Pb Vinyl Chloride / Sorption Methods

# THE DETERMINATION OF VINYL CHLORIDE MONOMER IN CHARCOAL-LOADED PERSONNEL MONITOR TUBES USING THE AUTOMATED GAS CHROMATOGRAPHIC HEAD SPACE TECHNIQUE

I/I REV 8(E)

*N. A. Sebestyen and W. B. Thompson*
*The Perkin-Elmer Corp.*
*Norwalk, Connecticut 06856*

R&S 004144

## ABSTRACT

The head space method described herein is a simple and accurate, totally automated, way to determine the amount of vinyl chloride monomer (VCM) which has been adsorbed in a personnel monitor collection tube containing activated charcoal. The relatively short analysis cycle time (6 minutes) and relative accuracy (about 2%) will allow for a high throughput (over 200 samples per day) of accurate results.

## INTRODUCTION

Gas chromatography (GC) has been shown (1-3) to be a preferred method for measuring residual vinyl chloride monomer (VCM) in many matrices. The preferred GC method for the analysis of absorption tubes used in personnel monitoring devices employs carbon disulfide as a desorbant. Alternate GC methods which avoid the use of $CS_2$ have been published (4, 5). This paper describes another alternative GC technique which avoids the use of $CS_2$. In this method, the "static head space" sampling technique is used in conjunction with relatively safe desorbants. The head space technique is widely used for determining volatile compounds in complex and/or non-volatile matrices (6, 7). Basically the head space sampling technique is accomplished by establishing an equilibrium between the sample and the gas phase above the sample, and subsequently sampling and analyzing the gas phase. Three relatively safe alternative desorbing agents were examined: ethyl alcohol (ETOH), benzyl alcohol (BA), N,N,dimethyl acetamide (DMAC).

A VCM loaded sample charcoal tube consisting of a 100 mg front portion and a 50 mg second portion, was opened and each section was placed into separate standard 24 ml sample vials. A measured amount of desorbing agent was added to each vial. The vial was then sealed and equilibrated in the water bath at a specific temperature. After equilibration had taken place, the F-42 automatically sampled the head space in the vial, which then consisted of a mixture of the desorbing agent and the VCM. After the VCM peak eluted, the desorbing agent was backflushed out of the column. When the chromatographic analysis was completed, the instrument automatically sampled the subsequent vials in sequence.

In selecting desorbing agents for headspace work, certain criteria must be met:

- There may be no peaks that interfere with the VCM.
- Must be able to be backflushed out of the stripper column.
- Must reach headspace equilibrium in a relatively short time.
- Must be a good desorber and have a good recovery rate.
- Must be relatively non-toxic.

The three desorbers that were tried met most of the above criteria.

## EXPERIMENTAL

The Perkin-Elmer Model F-42 automated gas chromatographic head space analyzer was used with the automatic backflush system and the Model 1 computing integrator.

The following procedure was used in evaluating each of the desorbing agents. Charcoal sample tubes were loaded with identical volumes of 5 ppm VCM gas. The volume pulled through was 571 mL at a sampling rate of 100 mL/min. After loading the sample tubes with a known amount of VCM gas, the tubes were opened and the charcoal was separated into two vials: the front section in one vial, the rear (backup) section in another. One mL of the desorbing agent was added to the front section (100 mg of charcoal). To the backup section (50 mg of charcoal), 0.5 mL was added. The vials were immediately sealed and were placed in the thermostatted sample turntable. Ten minutes was allowed before sampling was started. Using a ten minute cycle time, a time study was made showing the equilibration period vs. time. When equilibration was reached (no large increase in area counts shown), the standard deviation was calculated using the concentration printouts of the Model 1. At the end of the run made for all front section charcoals, the "backup" section was run to make sure no breakthrough occurred; and none had occurred. Table 1 shows time vs. conc. for each of the three desorbing agents.

All three of the desorbing agents met the first two criteria previously listed. The differences are in the last three criteria. As can be seen in Table 1, the ETOH desorbed VCM samples reached equilibrium first, followed by the DMAC samples and last by the BA samples. Due to the close retention of the ETOH peak to the VCM peak, the set up of the backflushing is not easy. For that reason ETOH is ruled out. The benzyl alcohol takes a long time to reach equilibrium. Therefore the authors recommend the use of DMAC as the desorbing agent, even though it has a lower recovery percentage (about 80%). DMAC has a short equilibrium time, about 30 minutes, and the backflush timing is also made easier.

*Instrumental* – The following conditions were set on instrument. The temperature settings were oven, 65 °C, injector, 150 °C; detector, 150 °C; needle, 150 °C; water bath, 60 °C for ETOH, 90 °C for BA and DMAC. The time settings were inject = 3 s, analysis = 30 s, F = BF set at 4 min, S = as needed, usually 0. The flows, with the instrument in the standby position, were set as follows: (1) Disconnect column from FID. (2) Measure and adjust flow to obtain 24 mL/min using column pressure regulator. (3) Start the instrument cycle. While the instrument is in the backflush cycle, measure the flow again. Flow should be adjusted to 24 mL/min, using the backflush pressure regulator. Connect the column to the FID, ignite the flame.

Run through an instrument cycle with range and attenuation at X1. Zero the baseline during the analysis time

using the course and fine suppression control. When the backflushing cycle occurs, adjust the backflush pressure regulator to correct for small offsets in the baseline. Check the baseline this way several times. Set the FID pressure regulators at optimum settings which are approximately: air - 3.7 atm. and $H_2$ - 2.4 atm.

Obtain the retention time for the VCM peak, about 60 s. Then obtain the retention time for the solvent peak. DMAC and BA have greater than 45 min retention time, so the retention time is not critical. The ETOH retention time is approximately 140 s.

First set the analysis time at about 1/3 of the retention time of the VCM peak. Run a sample of VCM + ETOH. Increase the analysis time by six seconds until the VCM peak appears on the recorder. If the analysis time is too long, the ETOH peak will elute. The optimum setting just allows the VCM peak and not the ETOH solvent peak to elute.

*Quantitation* – Calibrate the charcoal tube with a known amount of VCM. Take a Tedlar bag, fill it with a known concentration, C (ppm) of VCM/air or VCM/$N_2$ gas mixture. Pull through a calibration charcoal tube, with a personnel monitoring pump, *n* counts of this gas mixture. If the personal sampling pump has a sampling volume of *L* mL/count and has a rate of *Y* counts per minute, then the volume (mL) pulled through the charcoal tube per minute is

$$V_M = (L \text{ mL/ct}) \times (Y \text{ ct/min})$$

The total volume (mL) pulled through the charcoal tube is

(1) $V_T = V_{VCM} = V_M \times t$,

where t is the time in minutes. The total weight of the adsorbed VCM is expressed by the formula

(2) $W_{VCM} = V_T \times C \times 2.58$ ng

(2.58 ng = weight of VCM in 1 mL of 1 ppm gas). value is proportional to the head space concentration of the VCM which is desorbed by a desorbing agent in a sealed vial that has been equilibrated at a specific temperature.

The loaded and desorbed charcoal is then used as the external calibration standard. (The external standard can be used because of the excellent repeatability of the sample size). Knowing that the desorption efficiency of the VCM on the calibration charcoal is the same as on the sample charcoal, the weight of the desorbed VCM in the unknown sample is

(3) $W_uVCM = A_uVCM/AVCM \times W_{VCM}$

where $A_{VCM}$ is the area counts of the calibration VCM peak of weight $W_{VCM}$ (as calculated earlier) in the desorbed calibration charcoal, and $A_uVCM$ is the area counts of the VCM peak of weight $W_uVCM$ in the desorbed unknown charcoal.

The average air concentration of the unknown VCM (in ppm) during the time the personnel monitor charcoal sample tube was worn is

(4) $C_u = W_uVCM/(V_u \times 2.58 \times 10^{-3})$

or combining equation (2), (3) and (4)

(5) $C_u = A_uVCM/AVCM \times V_T/V_u \times C \times 10^{-6}$

The concentration for each unknown can be calculated automatically using the Model 1 automatic integrator or similar data system. The $V_T$ and $V_u$ are entered for each sample.

## DISCUSSION

Having selected DMAC as the best overall desorbing nt, runs were made with varying concentrations and olumes of VCM gas loaded on sample charcoal tubes. These runs were made to assure that the desorption rate of the VCM from the charcoal remains constant for varying amount loaded.

Although this study was written using the approved NIOSH charcoal tubes for sampling, the desorption method from charcoal can be used on different amounts of charcoal loaded in different ways. Adjustments may be needed in the volume of desorbing agents used or desorption times. But overall results should be as good as shown in this paper.

TABLE I
Test of Desorption Reagents*

| | *ETOH 60°C Thermostatted Samples* | *BA 90°C Thermostatted Samples* | *DMAC 90°C Thermostatted Samples* |
|---|---|---|---|
| *Min* | *Conc.* | *Conc.* | *Conc.* |
| 10 | 100.6 | 85.0 | 5.0 |
| 20 | 129.3** | 95.4 | 102.0 |
| 30 | 112.5 | 105.5 | 114.0** |
| 40 | 115.6 | 122.0 | 112.5 |
| 50 | 115.4 | 129.8 | 113.2 |
| 60 | 125.4 | 140.6 | 115.1 |
| 70 | 123.8 | 138.2 | 110.8 |
| 80 | 134.7 | 141.7 | 116.7 |
| 90 | 118.5 | 147.0** | 114.3 |
| 100 | 127.6 | 146.9 | 111.3 |
| 110 | 127.0 | 154.9 | 115.9 |
| 120 | 129.2 | 152.3 | 116.4 |
| 130 | 121.5 | 149.1 | 117.7 |
| 140 | 126.1 | 146.1 | 115.9 |
| 150 | 125.9 | 151.3 | 112.1 |
| 160 | 129.4 | 152.4 | 109.3 |
| 170 | 134.0 | 150.7 | 113.2 |
| 180 | 116.1 | 155.0 | |
| 190 | 122.3 | 151.5 | |
| 200 | | 150.6 | |
| Mean = | 124.2 | 150.7 | 113.9 |
| Sigma = | 6.5 | 2.9 | 2.4 |
| RSD = | 5.2% | 1.9% | 2.1% |
| Recovery = | 95% | 94% | 80% |

*The experimental conditions were: Column: 0.2% Carbowax 1500 on Carbopack C. Col. temp.: 65°C. VCM retention time: 60 s. FID - x 80 Attn.

**Equilibrium reached.

R&S 004145

## REFERENCES


1. Method No. P&CAM-178 in *NIOSH Manual of Analytical Methods.* Dept. HEW, USPHS, NIOSH, 1014 Broadway, Cincinnati, Ohio, 45202.
2. L. D. White, D. G. Taylor, P. A. Mauer, and R. E. Kupel, Am. Ind. Hyg. Assoc. J. 31, 225 (1970).
3. A. R. Berens, L. B. Crider, C. J. Tomanek and J. M. Whitney, J. Appl. Poly. Sci. 19, 3169 (1975).
4. J. E. Purcell, Amerb. Lab., May, p. 99 (1975).
5. D. H. Ahlstrom, R. J. Kilgour and S. A. Liebman, Anal. Chem. 47, 1411 (1975).
6. H. Hachenberg and A. P. Schmidt, "Gas Chromatographic Headspace Analysis", Heyden & Son, New York, 1977.
7. B. Kolb, J. Chromatogr. 122, 553 (1976).