Determination of Vinyl Chloride Monomer at the Sub-ppm Level Using a Personal Monitor

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A method is given for personal-breathing-zone sampling of vinyl chloride in ambient air. The procedure utilizes adsorption of the gas on activated charcoal followed by thermal elution onto a gas chromatograph. The furnace used to desorb the vinyl chloride is described in detail. The method was found to have a standard deviation of 0.04 at the 1-ppm level and a limit of detection of 20 ppb or lower. The method can also be used to monitor other organic material with high sensitivity.

Introduction

SAMPLING OF ORGANIC VAPORS by collection on solid adsorbents followed by thermal desorption onto a gas chromatograph has been reported in the literature.[1-9] Our laboratories have been using this technique for several years to measure trace quantities of organic materials in workroom environments.[10-12] Recent government permanent standards for vinyl chloride monomer (VCM) have necessitated a sampling and analytical method capable of detecting VCM at below 1 ppm.[13] The technique described here provides a method for taking breathing-zone samples of industrial workers with a sensitivity in the sub-ppm range for VCM.

The method consists of drawing a known volume of air through a glass tube packed with activated charcoal using a portable battery-operated pump. Breathing-zone samples are collected by attaching the adsorption tube to the individual's lapel and hence represent a sample of the air being breathed. The sample is returned to the laboratory and the collected organic material is backflushed with the aid of heat into a flame ionization gas chromatograph. With the exception of minor modifications, all the equipment necessary for this test is available commercially or can readily be prepared in the laboratory.

Apparatus

Adsorption Tubes: (See Figure 1.) Prepared by cutting 80-mm lengths of 5-mm o.d. glass tubing. Both ends were fire-polished with the inlet end of the tube partially constricted. Glass wool was packed into the inlet end of the tube to a length of approximately 0.5 mm. The tube was filled with 60-80 mesh activated charcoal (Coast Engineering Laboratory, Redondo Beach, California-Gas Chromatographic Grade) within about 1cm of the open end, and a second wad of glass wool was used to retain the adsorbent in the tube. The tubes were condi-

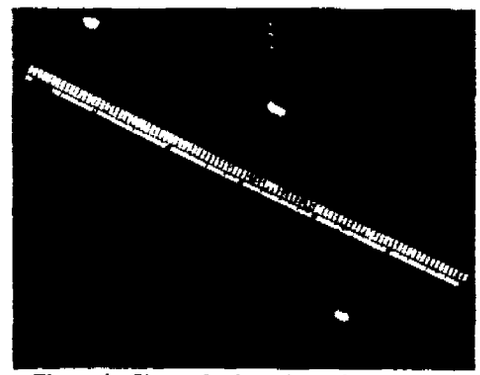

Figure 1. Charcoal adsorption tube.

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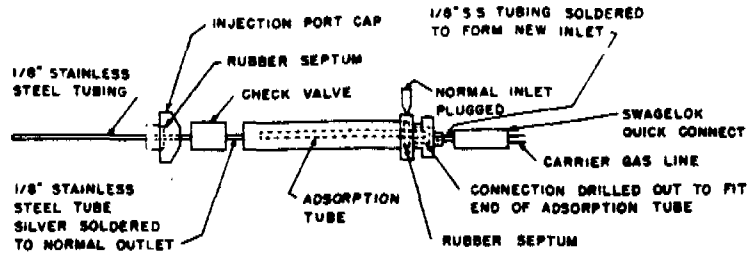

Figure 2. Diagram showing modifications to Burrell Pyrolyzer furnace.

tioned by heating at 300°C under a flow of 10 ml/min nitrogen for 10 minutes. After conditioning, the tubes were immediately capped to prevent pick-up of organic matter from the ambient air. Satisfactory caps can be purchased from Thomas-Packard, 48 Notch Road, Little Falls, N.J. 07424. (catalog number 521).

Gas Chromatograph: Varian Aerograph Model 1200 or equivalent instrument with a flame ionization detector.

Conditions: Column—6' x ⅛" stainless steel packed with 60-80 mesh Chromosorb 101. Oven Temperature—100°C isothermal. Attenuation—1 ×. Range—10^{-10} amps/mv. The area of the peaks was determined by an EAI 640 computer with a PACE III program.

Burrell Pyrolyzer: Model #340-017-35. The pyrolyzer oven was modified by plugging the normal inlet to furnace and relocating the carrier input to the screw cap of the oven. The inside of the screw cap is drilled out to at least 6 mm to accommodate the 5-mm adsorption tube. A short length of ⅛-inch stainless steel tubing was silver soldered to both the inlet and outlet of the furnace (see Figure 2). The pyrolyzer oven was attached to the gas chromatograph as shown in Figures 3 and 4.

Personal Monitoring Apparatus: Consists of a MSA portable pump Model G with a MSA multiple tube assembly (see Figure 5). In actual use, the pump is clipped to the belt and the holder to the lapel of the individual under test. Four tubes are exposed simultaneously to allow for replicated determinations

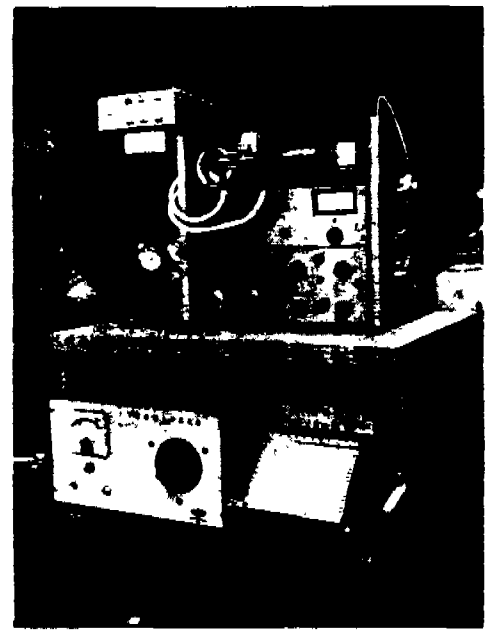

Figure 3. Burrell Pyrolyzer attached to gas chromatograph.

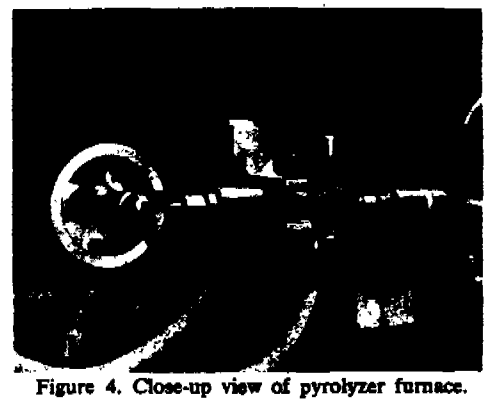

Figure 4. Close-up view of pyrolyzer furnace.

of the same sample. The critical orifices in the multiple tube holders were not removed.

Standardization

One ml of vinyl chloride was diluted to 100 ml with air in a 100-ml glass syringe. The contents were allowed to equilibrate for 30 minutes after which time a uniform mixture of air and VCM was achieved. The end of the syringe was fitted with a rubber serum bottle cap which allowed aliquots to be removed with a Hamilton 250-μl gas syringe. The aliquots were injected into the calibration apparatus (see Figure 6) and pulled on to the adsorption tube by applying a vacuum and flushing the injection port with approximately 0.15 liters of clean air. This volume was measured by attaching a rotameter to the inlet of the scrubber. The standard was then analyzed as described below under Procedure. A typical calibration curve and chromatogram are shown in Figures 7 and 8.

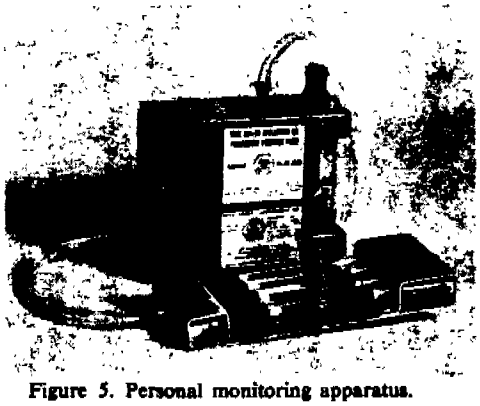

Figure 5. Personal monitoring apparatus.

Figure 6. Calibration apparatus.

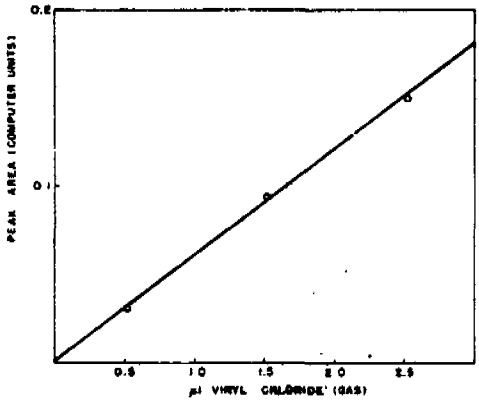

Figure 7. Vinyl chloride calibration curve.

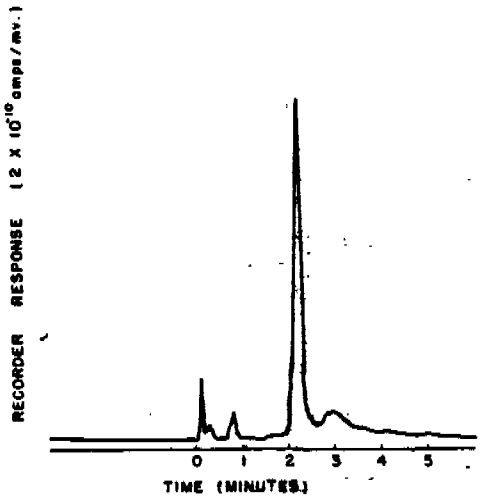

Figure 8. Chromatogram of 0.25μl vinyl chloride.

Sampling

In an area of uncontaminated air, the caps from four clean adsorption tubes were removed and mounted in the multiple tube holder, and the holder was connected to the portable pump. The pump was turned on, and the flow through each tube was measured against a calibrated rotameter. The flow rate was adjusted so that at least one liter of air was collected through each tube during the sampling period. Each tube was recapped until the actual time of sampling and recapped immediately after sampling. The tubes were analyzed as described under Procedure.

Procedure

With the three-way valve in the carrier gas line in the by-pass position (see Figure 9A), the tube to be analyzed was placed in the pyrolysis furnace. In all cases, the tubes were inserted so the input end was in the portion of the furnace closest to the injection port of the gas chromatograph (*i.e.*, so the contents of the tube are backflushed by the carrier gas). The tube was sealed in place and the temperature was brought rapidly to about 300°C. This was done by turning the pyrolyzer on, applying a voltage to the heater which will bring the temperature to 250°C in about 5 to 10 seconds, then reducing the setting to a predetermined value which would maintain the final temperature of 300°C. The temperature was held for 30 seconds then the three-way valve was placed in the inject position (see Figure 9B), and the area of the peaks in the resulting chromatogram were integrated. The results were calculated by comparison with standards.

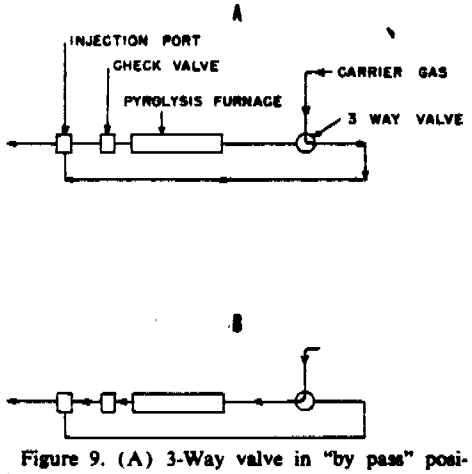

Figure 9. (A) 3-Way valve in "by pass" position (upper view). (B) 3-Way valve in "inject" position (lower view).

Precision

To test the reproducibility of the method, a standard sample was prepared by mixing 50 μl of vinyl chloride monomer with 50 liters of air in a Teflon bag. The volume of air used for dilution was measured from a gas cylinder through a rotameter and into the bag.

Thirteen replicate samples consisting of one liter each were taken through individual charcoal tubes from the bag. The data are given in Table I.

Breakthrough and Stability

Breakthrough was determined by injecting equal quantities of vinyl chloride into the calibration apparatus and then progressively increasing the volume of air used to flush

TABLE I
Replicate Analysis of a Standard Atmosphere Containing Approximately 1-ppm Vinyl Chloride

	Results ppm Vinyl Chloride
	1.20
	1.25
	1.27
	1.17
	1.30
	1.22
	1.30
	1.27
	1.27
	1.23
	1.27
	1.25
	1.25
Average	1.25
Standard Deviation	0.037

the VCM onto the absorption tube. In this manner, it was found that at least 5 liters of air could be passed through the tube before significant quantities of VCM were lost. When desired to check for breakthrough under field conditions, a fifth back-up adsorption tube can be placed in series between the multiple tube holder and the portable pump.

Tubes to which a known quantity of vinyl chloride was added have been kept in the laboratory up to two weeks before analysis without significant losses.

Discussion

The technique described represents a method of sampling and analysis which meets the current Federal requirements for monitoring vinyl chloride. The sensitivity is such that a level of 100-ppb VCM can easily be detected in a 1-liter sample or 20-ppb in a 5-liter sample. Since the electrometer used in the above work was on the 10^{-10} range, it is conceivable that the lower limit of detection could be reduced to 1 ppb by increasing the operating sensitivity of the instrument.

Although written specifically for VCM, the procedure is generally applicable to a large number of organic vapors. Our laboratory has used adsorption tubes packed with Porapak Q, silica gel, activated alumina, and activated charcoal to sample air for acrylic and methacrylic esters as well as various industrial organic compounds and solvents (see Table II).

TABLE II
Breakthrough Volumes of some Organic Compounds

Compound	Adsorbant	Breakthrough Volume (liters)
Butyl acrylate	Porapak Q	>7
Benezene	Porapak Q	>7
Chloroform	Porapak Q	>7
Ethyl acetate	Porapak Q	2
Ethyl acrylate	Porapak Q	>7
Ethyl propionate	Porapak Q	>7
Ethylene dichloride	Porapak Q	>7
Methanol	Silica Gel	1.5
Methyl acrylate	Porapak Q	>7
Methyl cellosolve	Porapak Q	>7
Methyl methacrylate	Porapak Q	>7
Methyl ethyl ketone	Porapak Q	5
Methylene dichloride	Porapak Q	0.15
Naptha	Porapak Q	6
t-Butanol	Porapak Q	3
Toluene	Porapak Q	>7
Vinylidene chloride	Activated Alumina	2.5
Xylene	Porapak Q	>7

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