

A solid sorbent tube (Patent No 4,292,042) employing an inhibited carbon preceded by a drying agent enables the hygienist to collect environmental air samples up to 90 liters at flow rates up to 1 liter per minute. Samples collected can be stored up to 10 days without loss of the vinyl acetate monomer. Analytical sensitivity of the method via gas chromatograph/flame ionization detection is 20 micrograms per milliliter which is equivalent to 1.33 milligrams per cubic meter or 0.4 parts per million by volume based on a 15 liter sample volume. Validation of the tube at the TLV, one-half the TLV and twice the TLV (recommended) shows greater than 98% recovery of known amounts of vinyl acetate generated through a dynamic dilution system at both low and high relative humidities. Breakthrough does not begin to occur until after sixty liters even at high relative humidity. No vinyl acetate is retained on the calcium sulfate. The use of calcium sulfate, a drying agent, as a precursor to the solid sorbent eliminates the effect of moisture on the monomer. Inhibiting the carbon prevents polymerization of the monomer after collection and during storage. The use of carbon as the adsorbent permits use of a liquid desorption medium. This technology is currently in use at several Union Carbide plants.

A solid sorbent tube for vinyl acetate monomer that eliminates the effect of moisture in environmental sampling

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introduction

Vinyl acetate is a liquid at room temperature with a boiling point of 72.9 °C at 760 mm Hg and a vapor pressure of 92 mm Hg at 20 °C. Vinyl acetate has industrial applications in emulsion paints, synthetic fibers, adhesives, pharmaceutical intermediates, textile finishes and sizes, paper and leather coatings, and non-woven fabric binders. It is a colorless liquid with a sweet odor and is completely soluble in many organic solvents. The toxicological health effects of vinyl acetate include indications that vapor concentrations below 250 mg/m³ are a primary irritant to the upper respiratory tract and eyes, and the liquid may irritate skin to the point of vesiculation. The irritations reported have all been reversible, and there are no known systemic effects.⁽¹⁾

The current threshold limit value (TLV) for VA is 10 ppm.⁽²⁾ A threshold limit value for vinyl acetate of 4 ppm in air measured as a ceiling concentration for any fifteen (15) minute period has been recommended.⁽¹⁾

A literature review revealed a method using chilled toluene in impingers as a collection medium⁽³⁾ and a NIOSH method⁽¹⁾ using a solid sorbent (Chromosorb 107) as the collection medium. Both methods used gas chromatography/flame ionization detection as the means of analysis. Limitations on flow rates, time of sampling and total volume make both methods unsuitable for long-term personnel sampling. In addition the NIOSH method uses thermal desorption which was unavailable in most of our plant facilities. The project request for development of a vinyl acetate personnel monitoring method included: (a) capability for long-term personnel sampling, (b) no interferences from other monomers used in the industrial process, (c) the collecting medium be charcoal or carbon, (d) the desorption medium be carbon disulfide, and (e) the analytical procedure be gas chromatography with flame ionization detection.

This paper describes the development and evaluation of such a procedure.

sampling technique

Vinyl acetate is a monomer that is subject to hydrolysis and polymerization. In developing a sound sampling procedure the following parameters were investigated: capacities of drying agents and sorbents, desorption efficiencies and

TABLE I
Solid Sorbents Evaluated

Adsorbent	ppm Generated	Relative Humidity	Percent Recovery
COLUMBIA® JXC Activated Carbon	10.0	<25	95
COLUMBIA® JXC Activated Carbon	10.0	>83	70
Bead Activated Carbon	10.0	>83	70
Activated Charcoal (Coconut Base)	10.0	<25	60
Porous Polymer Chromosorb 107	10.0	<25	50
Porous Polymer XAD-2 Resin	10.0	<25	50
COLUMBIA® JXC Activated Carbon Inhibited with Hydroquinone	10.0	>83	78
COLUMBIA® JXC Activated Carbon Inhibited with Hydroquinone Preceded by Drierite® (Calcium Sulfate)	10.0	>83	98.6

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humidity effects, sampling rates, maximum sample volume, and shelf life studies of the sampled tubes.

collection medium

Solid sorbents offer many advantages over other collection media for personnel sampling. Several adsorbents were evaluated as shown in Table I. Carbon was inhibited with hydroquinone using the following procedure:⁽⁴⁾

- 2.0 grams of carbon into a 25 mL beaker;
- add 4.0 mL of 5.0 (w/v) percent hydroquinone in 200 proof ethanol;
- stir to wet all the carbon granules and let stand for 15 minutes;
- place in vacuum dessicator and slowly evacuate all visible ethanol;
- place in a vacuum oven and evacuate overnight at 80 mm of Hg using dry nitrogen on the inlet side of the oven as the effluent, oven temperature 140 °C;
- store in a tightly stoppered container.

drying agents

To allow the use of a drying agent in the sampling apparatus, tubes were constructed according to the configuration shown in Figure 1 (patent application allowed). This allowed

the use of 1.8 grams of drying agent and 150/75 milligram two section carbon tube. Calcium sulfate 20 mesh (Drierite®) and molecular sieves sizes 3A and 4A (1/16-inch pellets) were evaluated as drying agents.

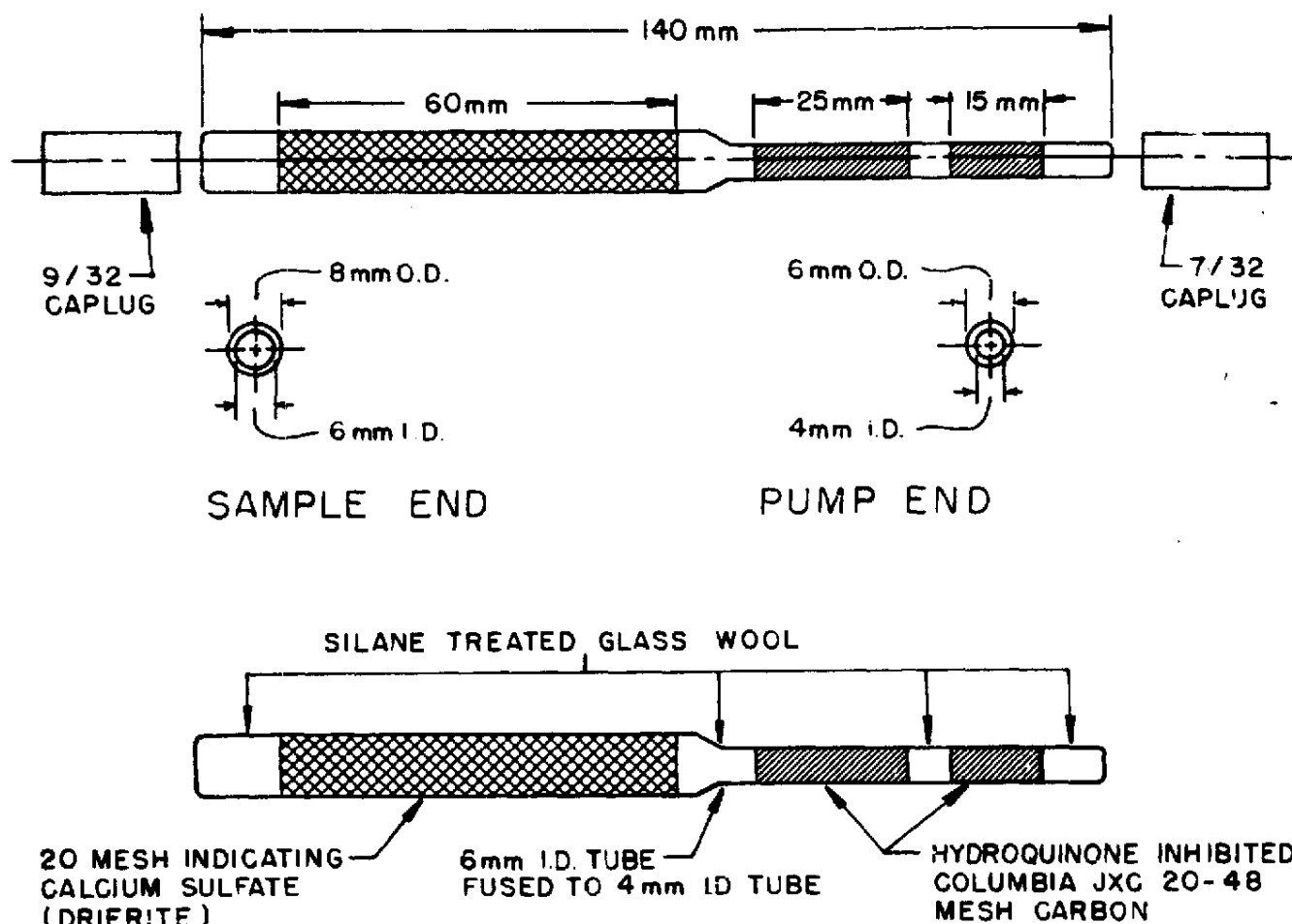
desorption solvents

Solvents evaluated include: (a) acetone, (b) acetonitrile, (c) carbon disulfide, (d) carbon tetrachloride, (e) methanol, (f) methylene chloride, (g) toluene, and (h) carbon disulfide containing 2 percent (v/v) acetone.

generation of known concentrations

A known concentration (1985 ppm vinyl acetate in nitrogen) was made up in a 239 pound water capacity cylinder. The concentration was verified by:

- pulling a known volume of the cylinder gas across a carbon tube, desorbing the carbon in carbon disulfide containing 2 percent (v/v) acetone;
- bubbling a known volume of the cylinder gas through midjet impingers containing the carbon disulfide-acetone mixture; and
- injecting a known volume into a chilled, septum capped vial, containing the carbon disulfide-acetone mixture. These were analyzed on the gas chromat-



graph and compared to a previously run standard calibration curve.

Known concentrations of vinyl acetate were generated in the 2-10 ppm range using a two (2) stage dynamic dilution system shown in Figure 2. A Wilkes Model 80 Infrared Computing Analyzer was calibrated with vinyl acetate in nitrogen and the sampling chamber of the dynamic system was analyzed.

Bag concentrations of vinyl acetate in nitrogen were made up and analyzed on a Hewlett Packard 5830A gas chromatograph equipped with a two (2) cc sample loop, a 3.05 m × 3.2 mm (10 foot × 1/8 inch) stainless steel FFAP column and a flame ionization detector. Samples were then taken from the dynamic sampling chamber with a 100 cc syringe and analyzed in the same manner. Bag concentrations were made up on a daily basis.

relative humidity

Relative humidity was controlled by using three (3) bubblers in series containing distilled water (Figure 2) and adjusting the flow of diluent into the second stage. The sensing unit of a Lab-Line Electro-Hygrometer was placed in the sampling chamber to measure relative humidity.

breakthrough

Breakthrough was determined by analysis of the backup section of the sample tubes after sampling at various flow rates, concentrations and relative humidities.

desorption efficiency

A desorption efficiency study was conducted on COLUMBIA® JXC 20-48 mesh carbon inhibited with a 5% solution (wt/v) hydroquinone in ethanol.

shelf life of the sample tubes

Storage studies were conducted on vinyl acetate collected on sample tubes at low and high relative humidities and were stored refrigerated and at room temperature.

analytical procedures

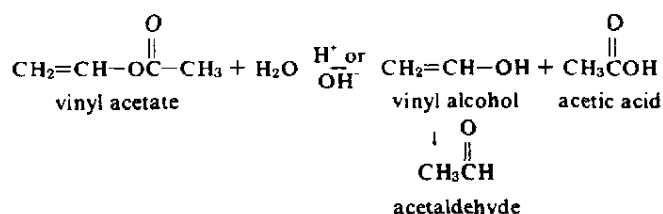
Gas chromatographs are common analytical instruments in industrial hygiene laboratories, and because of the expressed desire to have a procedure to simultaneously qualitate other monomers this was the only analytical tool evaluated.

A 9.2 m × 3.2 mm (30' × 1/8") stainless steel column packed with 15% Igepal CO-990 on 60/80 mesh Chromosorb W,AW and a flame ionization detector were used for separation and quantitation, respectively. Parameters are given in the appended method.

results and discussion

moisture effects

During this evaluation it became apparent hydrolysis was occurring. Mass spectrometer analysis of a sampled carbon tube showed the presence of both acetic acid and acetaldehyde. The vinyl acetate hydrolysis occurs as follows:



A procedure to eliminate the effect of moisture on the sampling and analytical procedure for vinyl acetate was needed.

Sampling the dynamic dilution system with no moisture added using the COLUMBIA® JXC carbon tube showed 90-100% recovery of vinyl acetate being theoretically generated. Introduction of moisture into the system reduced recovery to 60-70%. Studies showed the molecular sieves adsorbed the vinyl acetate to some degree but there was no adsorption of vinyl acetate by the calcium sulfate during validation or field testing. The drying agent eliminated hydrolysis of the vinyl acetate after collection and the inhibited carbon prevented polymerization after sampling.

columns and solvents

The literature search revealed a method⁽³⁾ that uses toluene as an adsorbent and a Porapak Q column for separation of vinyl acetate. The NIOSH procedure⁽¹⁾ uses a 10% FFAP column for separation. When toluene was evaluated using Porapak Q columns excellent analytical results were achieved. Vinyl acetate eluted before toluene, thus solvent tailing is not a problem. However, toluene caused an unstable baseline which resulted in a long analysis time. Carbon disulfide containing 2 percent (v/v) acetone was found to be the best desorption solvent. This solvent mixture was chosen for its ability to desorb other monomers in addition to vinyl acetate.

Standards were prepared and analyzed by gas chromatography. A standard calibration curve of eight concentrations was run ranging from 7.2 to 927.1 µg/mL. A linear regression analysis of concentration versus area response gave a correlation coefficient of 0.999 with 1.0 being a perfect fit.

Porapak Q and FFAP columns were evaluated using carbon disulfide as the desorption solvent but separation could not be achieved due to tailing of the solvent peak.

A Carbowax C plus 0.1% SP-1000 column did a good job of resolving vinyl acetate from carbon disulfide. The packing apparently adsorbed the vinyl acetate, however, and sensitivity was limited to approximately 200 µg/mL.

The need to have a method compatible with a method for one or more of the other monomers used in the industrial process led to an investigation of a column used for another monomer. This method calls for a 4.6 m × 3.2 mm (15' × 1/8") stainless steel column packed with 15% Igepal CO-990 on 60/80 mesh Chromosorb W,AW. A separation of the solvent (carbon disulfide containing 2% (v/v) acetone) and vinyl acetate was not obtained. Doubling the length produced a column capable of quantifying vinyl acetate in the presence of other monomers. Figure 3 shows a typical chromatogram.

desorption efficiency

Desorption efficiencies were run by transferring 150 milli-

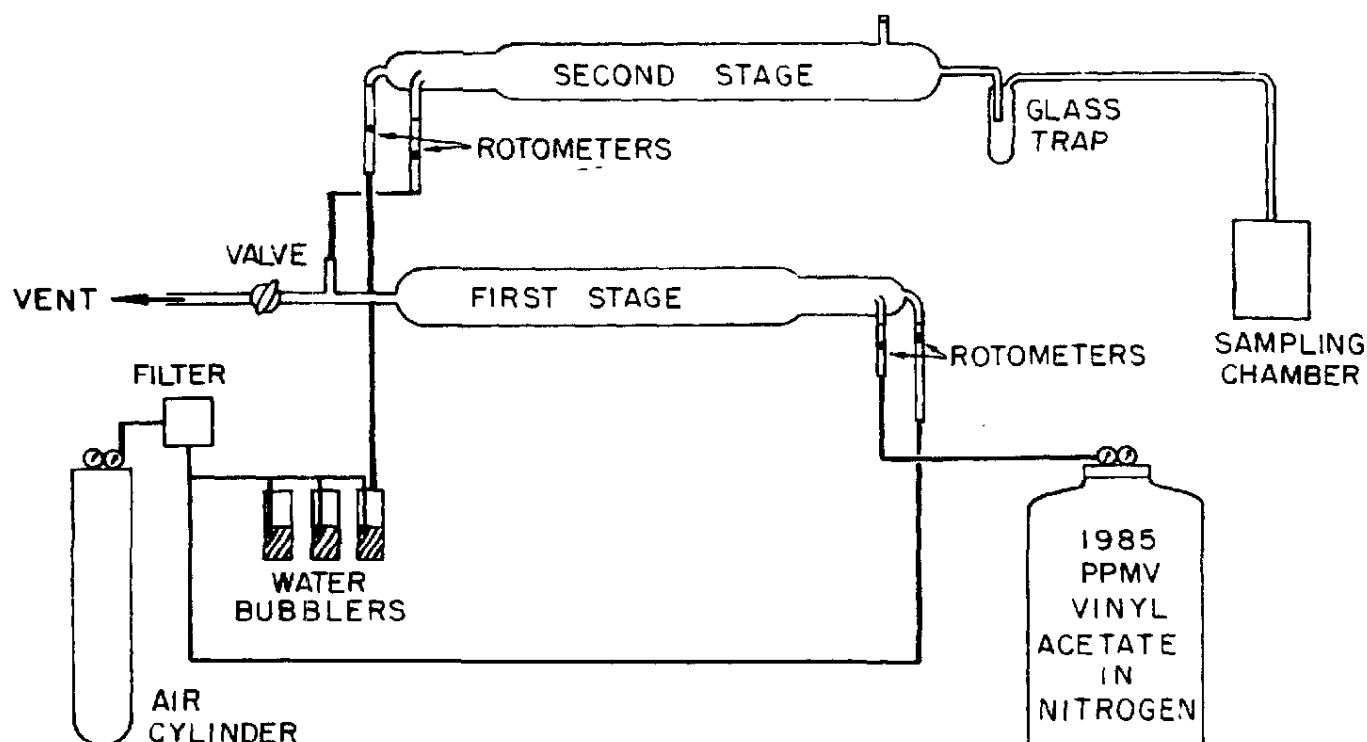


Figure 2 — Dynamic dilution system with relative humidity controlled.

grams of hydroquinone inhibited COLUMBIA® JXC 20-48 mesh carbon to each of 14 desorption vials. Two vials were left as blanks and 100, 200, 1000 and 2000 μg of vinyl acetate in acetone was injected into each of 3 vials, respectively. They were capped with parafilm and left overnight to allow the vinyl acetate to permeate the carbon. They were then desorbed in 1-mL of carbon disulfide containing 2 percent (v/v) acetone by sonifying 5 minutes in a water bath at room temperature. Results were compared to standards prepared at the same concentrations.

A mean desorption efficiency of 98.5% with a standard deviation of 2.25, was obtained for the desorption efficiency studies. The confidence interval of the standard deviation was determined by chi-square statistic. At 95% confidence level the true standard deviation will be included in a range of 1.59 to 3.82.

breakthrough evaluation of method

Breakthrough studies were conducted with the carbon tube (Table II). Area sampling can be done at a flow rate of up to one (1) liter per minute at 85% relative humidity for a period of up to ninety (90) minutes. This allows a total volume of 90 liters versus 3 liters maximum for the NIOSH procedure.⁽¹⁾ Above 85% relative humidity total volume should be limited to 60 liters.

validation

Vinyl acetate was collected at the TLV, half the TLV and two times the TLV (recommended) at both low and high relative humidity conditions to determine reliability of the method. Results are shown in Tables III and IV. The mean recovery

at low relative humidity (<50%) was 99.68%. The mean recovery at high relative humidity (>83%) was 98.62%.

A theoretical 4 ppm of vinyl acetate at 70-80% relative humidity showed less than 1 ppm vinyl acetate on the Model 80. Discrepancies between known concentrations of vinyl acetate and concentrations found with the Model 80 were attributed to hydrolysis of vinyl acetate.

The use of known bag concentrations as standards to ascertain generated analyte concentrations resulted in recoveries of 98% + for validation studies.

The precision of the sampling and analytical method at low and high relative humidity conditions was compared to check the homogeneity of the data by the F-test statistic. The calculated F-test value is equal to 1.477 whereas the critical F-value at 95% confidence level is equal to 2.7 ($F_{0.5/2, 16, 17} = 2.7$) suggesting that the test did not detect any difference in the precision for measuring vinyl acetate at low and high relative humidity conditions. The precision of the method is equal to 2.75% determined by pooling of variances.

The average recovery of vinyl acetate concentrations under low and high relative humidity conditions are shown in Tables III and IV. These averages were statistically evaluated by t-test to check whether these averages are significantly different from each other. The calculated t-test value is equal to 1.140, whereas the critical value of t at 95% confidence level is equal to 2.03 ($t_{0.05/2, 33} = 2.03$) suggesting that the test did not detect any difference in the averages of the vinyl acetate recovery under low and high relative humidity conditions.

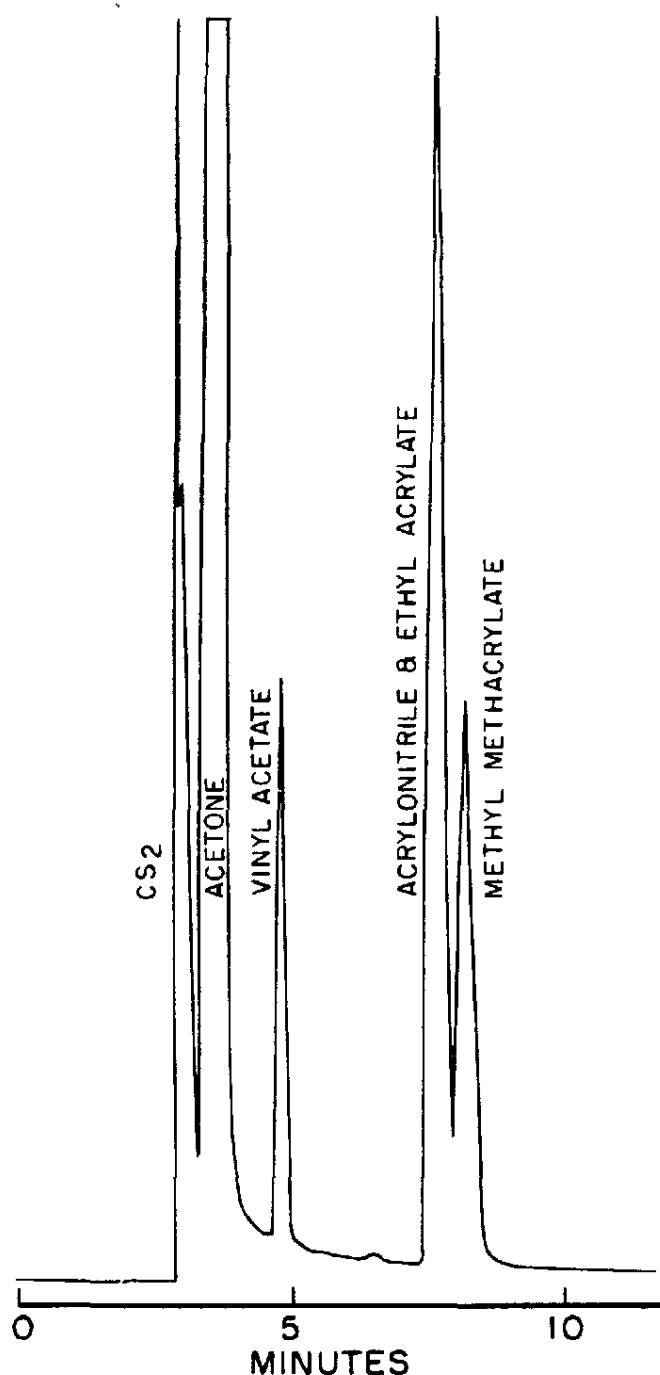


Figure 3 — Typical chromatogram @ 128×10^{-11} approximately 450 microgram of each monomer.

To evaluate the accuracy of the method the data in Table III were evaluated by the student t-test to determine the agreement between the experimentally determined average recoveries at several vinyl acetate concentrations and the theoretical reference value of one hundred percent recovery. The calculated t-test value is equal to 0.564 whereas the critical t-test value at 95% confidence level is equal to 2.11 ($t_{0.05/2; 17} = 2.11$) suggesting that the test did not detect any

difference of the average recovery from the theoretical one hundred percent recovery at 95% confidence level.

shelf life

Results of four sets of shelf life studies (24 samples plus blanks) collected and stored under various conditions was statistically evaluated. The averages were tested by Duncan's test for separation of means to detect if any of the averages

TABLE II
Breakthrough Studies on Tubes Containing
Inhibited Carbon and Drierite Precursor

Actual ppm Generated	% Relative Humidity	Flow Rate cc/min	Liters Collected	Percent Breakthrough
48.0	5	464	57.5	0.00
2.6	38	434	108.5	0.00
10.0	38	658	78.9	0.12
10.0	38	1054	126.5	1.26
2.2	48	1267	252.0	0.15
4.2	83	379	77.3	0.00
4.2	83	1117	126.3	0.71
4.3	83	179	32.7	0.00
10.0	92	1018	149.0	53.4
10.0	92	638	153.2	40.6
6.3	95	1122	16.8	0.00
6.3	95	1009	30.3	0.00
6.3	95	984	59.0	0.12
6.3	95	1154	103.9	21.90
6.3	95	1227	115.3	14.60
6.3	95	1112	90.5	8.40
6.3	95	1083	97.5	15.60

TABLE III
Evaluation of Method in The Presence
of Low (<50%) Relative Humidity

	ppm Vinyl Acetate Generated	ppm Vinyl Acetate Recovered	Volume (liters sampled)	Percent Recovery*
1	2.2	2.24	25.6	103.4
2	2.2	2.13	21.3	98.3
3	2.2	2.09	36.1	96.4
4	2.2	2.17	36.5	100.1
5	2.2	2.15	36.1	99.2
6	2.2	2.12	38.7	97.9
7	4.3	4.36	42.7	102.9
8	4.3	4.16	30.9	98.2
9	4.3	4.13	27.1	97.5
10	4.3	4.15	30.6	98.0
11	10.0	9.92	31.1	100.7
12	10.0	9.74	24.7	98.9
13	10.0	9.42	29.6	95.6
14	10.0	9.88	20.0	100.3
15	10.0	10.05	33.4	102.0
16	10.0	10.07	34.3	102.2
17	10.0	10.22	34.1	103.8
18	10.0	9.73	36.7	98.8
				($\bar{X}$) 99.68
				(SD) 2.41
				(*CV) 2.41

*Corrected for desorption efficiency of 98.5%

TABLE IV
Evaluation of Method in The Presence
of High (>83%) Relative Humidity

	ppm Vinyl Acetate Generated	ppm Vinyl Acetate Recovered	Volume (liters sampled)	Percent Recovery*
1	2.1	1.99	24.7	96.2
2	2.1	2.14	29.1	103.5
3	2.1	2.05	18.9	99.1
4	2.1	2.01	35.6	97.2
5	2.1	2.09	33.5	101.0
6	2.1	1.99	35.6	96.2
7	4.2	4.27	40.4	103.2
8	4.2	4.10	36.5	99.1
9	4.2	4.01	40.6	97.0
10	4.2	4.06	31.9	98.2
11	4.2	4.06	40.4	98.2
12	10.0	9.29	28.2	94.3
13	10.0	9.31	33.2	94.5
14	10.0	9.52	21.5	96.6
15	10.0	10.03	38.3	101.8
16	10.0	10.04	40.1	101.9
17	10.0	10.04	41.6	101.9
				($\bar{X}$) 98.81
				(SD) 2.94
				(*CV) 2.98

*Corrected for desorption efficiency of 98.5%

differed significantly from the others. At 95% confidence level the test detected a significant difference in the average recovery of vinyl acetate when samples in the presence of high relative humidity and analyzed after ten (10) days of storage at room temperature. Samples to be stored longer than five (5) days should be refrigerated.

evaluation of 3M organic vapor monitors (no. 3500)

3M Organic Vapor Monitors (No. 3500) were evaluated during the testing of this method. Concentration ranges were four (4) to ten (10) ppm at low and high relative humidity

conditions. An attempt was made to inhibit the charcoal absorbent pad of the monitor with hydroquinone but this proved futile. Results indicate the 3M Organic Vapor Monitors are not suited for monitoring vinyl acetate. Recovery at high relative humidity conditions are low and the monitors show a loss of vinyl acetate after being stored.

field evaluation of method

The method was field tested in May, 1979. Area and personnel samples were collected and analyzed. No problems were encountered with the method. Results of the field test concentrations ranged from 0.12 to 1.22 ppm on personnel samples and 0.1 to 5.5 ppm on area samples. The method has since been used successfully by several UCC Industrial Hygiene Laboratories.

conclusion

A proven air sampling and gas chromatographic method for measuring vinyl acetate in the occupational environment has been developed, validated and successfully field tested.

acknowledgements

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references

1. NIOSH: *Criteria for a Recommended Standard, Occupational Exposure to Vinyl Acetate* (September, 1978).
2. Threshold Limit Values for Chemical Substances in Workroom Air Adopted by ACGIH, Intended Changes for 1980.
3. Union Carbide Corporation: Method for collection and quantitation of vinyl acetate in air.
4. Hurley, G.F. and N.H. Ketcham: *Am. Ind. Hyg. Assoc. J.* 39:615 (1978).

APPENDIX A

Vinyl Acetate Determination in Air by Adsorption
on Activated Carbon Tubes and Analysis
by Gas Chromatography

purpose and limitations

This paper describes a procedure for measuring the exposure of personnel to vinyl acetate in the working environment and a grab sample technique for determination of vinyl acetate in air.

Based on results of injections of standard solutions of vinyl acetate in the carbon disulfide-acetone desorption solvent, the gas chromatography is capable of detecting 20 micrograms of vinyl acetate in the 1.0 mL desorption

volume. This would be equivalent to 0.3 ppm by volume vinyl acetate, based on a 18 liter air sample. The procedure as written describes the preparation of standards to determine vinyl acetate in the range of 2.0 to 8.0 ppm by volume in air. Higher or lower concentrations can be determined by preparing additional standards to cover the range desired.

principle

The sample is collected by passing air through a glass tube containing calcium sulfate to remove moisture and hydroquinone inhibited activated carbon which adsorbs any vinyl acetate vapors present. The vinyl acetate is then desorbed from the carbon by carbon disulfide containing 2 percent (v/v) acetone and analyzed by gas chromatography.

instrument parameters

Chromatograph	Varian Model 3700 gas chromatograph or equivalent equipped with a flame ionization detector
Column	9.2 m × 3.2 mm (30 feet × 1/8-inch) stainless steel column packed with 15% Igepal CO-990 on 60/80 mesh Chromosorb W, AW
Column temperature	90 °C isothermal
Injection port temperature	220 °C
Detector temperature	220 °C (critical)
Carrier gas (nitrogen)	35 cc per minute
Air flow rate	250 cc per minute
Hydrogen flow rate	30 cc per minute
Approximate retention time	5.0 minutes

apparatus and reagents

- Sampling Pumps, MSA Models (MSA Company), SIPIN Model SP 2 (Anatole J. Sipin Company), SKC Models 222-3 (SKC, Incorporated), or equivalent.
- Special vinyl acetate tubes, SKC-ST-226-68, SKC Inc., Eighty Four, PA 15330.
- Vinyl acetate UCC, LHQ, Inhibited with hydroquinone.
- Carbon disulfide, Mallinckrodt ACS grade or equivalent. Acetone, Spectroquality Matheson, Coleman & Bell or equivalent.
- Hypodermic syringes 10, 50 and 100- μ L sizes.
- Close-mesh Polynet 1/4"-3/8" No. 9405-10 Cole-Parmer Instrument Company, or equivalent.
- Cotton tipped applicators, 6-inch, Diamond International Corp. or equivalent.
- Sonic bath, Sonatron Corp. or Burrel Shaker, Burrel Corp., or equivalent.
- Volumetric flasks, 10-mL size.
- Soap bubble flowmeter calibrator.
- Stopwatch.
- Rotometers to cover range of 10 to 100 cc and 800 to 1200 cc per minute.
- Glass vial, 4.0-mL, with Teflon Septum, Supelco 2-2954 or equivalent.

preparation of carbon tubes

Tubes are available from SKC Inc., RD 1, 395 Valley View Road, Eighty Four, PA 15330, Catalog Number SKC-ST-226-68.

sampling procedure

- Immediately before sampling, break the tips of the tube to provide an opening of at least 2 mm.

- Attach the tube to a portable personnel pump with the back-up section next to the pump.
- Long-term sampling.* Set the air flow rate through the carbon tube from 50 cc to 100 cc per minute.
- Short-term sampling.* Flow rates of up to one liter per minute can be used to collect sufficient quantities of vinyl acetate to measure quantitatively. Use a MSA Model S personnel pump or equivalent to obtain these flow rates.
- If a personnel sample is to be taken, put the tube in an appropriate holder to protect the individual from the glass tube. (The Poly-net, paragraph 4f, works well with these tubes.)
- A total of 15-40 liters for personnel and 15-90 liters for area samples of air should be sampled. Record the temperature and the barometric pressure at the sampling site. Record the total liters of air pulled through the tube.
- Cap the ends of the tube with the polyethylene Caplug provided and send the tubes to the laboratory for analysis. Tubes must be kept refrigerated unless they are analyzed within 5 days of sampling.
- Send a tube which has had no air pulled through it to the laboratory at the same time to serve as a blank.

analytical procedure

- Remove the Caplug from the carbon section.
- Make a small hook at the end of a piece of wire and remove the glass wool retainer plug and discard. Make sure no carbon particles adhere to the glass wool plug.
- Transfer the carbon from the primary section and backup section of the tube into separate Supelco desorption vials. Cool in wet ice 5 minutes while capped.
- Pipet 2 mL of acetone into 98 mL of carbon disulfide and mix well. Pipet 1.0 mL of this solvent into each desorption vial and cap securely.
- Sonify for 5 minutes at ambient temperature or shake on the Burrel shaker for 15 minutes. Do not allow to stand more than 90 minutes before analyzing. The vials should be shaken vigorously to desorb the vinyl acetate, if no mechanical device is used.
- Solvent flush injection technique. This injection technique is designed to eliminate difficulties arising from blow-back or distillation within the needle of the microliter syringe.
- Flush a 10- μ L syringe with CS₂-acetone several times to wet the barrel and plunger.
- Draw 1- μ L of CS₂-acetone 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 CS₂-acetone from the sample with a pocket of air.
- Dip the needle into the sample solution in the

desorption vial and withdraw the plunger until the air bubble between the solvent and the sample has passed the 2- μ L mark on the syringe.

- j) Remove the top 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.
- k) Pull the plunger back an additional 0.5 μ L to prevent the sample solution from evaporating from the tip of the needle.
- l) Inject the entire contents of the syringe into the chromatograph.
- m) Measure the peak area or height and determine the organic content from a previously prepared calibration curve.
- n) Analyze the backup (small) section of carbon tube in the same manner as the primary.

calibration curve

- a) By means of a microliter syringe, inject 10.0 μ L of vinyl acetate into a 10-mL volumetric flask containing the carbon disulfide - 2 percent acetone desorption solvent. Dilute to the mark with additional CS₂-acetone. This solution contains 928 μ g of vinyl acetate per mL.
- b) Pipet .25, 0.5, 1, 2, and 4-mL aliquots of the 928 μ g per mL solution into respective 10-mL volumetric flasks and dilute to the mark with CS₂-acetone. These solutions contain 23.2, 46.4, 92.8, 185.6, 371.2 μ g per mL of vinyl acetate respectively.
- c) Inject these standards into the chromatograph using the procedure described in Section 7, paragraph f through i.
- d) Plot peak height or area versus micrograms of vinyl acetate per mL.

desorption efficiency

- a) The desorption efficiency (percentage of the adsorbed vinyl acetate removed from the carbon by the CS₂-acetone) can vary from one laboratory to another and from one batch of carbon to another. The desorption efficiency may vary with the quantity of vinyl acetate adsorbed on the carbon.
- b) Remove the Caplug from the same lot to be used for sampling. Remove the glass wool retainers. Transfer the content of the primary section (150 mg) into respective desorption efficiency test tubes.
- c) Remove the glass wool separators from the carbon

tubes and fill 2 additional desorption efficiency test tubes by combining the backup section (75 mg) from two carbon tubes into one desorption tube.

- d) Cap the open end of the desorption test tubes with Parafilm.
- e) Pipet 0.5 mL of vinyl acetate into a 10-mL volumetric flask containing 7 to 8 mL of hexane. Dilute to the mark with additional hexane.
- f) By means of a 10- μ L syringe, inject 2- μ L of this solution into each of four desorption tubes containing the carbon. Insert the needle of the microliter syringe through the Parafilm and inject directly into the carbon, moving the needle at intervals to spread the solvent on the carbon. These tubes contain 92.8 μ g of vinyl acetate.
- g) Into each of the 2 remaining tubes, inject 2- μ L of hexane. Reserve these tubes as blanks. (Make sure the microliter syringe is thoroughly clean before injecting the hexane. If the same syringe from paragraph f is used, a memory effect could cause a false blank.)
- h) Reseal the tubes with an additional piece of Parafilm. Allow the tubes to stand overnight before analyzing to assure complete adsorption of the organic onto the carbon.
- i) Follow the procedure as outlined in Section 7, paragraphs c through m for desorption and analysis of the carbon, including the blank tubes.
- j) Calculate the desorption efficiency as follows:

$$\frac{\text{Average weight } (\mu\text{g}) \text{ recovered} - \text{Blank, } \mu\text{g}}{\text{weight } (\mu\text{g}) \text{ added}} = \text{D.E.}$$

calculations

$$\frac{(A-B) \times 24.45 \times 760 \times (T+273^\circ)}{\text{D.E.} \times L \times 86.09 \times P \times 298} = \text{vinyl acetate, ppm by volume at } 25^\circ\text{C and } 760 \text{ mm Hg}$$

A = micrograms of vinyl acetate per mL in sample carbon tube read from calibration curve

B = micrograms of vinyl acetate on the blank carbon tube

D.E. = desorption efficiency, paragraph 9j

L = total volume of air sampled in liters

P = pressure (mm Hg) of air sampled

T = temperature ($^\circ$ C) of air sampled

interferences from other contaminants

The CO-990 column is capable of resolving the following compounds from vinyl acetate: Acrylonitrile, ethylacrylate, methyl methacrylate.