ETHYL CORPORATION
RESEARCH AND DEVELOPMENT DEPARTMENT

BATON ROUGE, LOUISIANA

THE DIFFUSIVITY OF VCM IN 8237 BOTTLE COMPOUND

A PRELIMINARY REPORT

December 19, 1975

G. A. Daniels
G. C. Gacke

THE DIFFUSIVITY OF VCM IN 8237 BOTTLE COMPOUND

Abstract

Diffusivity values for VCM in 8237 PVC bottle compound have been measured for cubes with initial VCM concentrations 0.04 mg/kg to 37 mg/kg when surrounded by air, water, and 50 percent aqueous ethanol at 75°F and 120°F. The cubes of PVC and the surrounding medium were sealed in 156 ml serum bottles and the quantity of VCM diffused out of the cubes was determined by measuring the concentration of VCM in the headspace as a function of time.

The results of the experiment indicate:

1. The quantity of VCM diffused from the PVC cubes is proportional to the initial VCM concentration. The diffusion process is linear.

2. The room temperature diffusivity of VCM in 8237 PVC bottle compound is greater than in PVC pipe compound by a factor of 2 to 3.

3. The surrounding medium is important. The diffusivity of VCM in 8237 PVC compound surrounded by water is 1.5-2 times the diffusivity of VCM in 8237 PVC compound surrounded by air while if the surrounding medium is 50 percent ethanol the diffusivity value is 5-7 times the value in the air experiments.

Introduction

The purpose of the experimental work presented in this report was to determine the effect of the concentration of vinyl chloride monomer (VCM) in the PVC on the diffusion rate and the diffusivity of VCM in 8237 PVC bottle compound and to determine the effect on diffusion rates of air, water, and a 50 percent aqueous ethanol solution as the medium surrounding the PVC. Earlier studies made of the diffusion of VCM from 8237 compound PVC bottles into 50 percent ethanol solutions were made at VCM levels of 100-400 ppm while 8237 PVC bottle compound manufactured at present contains less than 1 ppm VCM. It is desirable, therefore, to determine if the diffusivity is the same at the 1 ppm level as at the higher levels. The question of the effect of the surrounding medium arises from a comparison of the room temperature (75°F) diffusivity of VCM determined for PVC pipe compound ($6.6 \cdot 10^{-13}$ cm^2/sec) surrounded by air or water as compared to the diffusivity determined for 8237 compound bottles filled with 50 percent ethanol ($1.04 \cdot 10^{-11}$ cm^2/sec). The composition of 8237 bottle compound is not the same as for PVC pipe compound (the major difference is the impact modifier in the bottle compound) so that the difference between pipe and bottle compound could be due to composition or to the solvent effect of the surrounding medium or to both reasons.

Experimental Design

Cubes (about 0.12") of 8237 PVC bottle compound were added to a 156 ml serum bottle and 50 ml of the surrounding solvent (if any) was added. For runs at room temperature and the runs at 120°F using water as the surrounding medium the charge of PVC cubes was 50 ml (65 g) while the charge was 100 g for the 120°F run using air as the surrounding medium. Four samples of PVC cubes were used 0.04, 0.43, 5.5, and 37 mg VCM/Kg PVC. Duplicate or triplicate serum bottles were prepared for each condition and time. The time schedule was 1, 3, and 6 weeks for the 120°F experiments with air, and 1, 3, 6, and 12 weeks for the 120°F experiments using water and air. For all the room temperature experiments, the time schedule is 3, 9, 18, and 36 weeks.

The concentration of VCM in the head space of the serum bottles is determined by a gas chromatograph with a flame ionization detector. The total quantity of VCM in the head space and the surrounding medium (if present) is calculated using the volume of the head space, the volume of the surrounding medium and experimental values of the distribution coefficient between the solvent and air. These values were 0.973 for concentration of VCM in air compared to water (g/ml in gas)/(g/ml in water) and 0.208 for the concentration of VCM in air compared to 50 percent ethanol).

Experimental Results

The experimental program for 8237 PVC bottle compound using air as the surrounding medium is complete. The 120°F run using water as the surrounding medium as well as all the room temperature runs are incomplete. The experimental results are given in Tables 1-5. The values given in Tables 1-5 represent average values for the replicated runs, except in a few cases where leaks appeared to occur, these values were not included in the averages.

Analysis of Experimental Data

A diffusion model has been used to analyze the experimental data and to estimate approximate diffusivity value of VCM in 8237 PVC bottle compound when surrounded by different materials. The following assumptions have been made in analyzing the data.

1. The fluid phases surrounding the PVC cubes is perfectly mixed.

2. The concentration of VCM at the surface of cubes is in equilibrium with the concentration of VCM in the fluid phases. This equilibrium is described by a Henry's law constant.

3. The rate controlling step is the diffusion of VCM in the solid phase. The diffusion coefficient is assumed to be independent of concentration.

4. The concentration profile in the solid at the start of the experiment is given by the solution of the diffusion equation with initial constant composition and zero on the boundary for the manufacturing and storage period before the experiment was started.

5. The cubes can be treated as spheres. Mathematical solutions are available[1] for the case of diffusion from a sphere into a finite mixed solvent for the case of constant initial composition and have been derived for the case of the initial concentration being the solution of the diffusion equation with zero on the boundary[2]. The corresponding equations for a cube are not available and appear to represent a formidable problem in solution. Diffusion coefficients derived from the equations for spheres are only approximations but comparison between the diffusion coefficients for various cases is valid.

A study of the experimental data in Tables 1-5 shows that the amount of VCM that has diffused into the headspace is proportional to the initial concentration of VCM in the PVC cubes. For the case of Sample 1 (0.04 mg VCM/Kg PVC) in air at 120°F the headspace analyses are of questionable validity as large interferring peaks were present

---

[1] Crank "Mathematics of Diffusion," page 84-98, Oxford, 1956.

[2] These equations are presented in the Appendix.

in the chromatographic charts. Except for these data, all concentrations dependent data for each case have been pooled. This linear behavior of the quantity of VCM diffused with initial VCM concentration is strong evidence that both the Henry's law constant and the diffusion coefficient in independent of concentration in the region studied. The approximate values of the diffusion coefficient calculated from this study are given in Table 6.

It is apparent from the data given in Table 6 that both the composition of the PVC compound and the surrounding medium can make significant changes in the diffusivity of VCM. As would be expected, temperature is a significant variable. Water did not appear to have a significant effect on the diffusivity of VCM in pipe compound but for 8237 PVC bottle compound the diffusivity of VCM for water as the surrounding medium is 1.5-2.0 times larger than for air while the diffusivity of VCM for 50% ethanol as the surrounding medium 5-7 times larger than for air. The diffusivity of VCM in 8237 bottle compound is 2-3 times the diffusivity in PVC pipe compound.

APPENDIX

TABLE 1

8237 PVC Bottle Compound at 120°F
Air is the Surrounding Medium

Sample	1	2	4	7
Initial VCM mg/Kg	0.04	0.43	5.5	37.
		1 Week		
PPM VCM in Headspace V/V	~ 1	5.7	77.	514.
µg VCM diffused out of cubes	0.25	1.42	19.4	135.8
		3 Weeks		
PPM VCM in Headspace V/V	~ 1.8*	9.9	118.	715.
µg VCM diffused out of cubes	0.44	2.48	29.7	179.3
		6 Weeks		
PPM VCM in Headspace V/V	~ 1.6*	11.1	134.5	827.
µg VCM diffused out of cubes	0.40	2.78	33.8	207.4

*Interferring peaks in chromatographic chart makes these data very uncertain.

TABLE 2

8237 PVC Bottle Compound at 120°F
Water is the Surrounding Medium

Sample	1	2	4	7
Initial VCM mg/Kg	0.04	0.43	5.5	37
		1 Week		
PPM VCM in Headspace V/V	0.46	4.8	69.5	468.
µg VCM diffused out of cubes	0.125	1.32	19.1	128.5
		3 Weeks		
PPM VCM in Headspace V/V	0.84	8.0	79.3	730.
µg VCM diffused out of cubes	0.23	2.20	28.2	202.
		6 Weeks		
PPM VCM in Headspace V/V	1.25	9.9	111.	764.
µg VCM diffused out of cubes	0.33	2.62	29.4	203.
		12 Weeks		
PPM VCM in Headspace V/V				
µg VCM diffused out of cubes				

TABLE 3

8237 PVC Bottle Compound at Room Temperature
Air is the Surrounding Medium

Sample	1	2	4	7
Initial VCM mg/Kg	0.04	0.43	5.5	37
		3 Weeks		
PPM VCM in Headspace V/V	0.125	0.98	13.0	77.4
µg VCM diffused out of cubes	0.035	.265	3.52	21.0
		9 Weeks		
PPM VCM in Headspace V/V	0.19	1.95	24.4	137.5
µg VCM diffused out of cubes	0.052	0.529	6.59	37.2
		18 Weeks		
PPM VCM in Headspace V/V				
µg VCM diffused out of cubes				
		36 Weeks		
PPM VCM in Headspace V/V				
µg VCM diffused out of cubes				

TABLE 4

8237 PVC Bottle Compound at Room Temperature
Water is the Surrounding Medium

Sample	1	2	4	7
Initial VCM mg/Kg	0.04	0.43	5.5	37.
		3 Weeks		
PPM VCM in Headspace V/V	0.11	1.3	18.0	120.5
µg VCM diffused out of cubes	0.03	0.355	4.92	33.2
		9 Weeks		
PPM VCM in Headspace V/V	0.20	2.6	33.5	239.
µg VCM diffused out of cubes	0.053	0.71	8.94	63.8
		18 Weeks		
PPM VCM in Headspace V/V				
µg VCM diffused out of cubes				
		36 Weeks		
PPM VCM in Headspace V/V				
µg VCM diffused out of cubes				

TABLE 6

Diffusivity of VCM in PVC Compounds

Compound	Surrounding Medium	Temperature °F	Diffusivity cm^2/sec
8237 Bottle	Air	120	$1.5 \cdot 10^{-11}$
8237 Bottle	Water	120	$3.3 \cdot 10^{-11}$
8237 Bottle	Air	75	$1.4 \cdot 10^{-12}$
8237 Bottle	Water	75	$2.1 \cdot 10^{-12}$
8237 Bottle	50% Ethanol	75	$8.0 \cdot 10^{-12}$
8237 Bottle*	Air - 50% Ethanol	120	$8.3 \cdot 10^{-11}$
8237 Bottle*	Air - 50% Ethanol	75	$1.04 \cdot 10^{-11}$
PVC Pipe	Air	75	$6.6 \cdot 10^{-13}$
PVC Pipe	Water	75	$6.6 \cdot 10^{-13}$

*Bottle extraction experiments.

Derivation of Diffusion Equation

for

Limited Fluid Volume and Initial Concentration Given by the Solution of the Diffusion Equation with Constant Initial Concentration and Zero on the Boundary

Spherical Geometry

Diffusion Equation $\frac{\partial C_s}{\partial t} = \mathcal{D}\left(\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r}\frac{\partial C_s}{\partial r}\right)$

Boundary Conditions

1. $K C_L = C_s (r=a)$ Equilibrium
2. $-\mathcal{D} 4\pi a^2 \left(\frac{\partial C_s}{\partial r}\right)_{r=a} = V_L \frac{dC_L}{dt}$ Material balance

Initial Condition

$$C_s(t_0) = -\frac{2C_0}{\pi}\frac{a}{r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\left(\frac{n\pi r}{a}\right)e^{-\frac{\mathcal{D}n^2\pi^2 t_0}{a^2}}$$

Solution

$$\frac{C_s}{C_0} = \frac{6}{\pi^2(1+\alpha)}\sum_{n=1}^{\infty}\frac{e^{-\frac{\mathcal{D}n^2\pi^2 t_0}{a^2}}}{n^2} +$$

$$36\frac{a}{r}\sum_{k=1}^{\infty}\frac{\sin\left(\frac{z_k}{a}r\right)e^{-z_k^2\frac{\mathcal{D}t}{a^2}}}{\sin(z_k)\left(9\alpha+9+4(\alpha z_k^2)\right)}\sum_{n=1}^{\infty}\frac{e^{-\frac{n^2\pi^2\mathcal{D}t_0}{a^2}}}{\left[(n\pi)^2 - z_k^2\right]}$$

at $r = a$ (boundary)

SPI-02943

$$\frac{C_s(a)}{C_0} = \frac{6}{\pi^2(1+\alpha)}\sum_{n=1}^{\infty}\frac{e^{-\frac{\mathcal{D}n^2\pi^2 t_0}{a^2}}}{n^2} +$$

$$36\left[\sum_{k=1}^{\infty}\frac{e^{-\frac{z_k^2\mathcal{D}t}{a^2}}}{\left[9\alpha+9+4(\alpha z_k^2)\right]}\right]\sum_{n=1}^{\infty}\frac{e^{-\frac{n^2\pi^2\mathcal{D}t_0}{a^2}}}{\left[(n\pi)^2 - (z_k)^2\right]} -$$

Average concentration

$$\frac{\bar{C}_s}{C_0} = \frac{6}{\pi^2(1+\alpha)} \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2 \frac{\mathcal{D}}{a^2} t_0}}{n^2} -$$

$$36\alpha \sum_{k=1}^{\infty} \frac{e^{-z_k^2 \frac{\mathcal{D}}{a^2} t}}{\left[9\alpha + 9 + (\alpha z_k)^2\right]} \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2 \frac{\mathcal{D}}{a^2} t_0}}{(n^2\pi^2 - z_k^2)}$$

z_k are the roots of

$$\tan z_k = \frac{3 z_k}{3 + \alpha z_k^2}$$

C_s = Concentration in the sphere

C_L = Concentration in surrounding fluid

$\mathcal{D}$ = Diffusion coefficient

K = Henry's Law constant

r = Radial coordinate

a = Radius of sphere

$\alpha = \frac{V_L}{4/3 \cdot \pi a^2 K}$

Predicted VCM Concentration
In The Contents of PVC Bottles
Manufactured From PVC Compound
Containing 1 mg/kg VCM (1 ppm)

The three attached charts show the VCM content of 50 per cent ethanol (Figure 1) and water (Figure 2 and Figure 3) calculated for a level of VCM in the PVC of 1 mg/kg assuming no VCM is lost during blowing. The diffusivity of VCM in 8237 bottle compound used for Figures 1 and 2 is $1.04 \cdot 10^{-14}$ cm^2/sec which was derived from our studies of 50 per cent ethanol in 2 ounce bottles presented in our January 17, 1975, repott. Figure 3 shows the same calculation using a value of $2.1 \cdot 10^{-12}$ cm^2/sec for the diffusivity of VCM in PVC exposed to water taken from our preliminary report of December 19, 1975, describing our studies of the diffusion of VCM from cubes into air, water and 50 per cent ethanol.

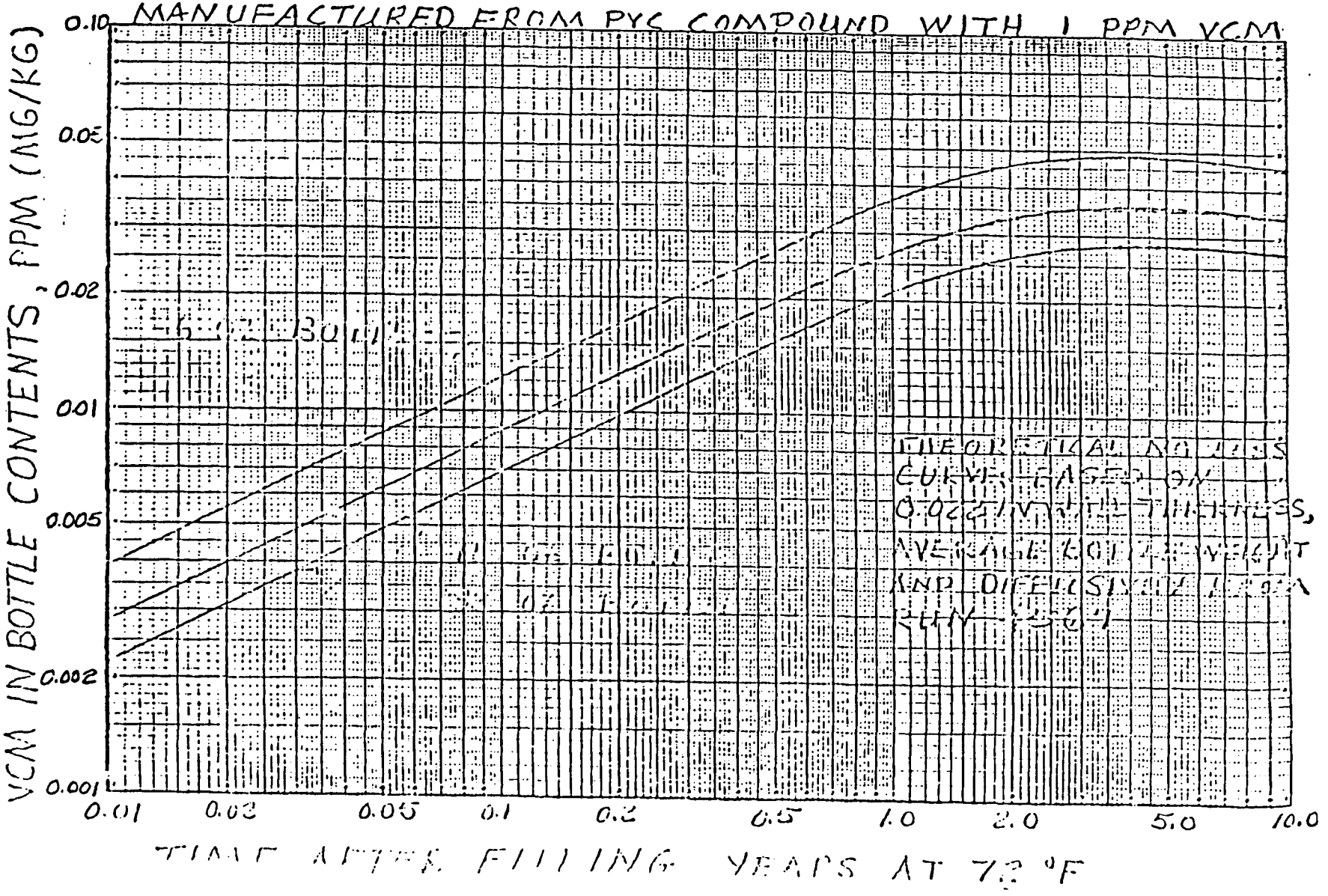
The lower value of the diffusivity changes the time scale of the diffusion of VCM into water but does not change the maximum concentration in the water.

GAD/bwb

SPI-02945

VCM CONTENT OF 50% ETHANOL STORED IN PVC BOTTLES

FIGURE 1



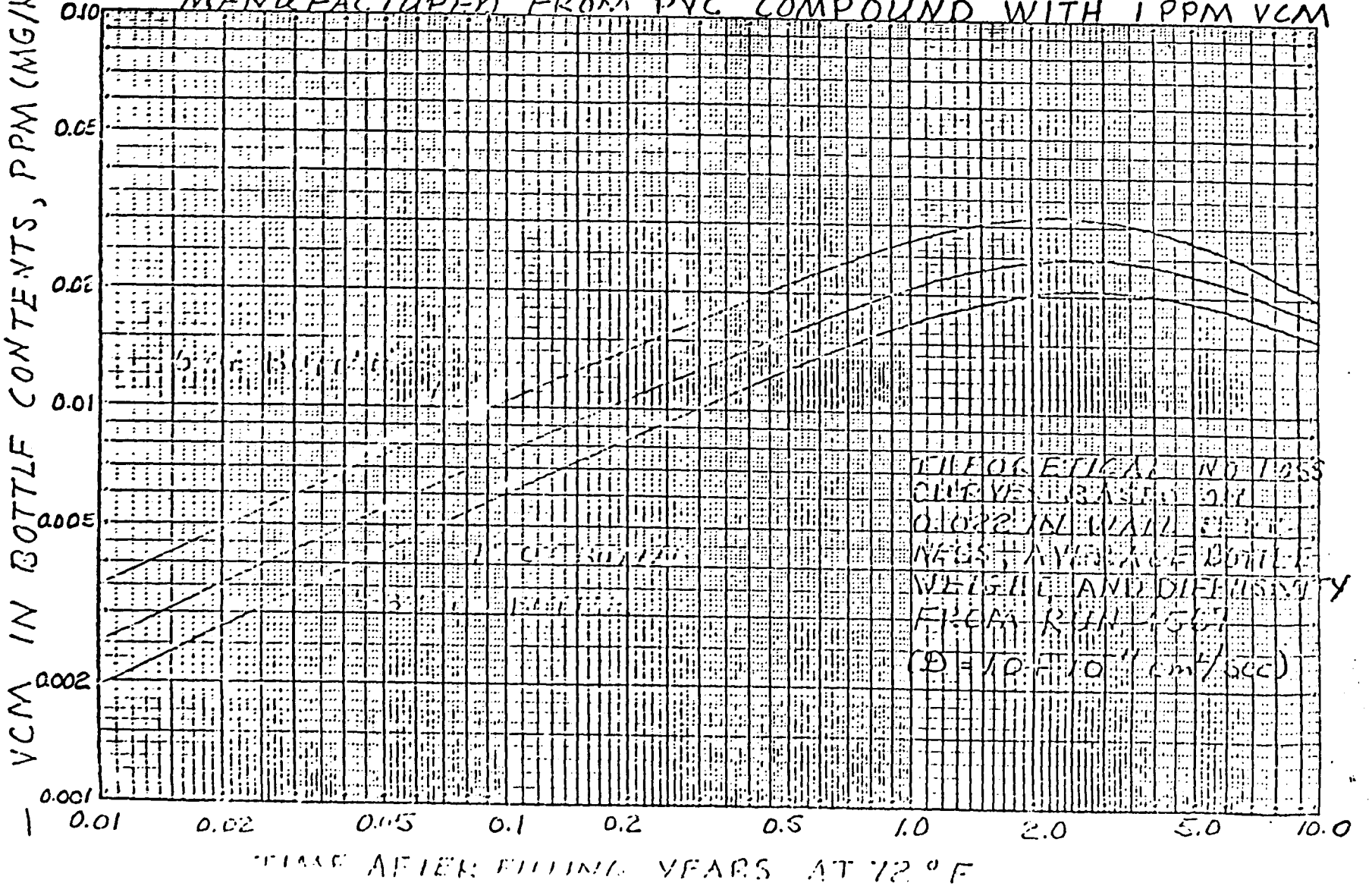
SPI-02946

NO. 31,123 LOGARITHMIC: THREE BY TWO 3-INCH CYCLES.

Codex IN STOCK DIRECT FROM CODEX BOOK CO., INC. NORWOOD, MASS. 02062

FIGURE 2

VCM CONTENT OF WATER STORED IN PVC BOTTLES MANUFACTURED FROM PVC COMPOUND WITH 1 PPM VCM

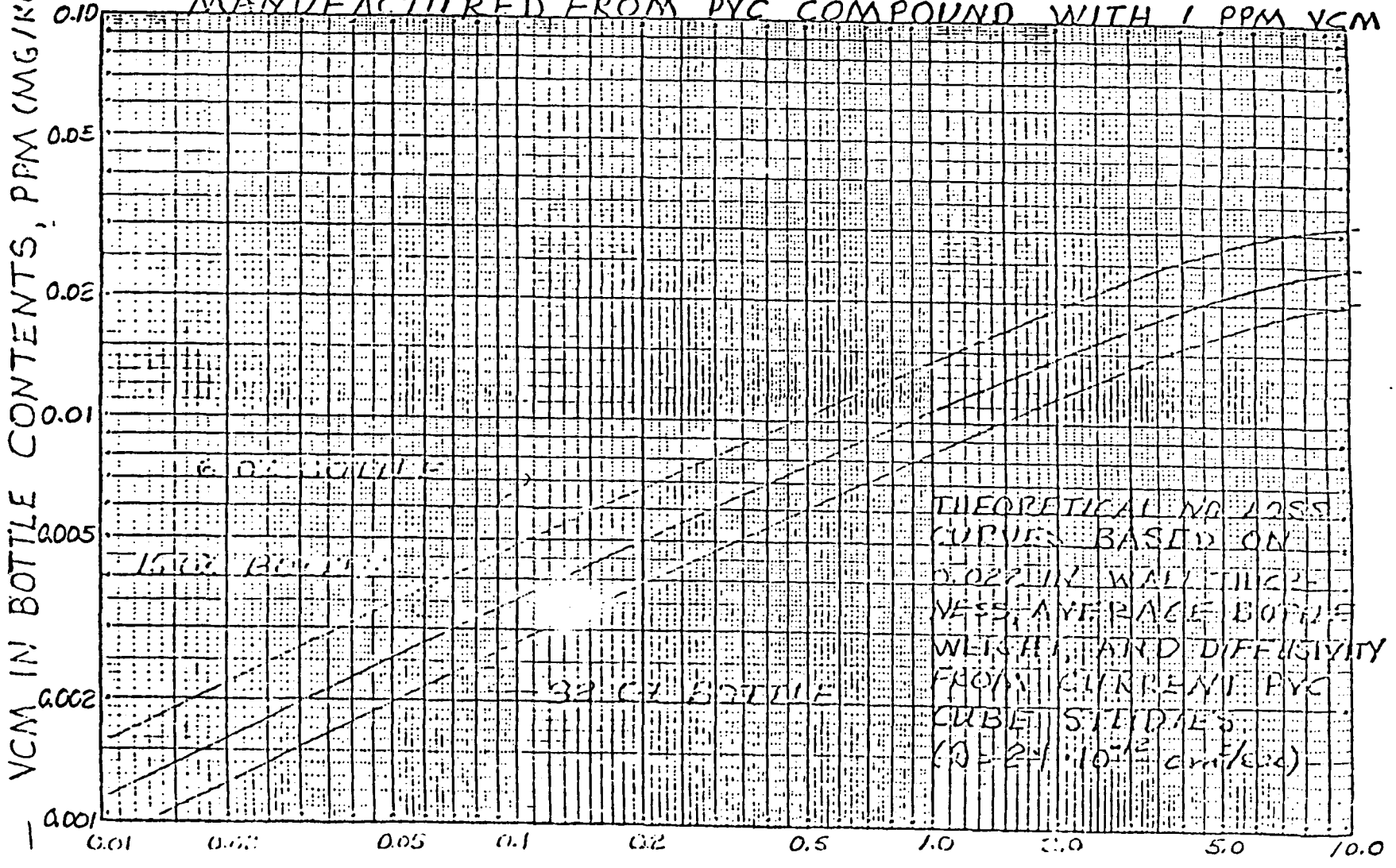


TIME AFTER FILLING, YEARS AT 72°F

SPI-02947

FIGURE 3

VCM CONTENT OF WATER STORED IN PVC BOTTLES MANUFACTURED FROM PVC COMPOUND WITH 1 PPM VCM



TIME AFTER FILLING, YEARS AT 75°F

SPI-02948

Part 2 - Additional Comments on Analytical Procedures (including the relevant analytical procedures as Attachment 1).

The analytical method used in this work is given in Attachment 1 to this addendum. The method used is a manual headspace analysis.

ATTACHMENT 1

A GAS CHROMATOGRAPHIC METHOD FOR THE MEASUREMENT OF PARTS PER BILLION VINYL CHLORIDE MONOMER IN WATER AND 50% ETHANOL BY HEADSPACE ANALYSIS

I. Scope

This method is designed to determine parts per billion quantities of vinyl chloride monomer in water and 50% ethanol by analysis of the gas in the headspace above the liquid by flame ionization gas chromatography.

II. Outline of Method

The liquid sample is sealed in a serum type bottle and stored at ambient temperature.

A one milliliter sample of the gas in the vapor space from the bottle is injected into the gas chromatograph. From the concentration found in the headspace and the partition coefficient, the concentration of VCl in the liquid is determined.

III. Apparatus

A. Gas Chromatograph - A Bendix 2200 gas chromatograph or the equivalent equipped with a flame ionization detector.

B. Gas Chromatographic Column - A 1/8" x 25' stainless steel column packed with 50% SE-52 on 80/100 mesh. Gas Chrom Q conditioned for 16 hours at 200°C.

C. Syringe - A 2.0 ml., gas tight, Series A-2 Pressure-Lok syringe from Precision Sampling Corp., Baton Rouge, Louisiana 70815.

D. Data Collection System - A Hewlett-Packard 3380 recording integrator or computer (IBM/7).

E. Serum Bottles - 125 ml nominal capacity, complete with serum stoppers (flat rubber with Teflon face) and aluminum caps.

IV. Reagents

A. Vinyl Chloride Monomer in Nitrogen Gas Standards:

IV. Reagents (Cont'd)

1. Minicyl Calibration Gas - 1 ppm and 10 ppm (v/v) available from MG Scientific Division of MG Tech. Prod., 1100 Harrison Ave., Kearny, N. J. 07029.

2. Calibration Gas Standards - 25 ppm and 50 ppm (v/v) available from Gas Analytical Services Department of Airco Industrial Gases, 4228 Rhoda Ave., Baton Rouge, Louisiana 70815.

B. Vinyl Chloride - High purity, available from Ethyl Corporation, P.O. Box 341, Baton Rouge, Louisiana 70821.

V. Gas Chromatographic Conditions

A. Carrier Gas - Helium at 30 cc/min.

B. Detector - Flame ionization.

C. Hydrogen Flow Rate - Refer to instrument manual for optimum conditions.

D. Air Flow Rate - Refer to instrument manual for optimum conditions.

E. Injection Part Temp. - 150°C.

F. Detector Temperature - 300°C.

G. Oven Temperature - Ambient (25-30°C)

VI. Calibration

A. Inject 1.0 ml aliquots of each gas standard into the gas chromatograph (each standard should be analyzed in triplicate) and determine the area of the VCl peak. From the concentration of the standards and their corresponding areas calculate a calibration factor for each analysis as follows:

$$CF = \frac{A}{C}$$

where: CF = calibration factor (area units/ppm)

A = Area of VCl peak

C = Concentration of VCl (ppm) in standard

This calibration should be carried out each time a series of samples is analyzed.

VII. Determination of Partition Coefficient

A. Transfer a known volume (100 ml) of liquid (water or 50% ethanol) to a 125 ml (156 ml actual volume) serum bottle. Seal the bottle with a serum stopper and aluminum cap. By means of a calibrated 10 µl gas tight syringe, inject 2.0 µl of pure vinyl chloride into the liquid in the sealed bottle. Prepare additional samples containing 5.0 µl and 10.0 µl of pure vinyl chloride per 100 ml of liquid. Shake the samples for 10 minutes and allow to stand for 15-30 minutes for vapor/liquid equilibrium to be established.

B. By means of a 2 ml gas tight syringe, withdraw approximately 1.4 ml of vapor space (headspace) from the sample bottle. Adjust the volume to 1.0 ml and inject into the gas chromatograph. Measure the area of the VCl peak. Repeat this procedure for the other samples.

C. Calculate the partition coefficient (vapor/liquid) as follows:

$$P.C. = \frac{C'_{(HS)} \times V_{(liq.)}}{(V_{VCl} \times 2.55) - (C'_{(HS)} \times V_{(HS)})}$$

where: P.C. = partition coefficient (vapor/liquid)

$C'_{(HS)}$ = concentration (µg/l) of VCl in headspace

$$C'_{(HS)} = C_{(HS)} \times \frac{62.5}{24.45}$$

$C_{(HS)}$ = concentration (ppm v/v) of VCl in headspace

62.5 = mol. wt. of VCl

24.45 = molar volume @ 25°C and 760 mm Hg

$V_{(liq)}$ = volume (liters) of liquid phase

$V_{(VCl)}$ = volume (µl) of VCl injected

2.55 = vapor density (µg/µl of VCl at 25°C and 760 mm Hg

$V_{(HS)}$ = volume (liters) of headspace

The partition coefficient for water is approximately one and the partition coefficient for 50% ethanol is approximately 0.2 based on experimental data obtained in the Ethyl R&D laboratories.

VIII. Procedure

A. Carefully transfer 100 ml of the liquid to be analyzed (water or 50% ethanol) to a 125 ml (156 ml actual) serum bottle. Insert a serum stopper and seal with an aluminum cap. Shake the bottle for 10 minutes and allow to stand for 15 minutes to establish vapor/liquid equilibrium.

B. Insert the needle of a 2 ml gas tight syringe into the vapor space of the bottle and withdraw about 1.4 ml of vapor (headspace) into the syringe. Adjust the sample volume to 1.0 ml and inject into the gas chromatograph. Measure the area of the vinyl chloride peak.

C. For 50% ethanol samples, heat the column oven to 100°C for about five minutes after the VCl peak has eluted to elute ethanol from the column. Reestablish the column at ambient (25-30°C) before analyzing any additional samples.

IX. Calculations

A. Calculate the original concentration of VCl in the liquid as follows:

$$C_{(liq)} = \frac{\frac{C'_{(HS)} \times V_{(liq)}}{P.C.} + C'_{(HS)} \times V_{(HS)}}{V_{(liq)}}$$

where: $C_{(liq)}$ = concentration (µg/l) of VCl in the liquid

$C'_{(HS)}$ = concentration (µg/l) of VCl in headspace

$C'_{(HS)} = C_{(HS)} \times \frac{62.5}{24.45}$

$C_{(HS)}$ = concentration (ppm v/v) found of VCl in headspace.

62.5 = mol. wt. of VCl

24.45 = molar volume at 25°C and 760 mm Hg

$V_{(liq)}$ = volume (liters) of liquid

P.C. = partition coefficient (Section VII)

$V_{(HS)}$ = volume (liters) of headspace

X. Precision and Accuracy

A. The precision of the method has been found to be ± 10-15% relative for concentrations below 100 µg/l (ppb). The accuracy is dependent on the accuracy of the determination of the partition coefficient which is ± 10-15% for water.

B. The limit of detection for water samples is estimated to be < 1 µg/l and the limit of detection for 50% ethanol samples is estimated to be about 3 µg/l.

/jdt
10-30-75

ADDENDUM D

This attachment is relevant to the Ethyl Corporation submission "Vinyl Chloride Migration from PVC Bottles to Vegetable Oils and Food Simulating Solvents" dated September 17, 1976:

Part 1 - The original submission reproduced in its entirety

Part 2 - Additional information requested and submitted October 20, 1976 reproduced in its entirety (includes chromatograms)

Part 3 - Additional Comments on Methodology

Part 4 - Additional Comments on Analytical Procedures with Analytical Procedures provided as Attachments No. 1 and No. 2