VINYL CHLORIDE
DETERMINATION IN AIR BY ADSORPTION ON ACTIVATED CHARCOAL AND ANALYSIS BY GAS CHROMATOGRAPHY

1 PURPOSE AND LIMITATIONS This paper describes a procedure for measuring the exposure of personnel to vinyl chloride in the working environment. This method will meet the monitoring requirements of the Occupational Safety and Health Administration Standard for Exposure to Vinyl Chloride (1). The method describes the preparation of standards to determine vinyl chloride in the range of 0.01 to 2.08 ppm by volume in air to determine the 8-hour Time-Weighted Average concentration. These same standards will determine vinyl chloride in the range of 0.13 to 66 ppm by volume to measure the 15-minute ceiling value. Higher or lower ppm ranges can be determined by preparing additional standards to cover the range desired.

2 PRINCIPLE The sample is collected by passing air through a glass tube containing activated charcoal which adsorbs any vinyl chloride vapors present. The vinyl chloride is then desorbed from the charcoal by carbon disulfide extraction and analyzed by gas chromatography.

3 INSTRUMENT PARAMETERS

Chromatograph	Hewlett-Packard 5831A gas chromatograph, dual column or equivalent
Column	Six-foot x 1/8-inch stainless steel packed with 10% di(2-ethylhexyl) sebacate on Chromosorb P, 80/100 mesh, NAW
Column temperature	30°C
Detector	flame ionization
Detector temperature	200°C
Injector temperature	150°C
Carrier gas	nitrogen at 40 cc per min
Air flow rate	235 cc per minute at 27 psi
Hydrogen flow rate	21 cc per minute at 11 psi
Sample size	2 µl, solvent flush techniqu
Approximate retention time	1.0 minute

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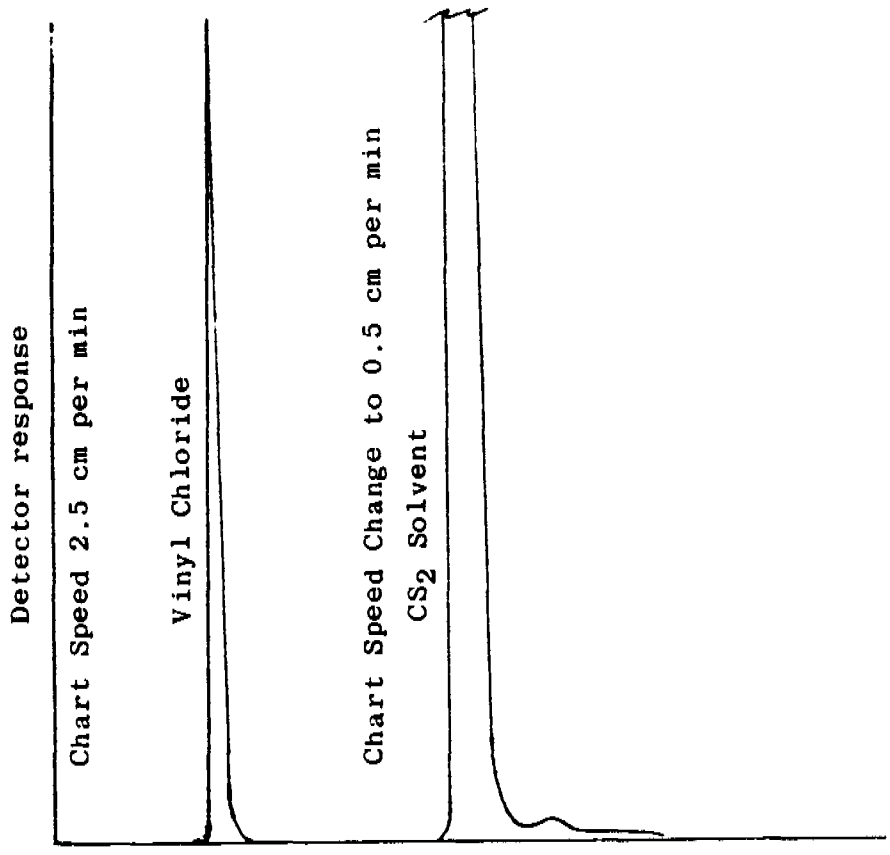

Alternate Column - Better Resolution (4)

Instrument	Hewlett-Packard 5831A gas chromatograph - dual column, or equivalent
Column	25-foot x 1/8 inch stainless steel packed with 25% by weight 75% CO880/25% TERGITOL E-35 on 40/60 mesh rescreened Chromosorb P
Detector	flame ionization
Column temperature	40° to 100°C at 4°C per minute
Detector temperature	125°C
Injector temperature	125°C
Carrier gas	helium, 30 ml per minute
Air flow	350 ml per minute
Hydrogen flow	30 ml per minute
Sample size	10 µl
Approximate retention time	6.5 minutes

4 APPARATUS AND REAGENTS

a) Personal sampling pump. MSA Models G or S, Bendix Micron-air, Sipin Sp-1, SKC 222-3 or equivalent
b) Hypo-vials, 15-ml size, Cat. No. 12911; Neoprene septa, Cat. No. 13233, alumina seals, Cat. No. 13214; and hand crimper, Cat. No. 13212, Pierce Chemical Company, Rockford, Illinois
c) Carbon disulfide, spectrophotometric grade
d) Activated charcoal, Cat. No. 580-26, Barnebey-Cheney, Columbus, Ohio
e) Soap film flow meter, 10-ml size
f) Stop watch

5 PREPARATION OF THE ACTIVATED CARBON ADSORPTION TUBE

a) Prepare the activated charcoal by placing the charcoal on a 40-mesh sieve and wash with demineralized water until no visible fines appear in the washings.
b) Dry the carbon in a drying oven at 110°C until dry and free flowing (overnight). Store in a screw-top, glass bottle until needed.
c) Cut 8-mm O.D. x 6-mm I.D. Pyrex glass tubing into 6-inch lengths and fire polish the ends.
d) Insert a Pyrex glass wool plug two-thirds of the distance into the glass tubes. The longer section of tubing will be designated as the primary end, while the shorter side of the tubing is the back-up end.
e) Pack the tubes with the activated carbon, using a length of 60 mm in the primary section and 35 mm in the back-up section. Retain the carbon with glass wool plugs.
f) Seal the tubes with a red rubber septum or parafilm until ready for use.

6 SAMPLING PROCEDURE

a) Remove the seals from the charcoal tube and attach the back-up section to a portable pump by means of a length of 1/4-inch Tygon tubing.
b) Ceiling value determination Air samples can be taken for periods up to 15 minutes to determine compliance with the 5 ppmv ceiling limit.
c) Set the air flow rate through the charcoal tube in the range of 50 to 150 cc per minute.
d) Determine the actual air flow rate through the charcoal tube by means of a soap film flow meter or a calibrated rotameter.
e) Record the time the air sampling is started.
f) At the end of the selected time period, stop the pump and record the time.
g) After sampling, recheck the flow rate and reseal the ends of the charcoal tube. Return the tube to the laboratory for analysis.

h) Time-w ight d average value determination Air samples can be tak n up to 8 hours to determine complianc with the 1 ppmv TWA limit and/or the 0.5 ppmv action limit.
i) Set the air flow rate at 50 cc per minute through the charcoal tube by means of a soap film flowmeter or a calibrated rotameter.
j) Repeat the step in paragraphs e through g above.

7 ANALYTICAL PROCEDURE
a) Make a small hook at the end of a piece of wire and remove the glass wool plug from the primary end of the charcoal tube. Make sure that no charcoal particles adhere to the glass wool plug.
b) Pour the charcoal into a 10-ml glass-stoppered volumetric flask and cool the flask and carbon in a wet-ice bath.
c) Pipet 3 ml of carbon disulfide (CS_2) into the cooled flask and stopper securely. (CAUTION: Carbon disulfide is toxic and should be handled under a hood.)
d) Agitate the flask periodically for at least 30 minutes.
e) Solvent flush injection technique. This injection technique is designed to eliminate difficulties arising from blow-back or distillation with the needle or the microliter syringe.
f) Flush a 10-µl syringe with CS_2 several times to wet the barrel and plunger.
g) Draw 2 µl of CS_2 into the syringe and remove the tip of the needle from the solvent. Withdraw the plunger an additional 0.5 µl to separate the CS_2 from the sample with a pocket of air.
h) Dip the needle into the sample solution in the volumetric flask and withdraw the plunger until the air bubble between the solvent and the sample has passed the 2-µl mark on the syringe.
i) Remove the tip of the needle from the sample solution and adjust the volume in the syringe until the meniscus of the air bubble rests on the 2-µl mark. Remove the excess sample solution from the tip of the needle.
j) Pull the plunger back an additional 0.5 µl to prevent the sample solution from evaporating from the tip of the needle.
k) Inject the entire contents of the syringe into the chromatograph.
l) Measure the peak height or area and determine the vinyl chloride content from a previously prepared calibration curve.

8 CALIBRATION CURVE
a) Pipet 10 ml of carbon disulfide (CS_2) into each of five 15-ml hypo-vials which have been cooled in wet ice. Cap the vials with the Neoprene septa and aluminum seals, using the hand crimper.
b) Place one of the vials in wet ice to reduce the vapor pressur at the CS_2.

c) Cap one of the valves on a steel sampl cylinder containing vinyl chloride with a 1/8-inch Swagelok tubing nut which has a chromatographic septum installed in the nut.
d) Insert a hypodermic needle through the septum on the cylinder, open the valve and allow the vinyl chloride to vent through the needle for about 10 seconds to purge the air from the system. Remove the needle.
e) Using a 1-cc gas tight syringe, insert the syringe needl through the septum on the cylinder and withdraw vinyl chloride into the syringe. Flush the syringe two tim s to remove any air which may have trapped in the needle.
f) Inject 1.0 cc of vinyl chloride into the hypo-vial which has been chilled. Shake well and allow the contents of the vial to warm to room temperature. This standard will contain 255 µgm of vinyl chloride per ml.
g) Into the remaining capped hypo-vials containing 10 ml of CS_2, inject 2.0, 1.0, 0.1 and 0.01 ml of the 255 µgm per ml stock solution into the respective hypo-vial. These standards will contain 42.5, 23.2, 2.53 and 0.255 µgm of vinyl chloride per ml.
h) Inject these standards into the chromatograph using the procedure described in Section 7, paragraph e through k. Shake the hypo-vials each time just prior to withdrawing a sample. Keep standards stored in dark and prepare new ones each day.
i) Plot peak height or area versus micrograms of vinyl chloride per ml.

9 CALCULATION

$$\frac{A \times 3 \times 24.5}{L \times 62.5} = \text{vinyl chloride, ppm by volume at } 25^{\circ}C \text{ and } 760 \text{ mm}$$

A = µgm per ml of vinyl chloride read from calibration curve
L = total liters of air sample (flow rate x time)

10 PRECISION DATA

Mean ppm by Volume Vinyl Chloride	Degrees of Freedom	Standard Deviation	95% Confidence Level
4.62	9	±0.21	0.67 ppm
0.98	9	±0.054	0.17 ppm
0.48	9	±0.046	0.15 ppm

11 TYPICAL CHROMATOGRAM A typical chromatogram is shown on page 2 for the di(2-ethylhexyl) sebacate column.

12 ORIGIN This procedure is based on a method originally developed and used by the Industrial Hygiene Department at the Texas City Plant. This revision of the method is the result of extensive testing by the R/D Environmental Health Group to ensure the procedure would meet the monitoring requirements of the Permanent Standard for Vinyl Chloride (1).

13 REFERENCES

1) Department of Labor, Occupational Safety and Health Standard, "Exposure to Vinyl Chloride" Federal Registar, Vol. 39, No. 194, pp 35890-35898, Friday, Oct. 4, 1974.
2) Deese, D. E., "Vinyl Chloride Personnel Monitoring Data - Texas City Plant Summary and Method", Letter, February 25, 1975.
3) Reid, F. H. and Halpin, W. R., "Determination of Halogenated and Aromatic Hydrocarbons in Air by Charcoal Tube and Gas Chromatography", Amer. Ind. Hyg. Assoc. J., 29, No. 4, pp. 390-396, July-August, 1968.
4) Haskins, J. and Fink, W. W., "Method for Determining Impurities in Vinyl Chloride Monomer", UCC R and D Project Report File No. 320610, January 12, 1966.
5) 6-RSC-72