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VINYL CHLORIDEDETERMINATION 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. The method describes the preparation of standards which will determine vinyl chloride in the range of 9 to 90 parts per million by volume in air, based on a 4-hour sample at a flow rate of 28 ml per minute. Lower or higher ppm ranges can be determined by preparing additional standards to cover the range desired. (Vinyl chloride can be determined to at least 0.05 ppm by volume in air by this procedure, using more dilute standards.)
- 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	AID (Analytical Instrument Development, Inc.) Portable Chromatograph, Model 511, or equivalent chromatograph, with flame ionization detector.
Column	Six-foot x 1/8-inch stainless steel packed with 10% di(2-ethylhexyl) sebacate on Chromasorb P, 80/100 mesh, NAW.
Column temperature	100°C isothermal
Injection temperature	100°C
Detector	flame ionization detector
Carrier	helium or nitrogen
Hydrogen flow rate	23 cc per minute
Air flow rate	133 cc per minute
Sample size	2 µl solvent flush technique
Retention time	0.5 minute (adjust carrier flow until vinyl chloride elutes at this time)

Alternate Column - Better Resolution

Instrument Hewlett-Packard 5750 gas chromatograph - dual column, or equivalent.
 Column 25-foot x 1/8 inch stainless steel packed with 25% by weight 75% CO880/25% Fergitol B-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 elution time 6.5 minutes

4 REAGENTS AND APPARATUS

- a) Personal sampling pump, MSA Model G or Bendix Micronair. Insert an in-line orifice made from a cut-off and restricted (pinched) hypodermic needle in the sampling line to the pump in order to obtain a 28 cc per minute flow on these pumps.
- 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 attached the back-up section to a portable pump by means of a length of 1/4-inch Tygon tubing.
- b) Set the flow rate at 28 ml per minute through the tube with a calibrated rotameter. (NOTE: The 10-ml soap bubble flow meter can be used to obtain a more precise reading of the air flow through the tube if desired).
- c) Record the time the air sampling was started and the time when the sampling is completed. A four-hour sample may be taken with this system.
- d) After sampling, recheck the flow rate and reseal the ends of the charcoal tube. Return the tube to the laboratory for analysis.
- e) Record the temperature and barometric pressure at the sampling site.

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, pipet 3 ml of carbon disulfide (CS_2) into the flask and stopper securely. (CAUTION: Carbon disulfide is toxic and should be handled under a hood.)
- c) Agitate the flask periodically for at least 30 minutes.
- d) Solvent Flash Injection Technique: This injection technique was designed to eliminate difficulties arising from blow-back or distillation with the needle of the microliter syringe.
- e) Flush a 10 μ l syringe with CS_2 several times to wet the barrel and plunger.
- f) Draw 2 μ l of CS_2 into the syringe and remove the tip of the needle from the solvent. Withdraw the plunger an additional 0.5 μ l to separate the CS_2 from the sample with a pocket of air.
- g) 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 μ l mark on the syringe.
- h) 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 μ l mark. Remove the excess sample solution from the tip of the needle.
- i) Pull the plunger back an additional 0.5 μ l to prevent the sample solution from evaporating from the tip of the needle.
- j) Inject the entire contents of the syringe into the chromatograph.
- k) Measure the peak height 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. Cap the vials with the Neoprene septa and aluminum seals, using the hand crimper.
- b) Place the hypo-vials in wet ice to reduce the vapor pressure of CS_2 .
- c) Cap one of the valves on a steel sample 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 the appropriate gas-tight syringe fitted with a number 27 gauge hypodermic needle, insert the needle through the septum on the cylinder and allow the pressure of the vinyl chloride to displace the volume of the syringe. Flush the syringe two times to remove any air which may have been trapped in the needle.
- f) Into the respective hypo-vials, inject 0.2, 0.3, 0.5, 1.0, and 2.0 cc of vinyl chloride from the syringe.
- g) Shake the hypo-vials for one minute to put the vinyl chloride in solution. These standards will contain 56, 82, 133, 260, 515 μ g of vinyl chloride per ml. (NOTE: These calculations are corrected for the dead space in the gas syringe needle. The cold CS_2 solutions in the hypo-vials are kept under slight negative pressure. Measurements have shown that the dead space in the syringe needle amounts to 0.04 cc, and 0.02 cc of this volume is pulled into the hypo-vial by the negative pressure.)
- h) Allow the standards to warm up to room temperature, then inject these standards into the chromatograph using the procedure described in Section 7, paragraphs d through j. Shake the hypo-vials each time just prior to withdrawing a sample.
- i) Plot peak height versus micrograms of vinyl chloride per ml.

9 CALCULATION

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

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

VINYL CHLORIDE

DETERMINATION IN AIR BY GAS CHROMATOGRAPHY

- 1 **PURPOSE AND LIMITATION** This method was developed to determine vinyl chloride in air by grab samples taken with a 50-ml hypodermic syringe. Air samples are introduced directly into the gas chromatograph by means of a 5-cc gas sampling valve. The minimum detectable concentration of vinyl chloride is about 0.1 part per million (ppm) by volume in air using this procedure. The method has been written for use with an Analytical Instrument Development portable chromatograph but can be used with other suitably equipped gas chromatographs.

2 **INSTRUMENT PARAMETERS**

Chromatograph	AID (Analytical Instrument Development, Inc.) Portable Chromatograph, Model 511, or equivalent chromatograph, with flame ionization detector.
Column	eight foot x 1/8-inch stainless steel packed with Poropak Q, 50/80 mesh.
Column temperature	100°C, isothermal
Injection temperature	100°C
Detector	flame ionization detector
Carrier, flow rate	nitrogen, 40 cc per minute
Hydrogen flow rate	26 cc per minute
Air flow rate	120 cc per minute
Sample size	5-cc gas sampling loop
Retention time	approximately 2.8 min.

3 **SAMPLING AND ANALYTICAL PROCEDURE**

- a) Grab samples are taken with a 50-ml hypodermic syringe without needle. After taking samples, cap the opening of the syringe with parafilm or a 7/32 Caplug to prevent diffusion of the vinyl chloride from the syringe. Sample must be analyzed within 30 minutes after taking, as losses of vinyl chloride will occur in the syringe. Samples may also be taken with pre-conditioned Saran plastic bag if desired.
- b) Turn the gas sampling valve to the load position and connect the 50-ml hypodermic syringe to the inlet. Allow the weight of the plunger to force the contents of the syringe through the 5-cc loop.

- c) Turn the gas sampling valve to inject position. Measure the peak height and read the concentration of vinyl chloride in ppm by volume in air from a previously prepared calibration curve.

4 CALIBRATION CURVE

- a) Cap one of the valves on a steel sample cylinder containing vinyl chloride with a 1/8-inch Swagelok tubing nut which has a chromatographic septum installed in the nut.
- b) 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.
- c) Using the appropriate gas-tight syringe fitted with a number 27 gauge hypodermic needle, insert the needle through the septum on the cylinder and allow the pressure of the vinyl chloride to displace the volume of the syringe. Flush the syringe two times to remove any air which may have been trapped in the needle.
- d) Prepare a series of vinyl chloride standards in air by measuring 10 liters of purified or cylinder air into each of four Saran bags while injecting 0.0, 0.10, 0.25, and 0.5cc of pure vinyl chloride gas into the respective bags. These standards will contain 0, 10, 25 and 50 ppm by volume vinyl chloride in air, respectively. If previously unused Saran bags are employed, it is necessary to precondition by filling with air and injecting 0.5 cc of vinyl chloride. Allow the bags to stand approximately 30 minutes then deflate. Refill with purified air deflate twice more before making the standards.
- e) Plot peak height versus concentration of vinyl chloride in parts per million (ppm) by volume in air.

- 5 CALCULATION Read the concentration of vinyl chloride in the sample, in parts per million by volume in air, directly from the calibration curve.

