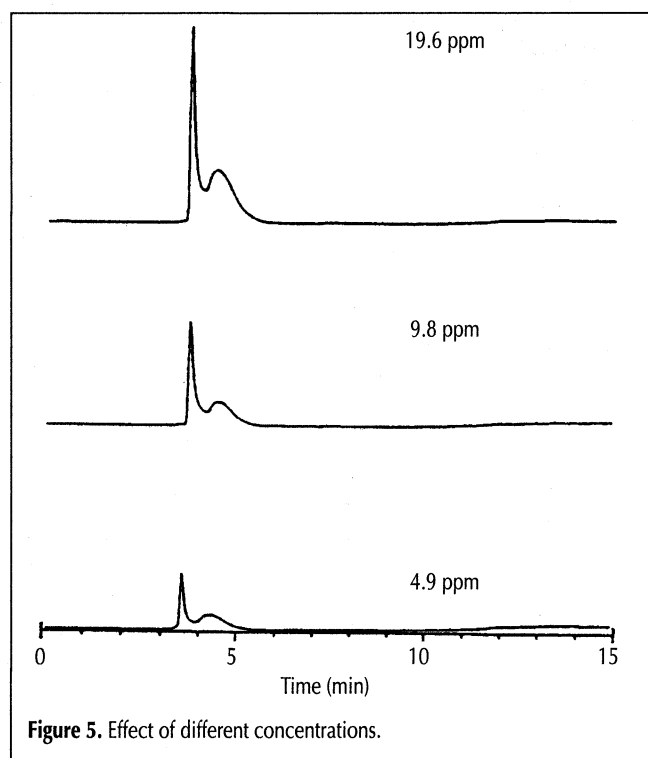


Figure 5. Effect of different concentrations.

Table II. Effect of Concentration on Vinyl Chloride Analyses

Concentration (ppm)	Average integrated area*	RSD (%)
1.0	844695 ( <i>n</i> = 7)	3.0
4.9	4459609 ( <i>n</i> = 3)	0.4
9.8	8788674 ( <i>n</i> = 3)	1.5
19.6	17725222 ( <i>n</i> = 3)	2.3

\* *n* = number of replicates.

bration curve. It is therefore necessary to include both peaks for the calculation of vinyl chloride concentration.

Vinyl chloride standards of different concentrations were then prepared and analyzed similarly to determine if there was any effect due to the difference in concentrations.

Chromatograms of vinyl chloride standards at three different concentrations are shown in Figure 5. These chromatograms have the same appearance of a double peak. The integrated area was calculated by including these two peaks together. The integrated area of these two peaks increased with increasing concentration. Results of these analyses are given in Table II. The RSD from the analysis of seven 1.0-ppm vinyl chloride standards was 3.0%, and the RSDs from the analysis of three each of the 4.9, 9.8, and 19.6 ppm vinyl chloride standards were 0.4, 1.5, and 2.3%, respectively. These were well within 5%. The linear correlation of this calibration curve was 0.9999. Thus, both peaks of the double peak should be included in the calculation of vinyl chloride concentrations. Otherwise, more than 50% of the actual concentration might not be accounted for if the second broader peak is not included in the calculation.

Subsequent GC-MS analysis using the ion of 62 amu for selective monitoring confirmed that both peaks of the double peak in the chromatogram were due to the response of vinyl chloride. This confirmation further supported previous demonstrations that both peaks were due to the response of the same compound and that they should be included in the calculation of vinyl chloride concentration.

Figure 6 shows chromatograms from the analysis of vinyl chloride standards prepared at 30°C and 80% relative humidity. Figure 6A was obtained when water in the adsorbent was not removed and vinyl chloride in the adsorbent was not thermally focused before analysis. Figure 6B was obtained when water in the adsorbent was not removed and vinyl chloride in the adsorbent was thermally focused before analysis. Figure 6C was obtained when water in the adsorbent was removed and vinyl chloride in the adsorbent was thermally focused before analysis. It is clear that a well-defined single peak was observed when the procedures of water removal and thermal focusing

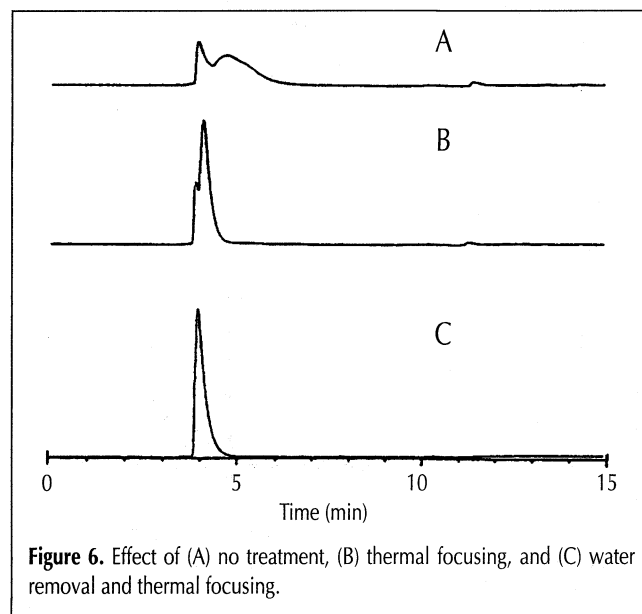


Figure 6. Effect of (A) no treatment, (B) thermal focusing, and (C) water removal and thermal focusing.

were performed prior to analysis. If only thermal focusing is conducted on the sample, the result is what is shown in Figure 6B. Therefore, the focusing step alone cannot eliminate the double peak problem. Water removal is the only way to solve this problem.

The procedure of water removal requires the attachment of an empty desorption tube to the focusing tube. An air stream with vinyl chloride and water vapor leaving the desorption chamber passes through the empty tube first. Water vapor condenses in the empty tube, leaving vinyl chloride in the adsorbent in the focusing tube. The flow rate in the tube was 6 mL/min, and the duration was 2 min for this procedure. This treatment is sufficient to remove water vapor from adsorbent to eliminate the artifact interference. The procedures of water removal and thermal focusing appear to have very little effect on the integrated area of the peak because the integrated areas of the vinyl chloride peak from these chromatograms have an RSD of 1.3%.

In a study on adsorbent tube evaluation for the preconcentration of volatile organic compounds in air by GC-MS analysis, McCaffrey et al. (5) reported the observation of a broad peak due to the presence of water. Poor peak shapes of propan-2-ol and 2-methylpropan-2-ol were reported as the result of the large amount of water present in the analytical column. A combination of Carboxen and Carbotrap adsorbent used for dry purging before desorption to the GC appeared to be effective in reducing the water content in the sample (6). The elimination of the effect due to water vapor in the analysis of VOCs has been studied by using multisorbent packings for compound accumulation and sample drying (7). Results from our study on sampling and analysis of vinyl chloride further confirm the observations of water vapor effect in thermal desorption GC analysis. This artifact is due to the presence of water in the adsorbent, and it can be eliminated entirely by the removal of water and thermal focusing prior to GC analysis.

## Conclusion

A thermal desorption GC method for sampling and analysis of airborne vinyl chloride has been developed in this laboratory. The method has been applied successfully in the monitoring of workplace air in a polyvinyl chloride production plant. This method is safer, more sensitive, more reliable, and more environment-friendly than the traditional solvent extraction method. However, the method suffers from the artifact interference in vinyl chloride analysis by water vapor adsorbed in the

adsorbent. The artifact present was a vinyl chloride double peak instead of a single peak normally observed in GC analysis. This artifact causes problems in compound identification and concentration calculation of the analyte. More than 50% of the actual concentration might not be accounted for if the second broadest peak is not included in the calculation of vinyl chloride concentration. This effect can be eliminated entirely by the removal of water vapor from the adsorbent and thermal focusing prior to analysis.

## Acknowledgments

This study was funded by the Institute of Occupational Safety and Health, Council of Labor Affairs, Executive Yuan, Taiwan, Republic of China by project #IOSH83-A205. The authors wish to thank all persons involved in this study.

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Manuscript accepted November 8, 1996.