Part 1 - Experimental Methodology (excerpt)

ETHYL CORPORATION
RESEARCH AND DEVELOPMENT DEPARTMENT
BATON ROUGE, LOUISIANA

EXTRACTION OF VINYL CHLORIDE FROM PVC BOTTLES BY THE BOTTLE CONTENTS

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Authors:

G. A. Daniels
D. E. Proctor

Experimental Program

An essential part of the experimental program is the analytical methods for VCM. These methods utilize flame ionization detector gas chromatography and are included as Appendix II.

One method is used for analyses of vinyl chloride in VCM-containing liquids and another for determining the VCM content of PVC in the form of powder, pellets or bottle walls. The method for VCM in liquid measurements involves the use of a long, small diameter column which provides adequate separation of VCM from other components of commercial products and solvents. The use of this method allows detection of as little as 10 ppb VCM. The penalties for using this type column are long elution and bake-out times between sample injections.

The method for VCM in PVC is an adaption of the prior method and involves injection of THF in which the PVC sample has been dissolved. A quantity of VCM corresponding to about one-quarter of a ppm in the dissolved sample can be detected. However, variable baseline interferences at the 1 ppm level adversely affect the accuracy.

Tables I to VI present the experimental data. The initial experiments included the use of standard FDA-recognized food-simulating solvents. A VCM level of 100-400 ppm in the compound was used to provide sufficient VCM to minimize analytical error. Table I shows the various solvents used; also note that two brands of vegetable oil are included in this series. This experiment was begun January, 1974, in response to an FDA request for room temperature storage VCM extraction data and the study continues. In April, 1974, 2-ounce capacity bottles made from <1 ppm VCM PVC were added to the series. The two-ounce bottles were used for several reasons: (1) to maximize VCM level potential in the product so it might be detected, (2) to reduce quantities of solvent used in migration testing, and (3) to allow filling of several bottles with each solvent so any particular bottle need not be resampled.

Table II is a table of results from another VCM extraction series begun in April. Both 16-ounce and 2-ounce bottles are used for storing weak VCM solvents in this series. The only real value of this series is to illustrate erratic results probable when using weak VCM solvents and poor sampling procedures. Largely on the basis of this experiment, methods were considerably altered. It was decided that subsequent experiments would involve using only strong VCM solvent (50% vol. ethanol) so that losses in sampling would not occur. Also, a procedure of filling numerous two-ounce capacity bottles was begun so that repeated sampling of the same bottle is unnecessary and so that duplicate and triplicate samples could be submitted for VCM analyses. The remaining results in Tables III, IV, V, and VI are for 2-ounce bottles with 50% ethanol.

TABLE I

Run 4555

Room Temperature VCM Migration - 72°F

Ethyl 8237 Octyl Tin Stabilized PVC Compound

Sample	Solvent	Bottle	Bottle VCM	PPM VCM in Contents 3 mos.	6 mos.	9 mos.	1 year
2	H_2O	16 oz. oval	7	0.03	0.09	0.07	
3	H_2O	2 oz. cylinder	< 1	< .01	< .01		
5	8% Ethanol	16 oz. oval	333	2.90	3.00	3.20	
6	8% Ethanol	16 oz. oval	7	0.08	0.05	< .01	
7	8% Ethanol	2 oz. cylinder	< 1	< .01	< .01		
9	50% Ethanol	16 oz. oval	333	4.90	4.70	6.02	
10	50% Ethanol	16 oz. oval	7	0.11	0.16	0.20	
11	50% Ethanol	2 oz. cylinder	< 1	< .01			
13	3% Acetic Acid	16 oz. oval	333	2.40	1.90	3.20	
14	3% Acetic Acid	16 oz. oval	7	0.06	0.06	0.06	
15	3% Acetic Acid	2 oz. cylinder	< 1	< .01	< .01		
17	n-Heptane	16 oz. oval	333	3.90	4.90	4.40	
18	n-Heptane	16 oz. oval	7	0.07	- -	0.19	
19	n-Heptane	2 oz. cylinder	< 1	< .01			
21	Soya Oil	16 oz. oval	333	2.70	4.80	6.45	
22	Soya Oil	16 oz. oval	7	0.065	0.115	0.15	
23	Soya Oil	2 oz. oval	< 1	< .01	< .01		
25	Cottonseed/Soya	16 oz. oval	333	2.10	4.25	6.60	
26	Cottonseed/Soya	16 oz. oval	7	.03	.095	.107	
27	Cottonseed/Soya	2 oz. oval	< 1	< .01	< .01		

(1) 16 oz. oval bottles are 36 gram bottles of the Imco Container Company's stock tapered oval design.

(2) Two 16 oz. bottles of each solvent are on test. Three month and six month samples were decanted from chilled PVC bottles into glass sample vial. Subsequent samples involve submitting storage bottles for sampling at chromatograph.

(3) 2 oz. bottles are sampled only once and discarded; multiple bottles filled.

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TABLE II

Run 4556

120°F Accelerated VCM Migration

Ethyl 9110 General Purpose Blow Molding Compound

Stock Cylinder Bottles

Sample	Solvent	Bottle Size (Oz.)	PPM VCM Bottle	PPM VCM Contents per Storage Time					
				1 wk.	2 wks.	3 wks.	4 wks.	5 wks.	8 wks.
1	H_2O	16	103	0.73	1.03	1.11	0.92	1.06	-
2	H_2O	16	173	1.02	0.12	1.94	0.03	<.01	0.03
3	H_2O	16	25	0.11	0.07	0.26	0.16	0.13	0.18
4	H_2O	2	103	1.27	1.72	2.15	1.74	2.00	2.80
5	H_2O	2	173	1.62	2.03	2.18	2.17	2.80	3.30
6	H_2O	2	25	0.09	0.20	0.19	0.14	0.18	0.22
7	8% Ethanol	16	103	0.92	0.17	0.16	1.16	1.50	1.08
8	8% Ethanol	16	173	0.96	0.46	0.12	1.40	1.70	0.93
9	8% Ethanol	16	25	0.14	0.16	0.23	0.17	0.20	0.02
10	8% Ethanol	2	103	1.61	1.30	-	1.66	-	2.05
11	8% Ethanol	2	173	1.62	1.95	2.91	1.87	2.40	3.70
12	8% Ethanol	2	25	0.13	0.21	0.19	0.21	0.14	0.14

(1) Each 16-oz. bottle resampled at least one time. Sample solvent was decanted into glass sample vials from chilled storage container.

(2) Two-ounce bottles were not resampled nor were solvent samples decanted into glass vials. Sample was taken at chromatograph.

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TABLE III

Run 4562

120°F Accelerated VCM Migration - 50% Ethanol

Ethyl 8237 - 82 PPM VCM - 2-Ounce Capacity Stock Cylinder

Storage Time	PPM VCM Contents	PPM VCM Bottle
3 days	0.49	
3 days	0.49	
3 days	0.54	
1 week	0.70	65
1 week	0.82	
1 week	0.66	
2 weeks	1.01	
2 weeks	1.37	
2 weeks	1.10	
2 weeks	1.30	56
2 weeks	1.08	
2 weeks	1.14	51
2 weeks	1.13	
2 weeks	1.05	
2 weeks	1.05	
2 weeks	1.02	
4 weeks	1.73	36
4 weeks	2.09	
4 weeks	1.96	37
2 mos.	3.84	29
2 mos.	3.58	26
2 mos.	3.51	31
4 mos.	4.28	13
4 mos.	3.78	14
4 mos.	4.10	15
5 mos.	4.76	
5 mos.	4.24	
5 mos.	4.55	

(1) Standard vinyl pulp cap liners used.

(2) No resampling of container, triplicate samples analyzed.

TABLE IV

Run 4564

Room Temperature VCM Migration - 50% Ethanol

Ethyl 8237 - 101 PPM VCM - 2-Ounce Capacity Stock Cylinder

Storage Time	PPM VCM Contents	PPM VCM Bottle
2 weeks	0.28	97
2 weeks	0.22	97
2 weeks	bad chart	94
4 weeks	- 0.88	
4 weeks	1.13	
4 weeks	0.76	
2 mos.	1.25	
2 mos.	1.00	
2 mos.	0.90	
4 mos.	1.43	
4 mos.	1.62	
4 mos.	1.65	

(1) Standard vinyl pulp cap liners used.

(2) No resampling of container.

TABLE V

Run 4566

120°F Accelerated VCM Migration - 50% Ethanol

Ethyl 8237 - 302 PPM VCM - 2-Ounce Capacity Stock Cylinder

Storage Time	PPM VCM Contents	PPM VCM Bottle
5 days	3.7	236
5 days	12.1 (reject)	245
2 weeks	5.7	204
2 weeks	4.6	208
2 weeks	4.4	211
4 weeks	11.0	149
4 weeks	11.7	148
4 weeks	11.25	141
6 weeks	14.1	130
6 weeks	14.7	143
6 weeks	13.8	107
3 mos.	18.5	36
3 mos.	17.3	43
3 mos.	15.6 (?)	44

(1) Foil liner heat-sealed over bottle mouth.

(2) No resampling of container.

(3) Chromatograph syringe needle breaks foil seal during sampling.

TABLE VI

Run 4567

Room Temperature VCM Migration - 50% Ethanol

Ethyl 8237 - 304 PPM VCM Bottle - 2-Ounce Capacity Stock Cylinder

Storage Time	PPM VCM Contents	PPM VCM Bottle
2 weeks	1.77	
2 weeks	1.70	
2 weeks	1.63	
1 month	2.94	267
1 month	2.84	270
1 month	3.00	272
2 months	5.11	236
2 months	4.61	251
2 months	4.95	237
3 months	6.60	
3 months	6.86	
3 months	6.70	

(1) Foil liner heat-sealed over bottle mouth.

(2) No resampling of containers.

(3) Chromatograph syringe needle breaks foil seal during sampling.

Experimental Procedure

The procedure that evolved from the succession of experiments can be briefly stated. First, a small batch of PVC molding compound is thoroughly mixed to insure that all bottles blown from it will contain like concentrations of VCM. Triplicate bottles from each batch are submitted for analyses at the time the bottles are filled with solvent. The analytical values are averaged to represent the beginning VCM level of the test bottles. Immediately after each bottle is filled with solvent to its rated capacity, a foil disc is heat-sealed over the mouth of the bottle which is then capped to protect the seal. (However, experiments indicate that commercial closure losses are negligible when 50% ethanol is used as the solvent.) The filled and sealed samples are kept at the appropriate temperature for the desired time interval. Triplicate samples are submitted for VCM analyses. The seals are broken only when the sample syringe pierces the foil. After sampling, many of the sample bottles are emptied and then analyzed for bottle wall VCM content.

Experimental Data Analysis

The experimental data shown by Tables III to VI is particularly useful for analysis because two sets, 4562 (Table III) and 4566 (Table V) were run at 120°F, while sets 4564 (Table IV) and 4567 (Table VI) were run at room temperature. The bottles for data sets 4566 and 4567 were blown the day before the bottles were filled, while the 4562 set was filled 78 days after the bottles were blown, and the 4564 set was filled 118 days after the bottles were blown. The compound for data sets 4566 and 4567 was from the same batch, while 4564 and 4562 were from different batches of compound. An analysis of the compound for 4566 and 4567 was not run when the bottles were blown, but a set of bottles were blown in January, 1974, from the same batch of compound. In January the compound analyzed 391 ppm VCM, while the bottles analyzed 333 ppm VCM. If the same amount of VCM were lost in blowing the bottles for 4566 and 4567, the compound would have contained about 356 ppm VCM as the bottles for 4566 and 4567 averaged 303 ppm VCM after blowing.

The contents for 4566 and 4567 are shown in Figure 4. All points for the 2 oz. bottles lie below the theoretical no initial loss curve. As the VCM loss during the blowing operation is about 15% (at least for the bottles blown in January), it is necessary to use the equations for Case II to determine the parameters of the model. The data sets 4566 and 4567 have two common parameters:

1. The initial concentration of the compound as bottles for both runs were blown from the same batch of compound.

2. The dimensionless time parameter which describes the VCM loss before filling, as all bottles used in 4566 and 4567 were blown and filled at the same times.

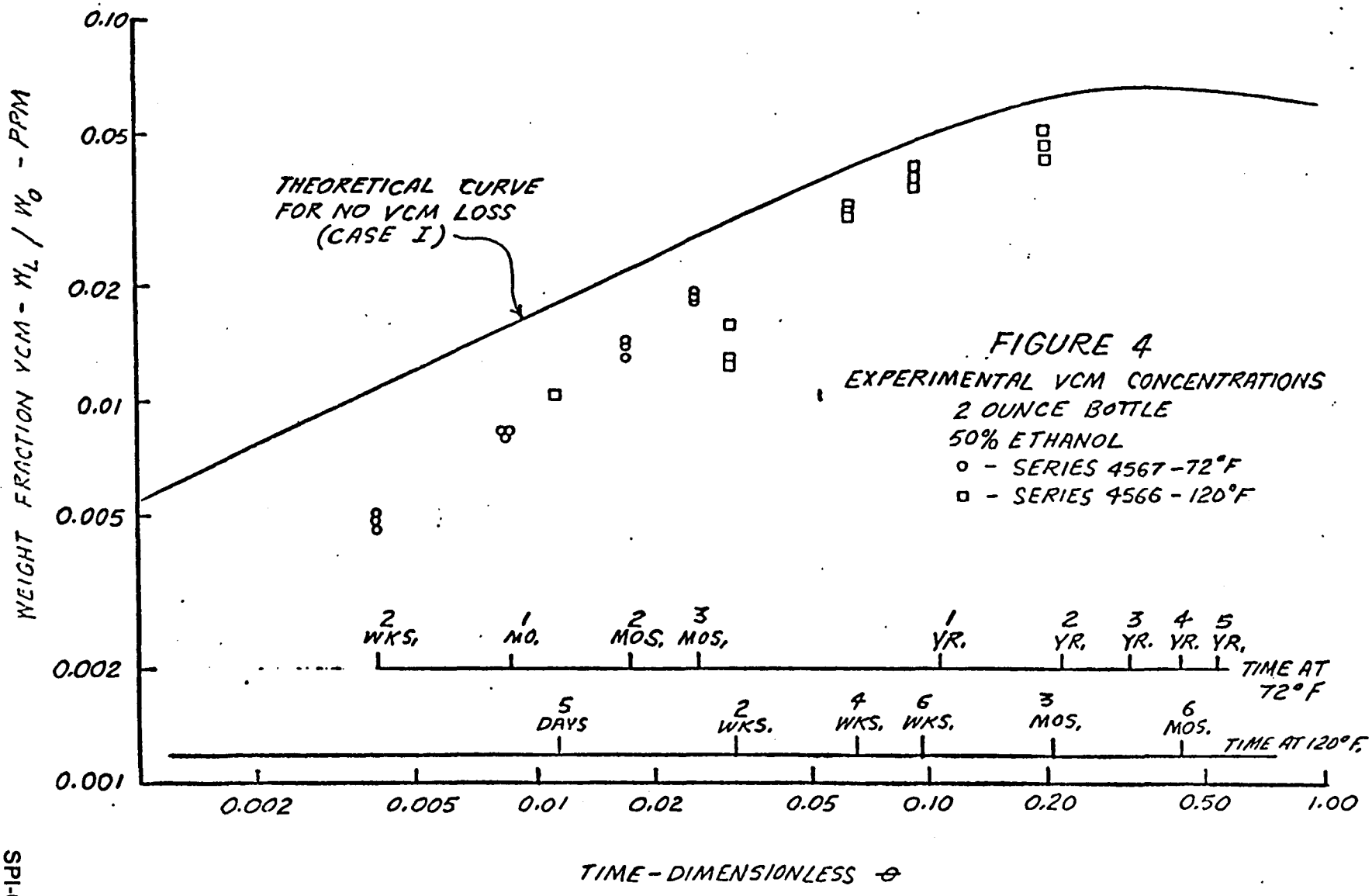

FIGURE 4

EXPERIMENTAL VCM CONCENTRATIONS
2 OUNCE BOTTLE
50% ETHANOL
o - SERIES 4567 - 72°F
□ - SERIES 4566 - 120°F

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The parameter D/l^2 is different for the two data sets as 4566 was run at 120°F, while 4567 was run at room temperature. Both the bottle content analyses and the bottle wall analyses have been included in the regression, using the appropriate equation for Case II given in Appendix I. The model parameters obtained by using a non-linear least square analysis are given as follows:

Runs 4566 and 4567

Parameter	Value	95% Confidence Limits	
		Lower	Upper
D/l^2 at 120°F, day^{-1}	$2.30 \cdot 10^{-3}$	$2.23 \cdot 10^{-3}$	$2.37 \cdot 10^{-3}$
D/l^2 at room temperature, day^{-1}	$2.88 \cdot 10^{-4}$	$2.64 \cdot 10^{-4}$	$3.13 \cdot 10^{-4}$
W_o, initial concentration of VCM in compound, ppm	346	336	357
θ_o, Dimensionless time corresponding to VCM loss before filling	$3.52 \cdot 10^{-3}$	$2.34 \cdot 10^{-3}$	$4.71 \cdot 10^{-3}$

Figure 5 shows the bottle content data for runs 4566 and 4567. The three data points of set 4566 at 2 weeks have been rejected during the regression.

Figure 6 shows the comparison of VCM concentration in the bottle wall for data sets 4566 and 4567. Some of the bottle wall data which deviates widely from the curve have been rejected during the regression.

A similar regression analysis has been made for the data of runs 4562 and 4564. The delay between blowing and filling has been included. For the 4564 series the 118 days of storage at room temperature plus about 12 days which corresponds to the vinyl chloride loss during blowing was used as the total delay time (130 days total). For the 4562 series the delay time at 120°F was estimated by dividing the sum of 78 days of storage at room temperature plus 12 days for blowing losses (90 days total) by the ratio of the 120°F diffusivity to the room temperature diffusivity determined from the analysis of the 4566 and 4567 data.

The D/l^2 parameter and the initial concentration of vinyl chloride were estimated from the regression.

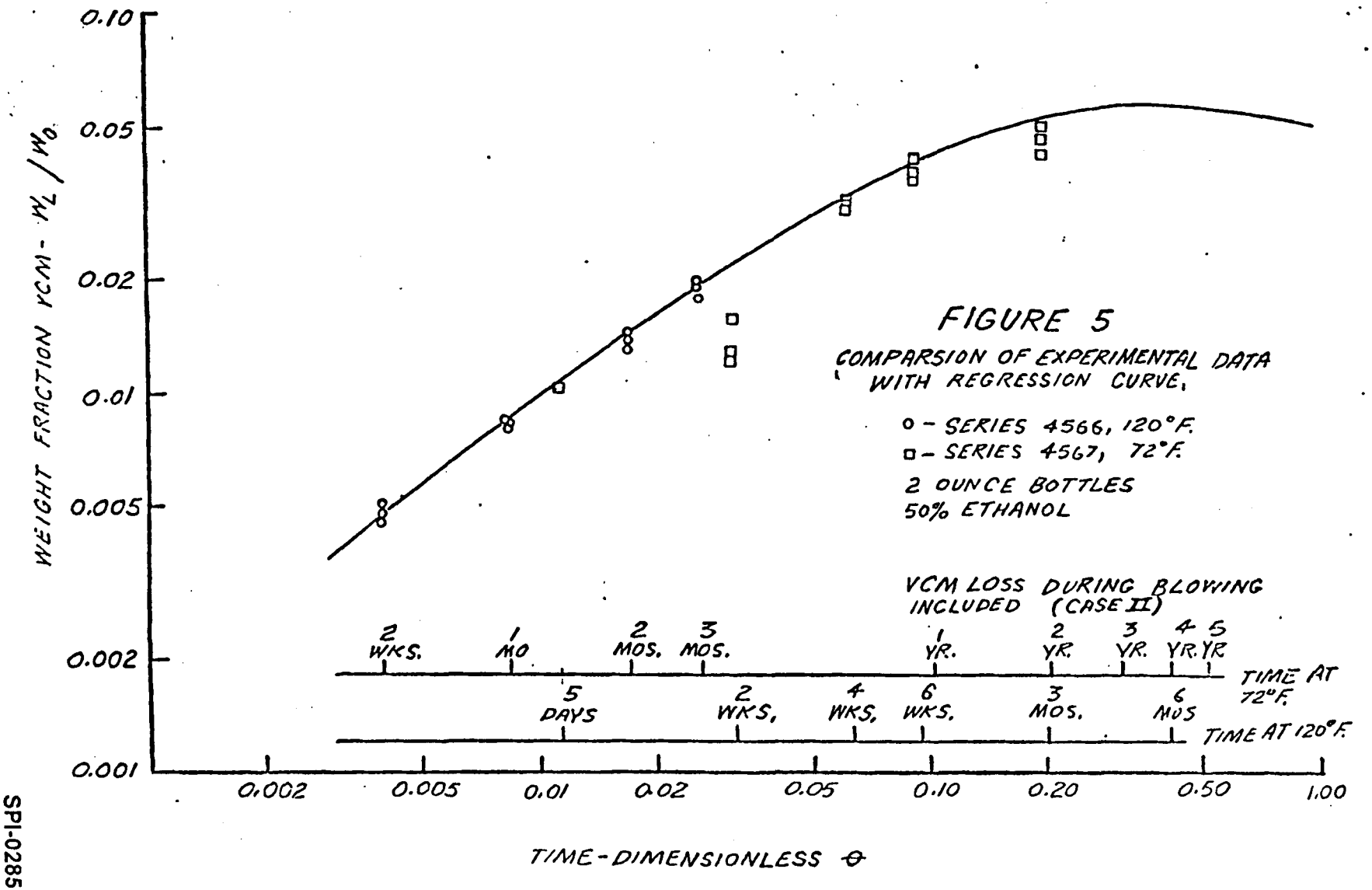

FIGURE 5

COMPARSION OF EXPERIMENTAL DATA WITH REGRESSION CURVE.

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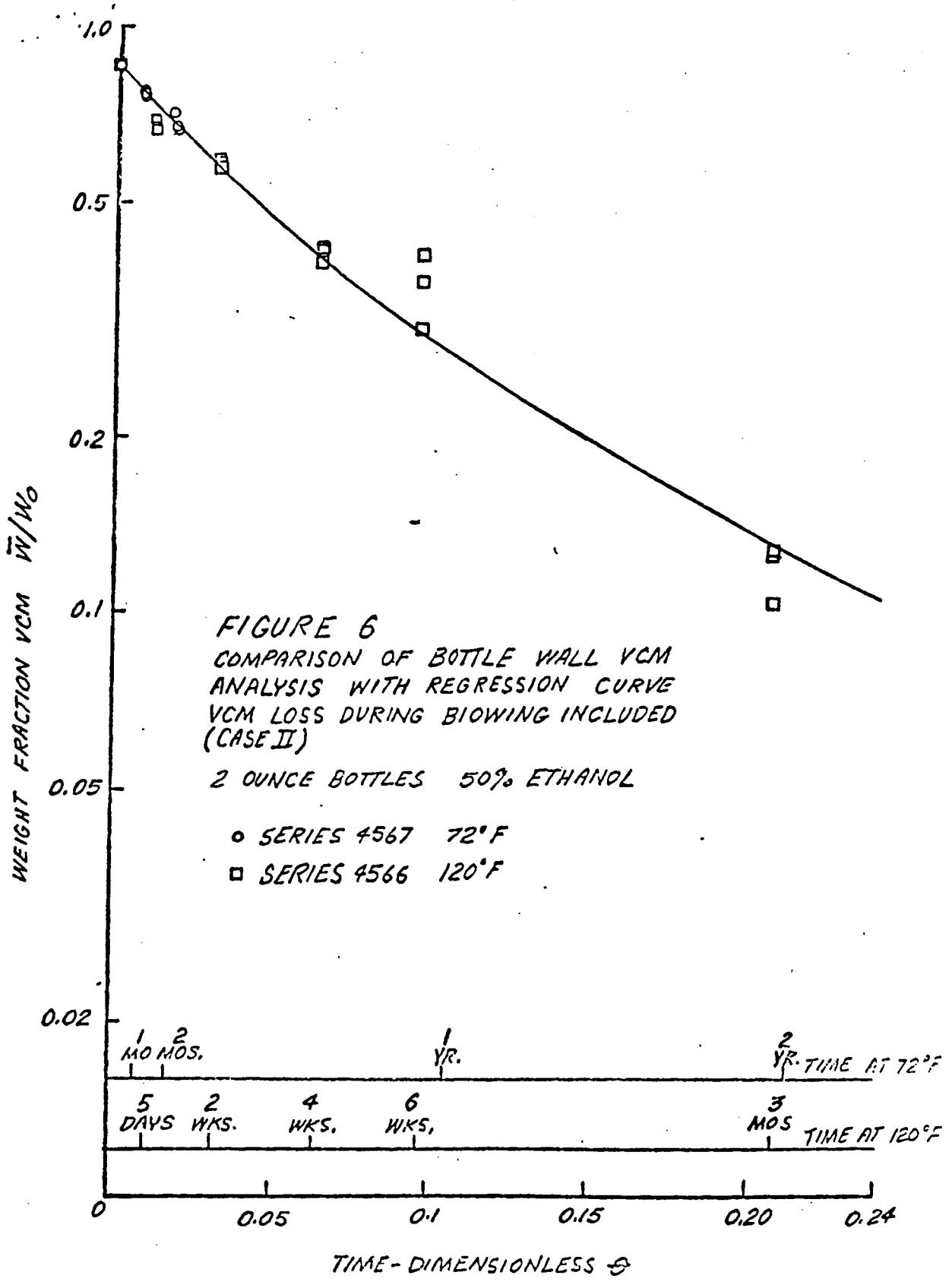

FIGURE 6
COMPARISON OF BOTTLE WALL VCM ANALYSIS WITH REGRESSION CURVE VCM LOSS DURING BIOWING INCLUDED (CASE II)
2 OUNCE BOTTLES 50% ETHANOL

○ SERIES 4567 72°F
□ SERIES 4566 120°F

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The results are given as follows:

Run 4562 - 120°F

Parameter	Value	95% Confidence Limits Lower	Upper
D/l^2, day^{-1}	$1.67 \cdot 10^{-3}$	$1.53 \cdot 10^{-3}$	$1.82 \cdot 10^{-3}$
W_o, Initial concentration, ppm	102	99	106

Run 4564 - Room Temperature

D/l^2, day^{-1}	$2.16 \cdot 10^{-4}$	$1.70 \cdot 10^{-4}$	$2.62 \cdot 10^{-4}$
W_o, Initial concentration, ppm	160	149	171

The VCM concentration in the bottle contents is shown in Figures 7 and 8. The bottle wall analyses are compared in Figure 9.

A reasonable comparison of the experimental data for runs 4566 and 4567 with the theoretical curve for no VCM loss can be made if half of the VCM lost during blowing were added to the observed values (the other half of the VCM diffuses to the exterior surface and does not appear in the contents) and if the time corresponding to the blowing operation is added to the actual time after filling. This approximation will yield numbers slightly greater than the true values. The results of this comparison are plotted in Figure 10.

Conclusions

Experimental extraction data, both the VCM concentration in the 50% ethanol contents and the VCM concentration in the bottle wall, determined using 2 oz. bottles are consistent with the diffusion controlled extraction model. This extraction model can be used to predict the effect of different bottle sizes and bottle contents on the VCM level in the bottle contents. Predictions for 2 oz. cylinderical and 16 oz. cylinderical bottles for several materials are shown in Figures 1 and 2.

Bottle weight as a function of bottle capacity is shown in Figure 11. Using the average curve from Figure 11, the following values for the maximum VCM concentration in 50% ethanol solution can be calculated for bottles made of PVC compound containing 1 ppm VCM.

Part 2 - Additional Comments on Methodology

The PVC compound used in the preparation of the sample bottles was compounded at Ethyl's Tiptonville, Tennessee plant. This compound was blown into the 16-ounce and 2-ounce bottles in our Baton Rouge laboratory. The bottles were made under conditions and on equipment that are used normally in commercial PVC bottle manufacturing plants. The bottles are of a quality (appearance and properties) comparable to those commercially produced.

The 16-ounce bottle is a tapered oval design with approximately 3.9 inch x 1.8 inch maximum oval dimension and 6.75 inch height with a standard 24 mm screw cap neck finish. The 2-ounce bottle is a nominal 1.35 inch diameter, 3.15 inch height flat bottom cylinder with a standard 8 mm screw cap neck finish. The 16-ounce bottles weighed 36 grams and the 2-ounce bottles weighed 10.5 grams.

The aqueous solutions were made with distilled water that was checked for zero VCM content. Solutions were mixed and stored in clean glass vessels. The heptane and vegetable oil were purchased locally in glass or PE containers.

The PVC bottles were not flushed prior to filling. The bottles were filled at 72°F by decanting the solvents from the storage vessel into the bottles. Bottles were filled to a point slightly above the shoulder of the bottle, which is the nominal capacity of the bottle. The bottles were immediately sealed after filling. The bottles were sealed with the following closures:

Run	Bottle Size	Seal
4555 and 4536	16 oz. oval	Cap with vinyl coated pulp liner
4555 and 4556	2 oz. cyl.	Cap with polyethylene plug liner
4562 and 4563	2 oz. cyl.	Cap with vinyl coated pulp liner
4566 and 4567	2 oz. cyl.	Heat sealed foil liner and cap

The room temperature storage work was carried out at a constant 72°F. The elevated temperature work was made in an air circulating oven at a constant 120°F.

After completion of the storage period, sample bottles were refrigerated at 35-40°F until VCM analysis was made on the contents.

Representative chromatograms from each of the series is attached.

Part 3 - Analytical Procedures (excerpt from "Extraction of Vinyl Chloride from PVC bottles by Bottle Contents", January 17, 1975.

The Determination of Vinyl Chloride Monomer in Various Solvents and in Alcoholic Beverages Stores in Polyvinyl Chloride Containers

T. G. Mungall

Introduction

Upon request from the Plastics Research Group a method was developed for the determination of vinyl chloride monomer in 50-50 ethanol-water, heptane, 3% acetic acid and alcoholic beverages stored in polyvinyl chloride containers.

This report covers the related development work and includes confirmatory data which were also gathered at their request.

A copy of this method was turned over to the Gas Chromatography Services Lab and they have been running samples submitted to them by the Plastics Research group using this method for the past several months.

Summary and Conclusions

1. A detailed method for the determination of vinyl chloride monomer (VCM) in various solvents including 50-50 ethanol-water, heptane, 3% acetic acid and alcoholic beverages is attached to this report. The method should also be applicable to the determination of VCM in other solvents.

2. The method, as written, can be used to determine as little as 0.01 ppm VCM in solution with a relative standard deviation of ±16%.

3. A computer or electronic integrator can be used, with this method, for samples containing 0.05 ppm or more VCM. It is necessary, however, to hand calculate the data for concentrations below 0.05 ppm.

4. Vinyl chloride monomer recovery factors for absolute calibration were in agreement regardless of the solvent medium. Factors were obtained for VCM in 50-50 ethanol-water solvent at various concentration levels from 0.01 ppm to 0.27 ppm, in heptane solvent from 0.01 to 3.6 ppm and in 3% acetic acid solution at the 0.25 ppm level.

5. Recovery data on VCM from "spiked" samples of 50-50 ethanol-water solution, actual samples of 50-50 ethanol-water and other solvents as well as alcoholic beverages stored in PVC, are included in this report.

6. Sample chromatograms are included to show the relative peak areas obtained with varying concentrations of VCM.

Discussion

In April, 1973, a request was made by the Plastics Research Group for the development of a method by which VCM in 50-50 ethanol-water and alcoholic beverages could be determined at the 1 ppm level or lower. Later on this request was extended to include the determination of VCM in heptane, 3% acetic acid solution, water and PVC (both the resin and finished products).

Initial work in this area was done using a Varian Aerograph 2800 equipped with a flame ionization detector (FID) and fitted with a 1/8" x 15' stainless steel column packed with 16.7% TCEP (tris-2-cyanoethoxy propane) on 70/80 mesh Chromasorb W, A.W. The limits of detection with this method were about 0.1 ppm VCM in liquids and 2 ppm in PVC.

Upon a request from the Plastics Research Group for greater sensitivity it was decided to try an electron capture detector. Electron capture proved to be little or no improvement over flame ionization as far as sensitivity for VCM is concerned; however, we were able to achieve the desired sensitivity by modifying our original FID method. The limits of detection of this new method, provided the peaks were hand-calculated, was 0.01 ppm VCM in solutions and 0.25 ppm in PVC. In this new method a different column was chosen to give a better separation between the VCM and heptane peaks than the TCEP column afforded and the flame ionization detector was operated at a much higher sensitivity. The size of the sample injected into the instrument was also several times larger than the former method.

Due to time considerations the gas chromatography service lab began integrating peak areas by means of the IBM S/7 computer. This practice resulted in a higher detection limit of approximately 0.03 ppm VCM in the 50%/50% ethanol-walter solvent.

The Plastics Research group requested data showing sensitivity, accuracy and precision of the routine analysis as applied to the 50%/50% ethanol-water system. Such data were obtained on the Bendix 2200 instrument by three different lab assistants. The S/7 computer was used for data processing.

First, a standard was prepared: VCM in 50-50 ethanol-water solution at the 0.27 ppm level. This was prepared three different times; on 8-14, 8-20 and 8-30-73 and each standard run two or more times. The overall relative standard deviation for this standard was ±5% and the vinyl chloride factor thus derived was 0.0338 ppm ViCl/unit (s/7) area (see Table I).

A standard was then prepared containing 0.054 ppm vinyl chloride in 50-50 ethanol-water. This standard was injected repeatedly and the areas for the vinyl chloride peaks obtained on the IBM S/7 (Table II).

Standards at the .027 and .011 ppm levels were prepared and an attempt made to collect the data on the IBM S/7; however, the noise to signal ratio at these levels was so high that only a few pieces of data at the .027 ppm level were obtained on this system (see Table III). The charts were hand-calculated to obtain numbers at the .011 and .027 ppm levels (see Tables IV and V).

Attached are typical chromatograms obtained at the 0.270, 0.054 and 0.011 ppm levels of vinyl chloride in 50-50 ethanol-water solution.

Vinyl chloride factors have been obtained in heptane and 3% acetic acid as well as 50-50 ethanol-water. Table VI summarizes these data.

Calibration

TABLE I

VINYL CHLORIDE FACTORS

50-50 Ethanol-Water Solution
(0.270 ppm ViCl level)

IBM System/7

Peak Area	Factor ppm/Unit S/7 Area
8.6113	.03135
8.3823	.03221
8.1879	.03298
7.8188	.03453
7.7846	.03468
7.8890	.03418
7.4410	.03629

$\bar{X}$ = 0.03375 (0.0338)

S = 0.00168

where:

$$S = \sqrt{\frac{n\Sigma X^2 - (\Sigma X)^2}{n(n-1)}}$$

Rel. Std. Dev. ± 5.0%

where:

$$\text{Rel. Std. Dev.} = \frac{S(100)}{\bar{X}}$$

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TABLE II

RECOVERY OF VINYL CHLORIDE MONOMER
FROM 50-50 ETHANOL-WATER SOLUTION

(0.054 ppm level)

Spiked Sample

IBM System/7

ppm in Solution
0.061
0.077
0.056
0.062
0.060
0.053
0.060
0.055
0.049

$\bar{X}$ = 0.059

S = 0.0079

Rel. Std. Dev. = ±13.4%

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TABLE III

RECOVERY OF VINYL CHLORIDE MONOMER FROM 50-50 ETHANOL-WATER SOLUTION

(0.027 ppm level)

Spiked Sample

IBM System/7

ppm in Solution

.031
.026
.028
.026

$\bar{X}$ = .028

S ≒ .0025

Rel. Std. Dev. = ±9.1%

TABLE IV

RECOVERY OF VINYL CHLORIDE MONOMER
FROM 50-50 ETHANOL-WATER SOLUTION

(0.011 ppm level)

Hand Calculated

0.016
0.020
0.014
0.014
0.014
0.015
0.014
0.016
0.014
0.022
0.019
0.017
0.017
0.016

$\bar{X} = 0.016$

$S = 0.0025$

Rel. Std. Dev. = ± 15.8%

TABLE V

RECOVERY OF VINYL CHLORIDE MONOMER
FROM 50-50 ETHANOL-WATER SOLUTION

(0.027 ppm level)

Hand Calculated

ditto

0.027
0.030
0.024
0.029

$\bar{X}$ = 0.028

S = .00263

Rel. Std. Dev. = ±9.4%

TABLE VI

VINYL CHLORIDE FACTORS OBTAINED IN OTHER SOLVENTS

Calibration

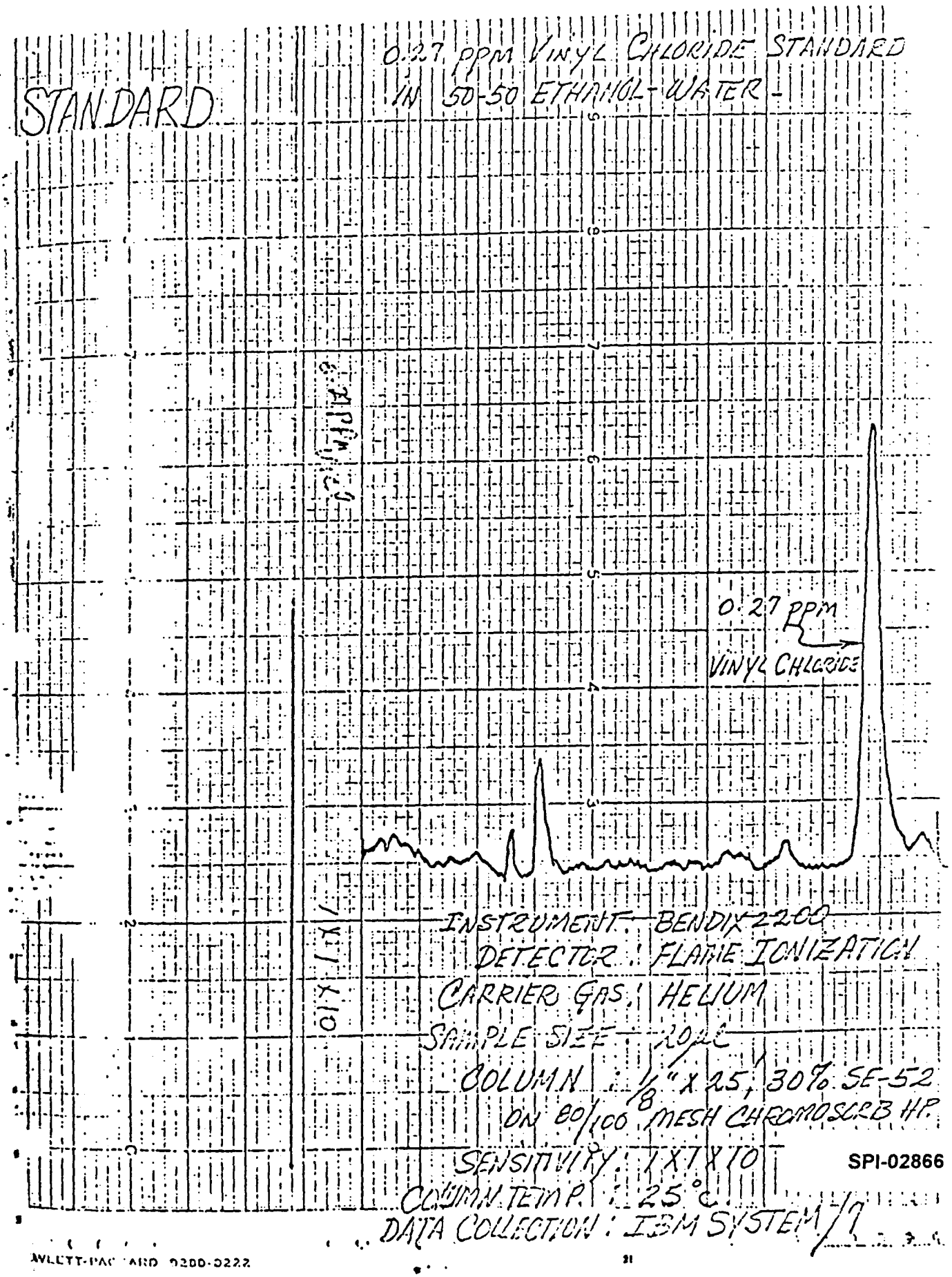
Heptane

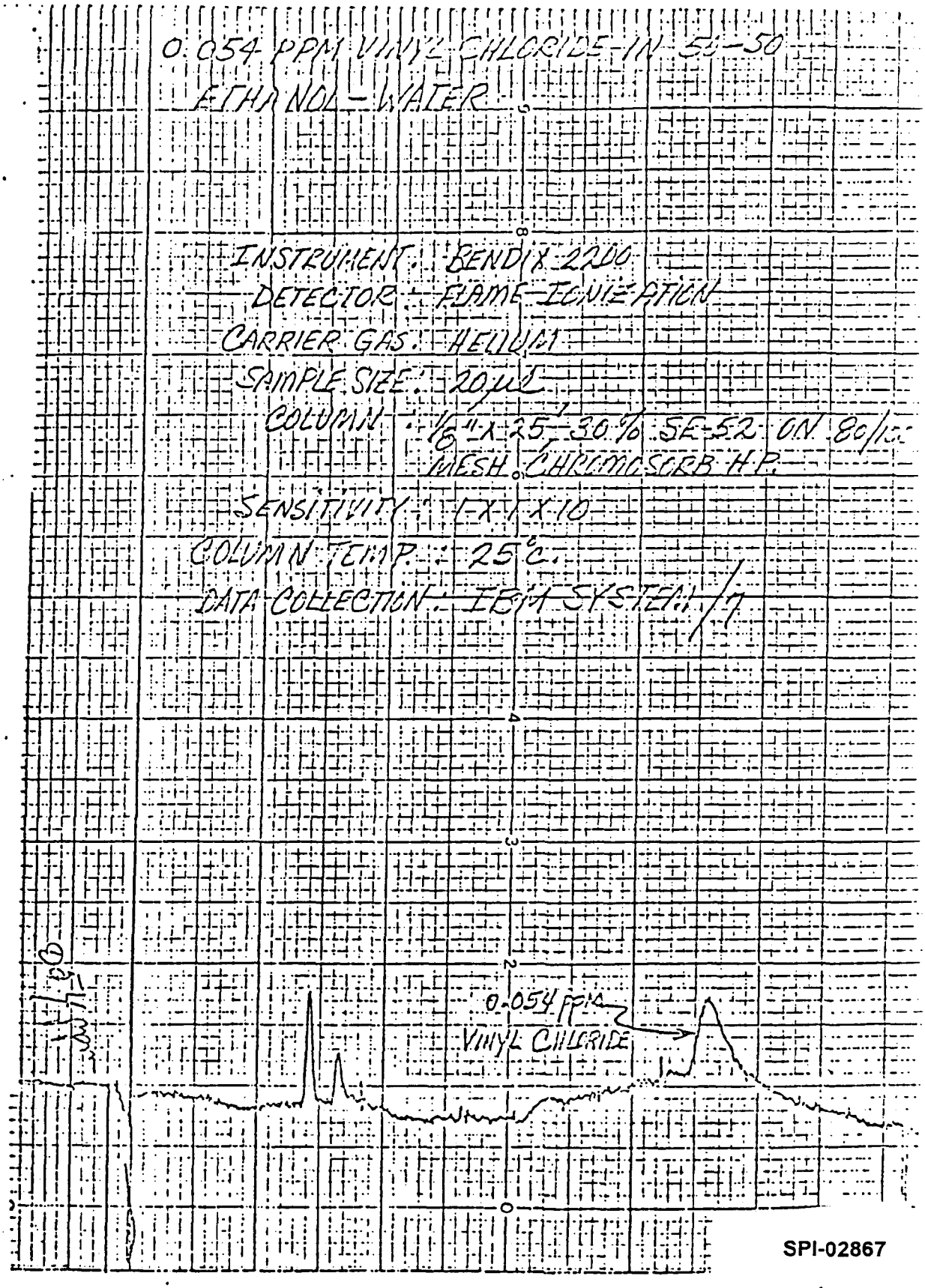
3.55 ppm Vinyl Chloride Level	ppm/Area Unit
	.0314
	.0283
	.0281

0.355 ppm Vinyl Chloride Level	ppm/Area Unit
	.0319
	.0334

3% Acetic Acid

0.249 ppm Vinyl Chloride Level	ppm/Area Unit
	.0280
	.0309
	.0301
	.0339
	.0290
	.0303

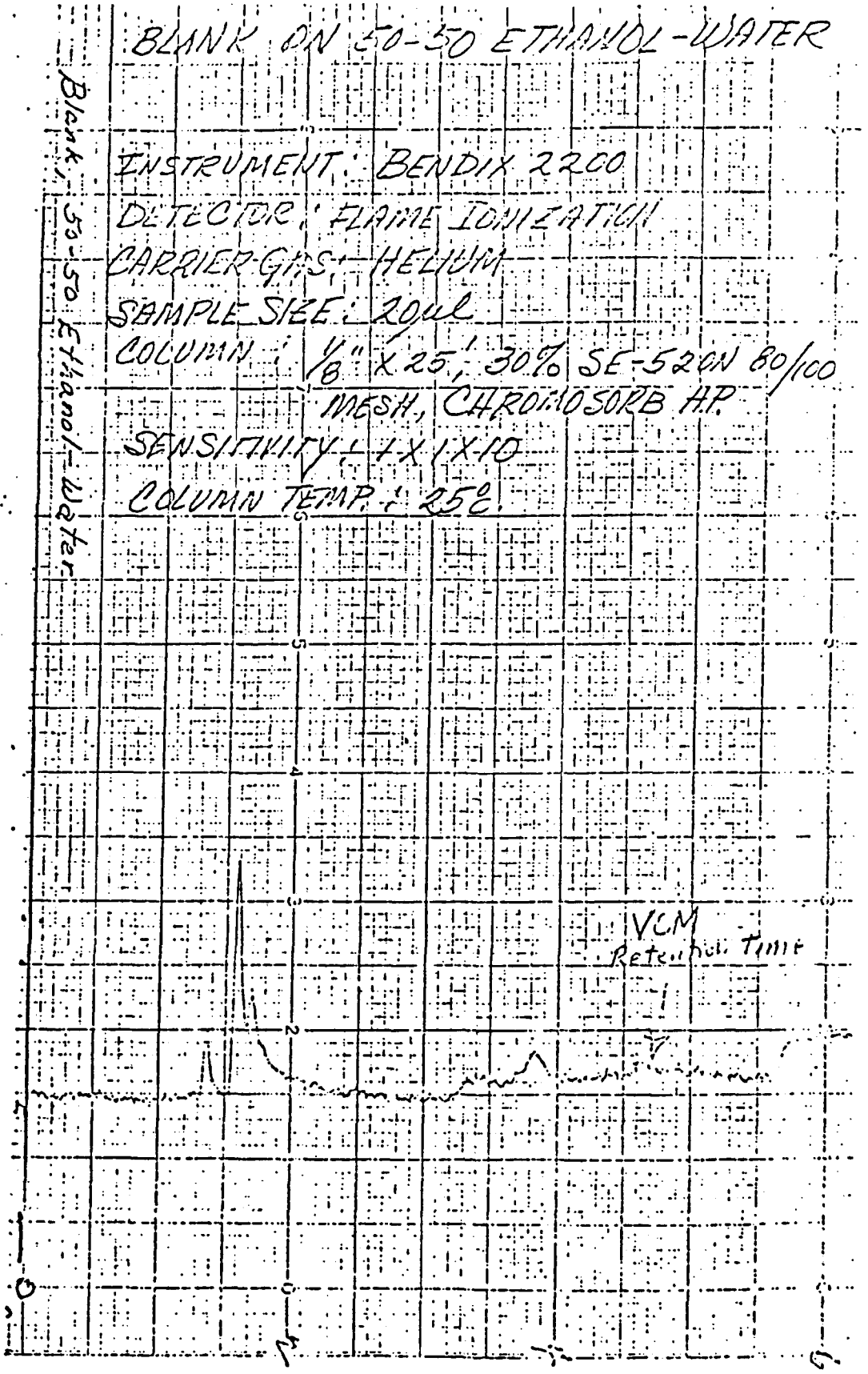

STANDARD
0.27 PPM VINYL CHLORIDE STANDARD
IN 50-50 ETHANOL-WATER
0.27 PPM
VINYL CHLORIDE
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20µL
COLUMN: 1/8" X 25' 30% SE-52
ON 80/100 MESH CHROMOSORB HP
SENSITIVITY: 1X1X10
COLUMN TEMP.: 25°C
DATA COLLECTION: IBM SYSTEM/7
SPI-02866


0.054 PPM VINYL CHLORIDE IN 50-50
ETHANOL-WATER
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME-IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20 µL
COLUMN: 6' X 1/4" 25% 5E-52 ON 80/100
MESH CHROMOSORB H.P.
SENSITIVITY: 1 X 1 X 10
COLUMN TEMP.: 25°C.
DATA COLLECTION: IEA SYSTEM
0.054 PPM
VINYL CHLORIDE
0
1
2
3
4

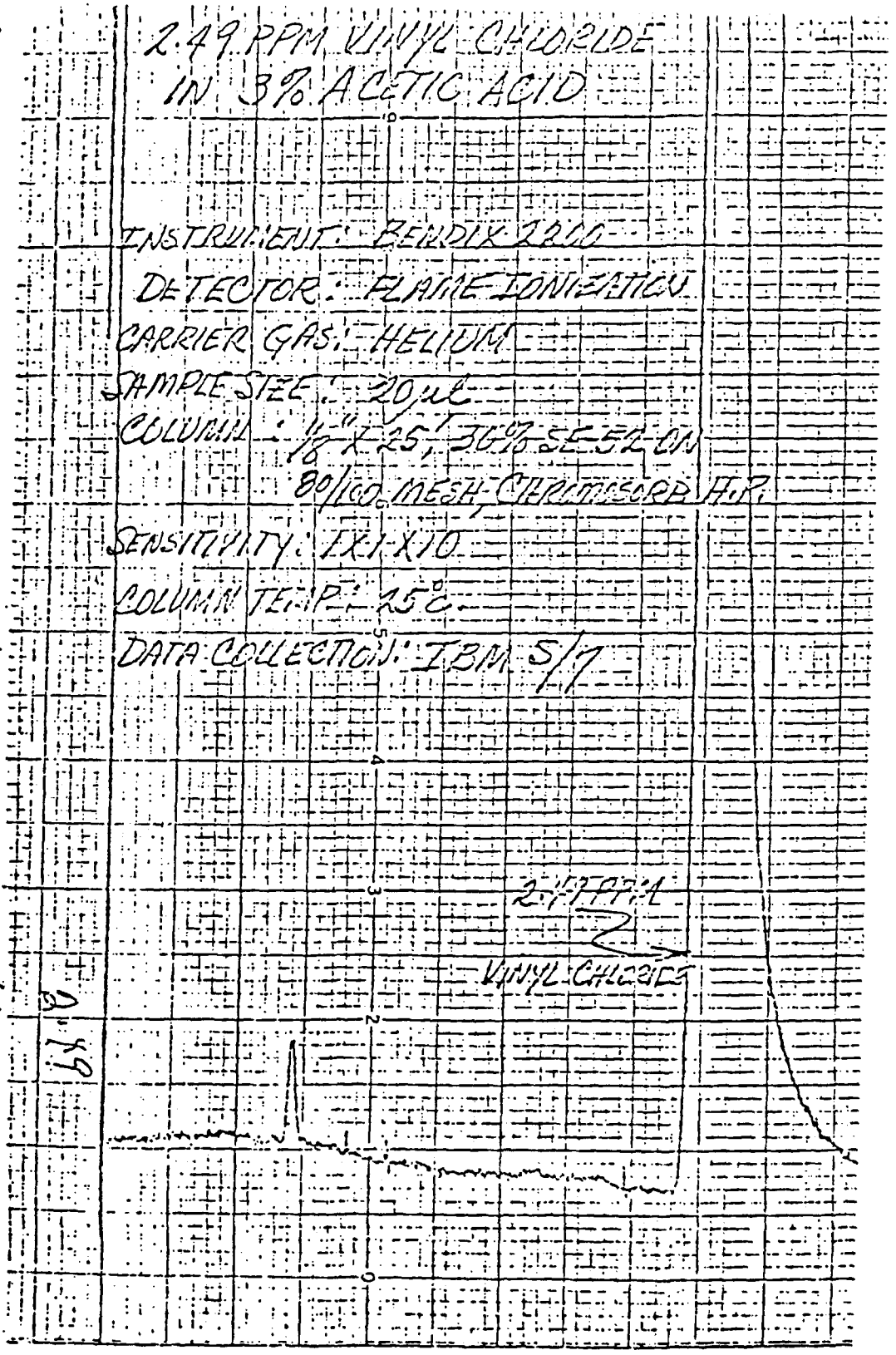
SPI-02867

0.01 PPM VINYL CHLORIDE IN
0.01 PPM VINYL CHLORIDE IN 50/50 ETHANOL-WATER
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 50 µl
COLUMN: 6' x 1/8" S.S. 10% SE-52 ON 80/100 MESH CHROMOSORB HP
SENSITIVITY: 1 x 10
COLUMN TEMP: 25°C.
.01 PPM VC
50/50 EtOH + H2O
1 x 1

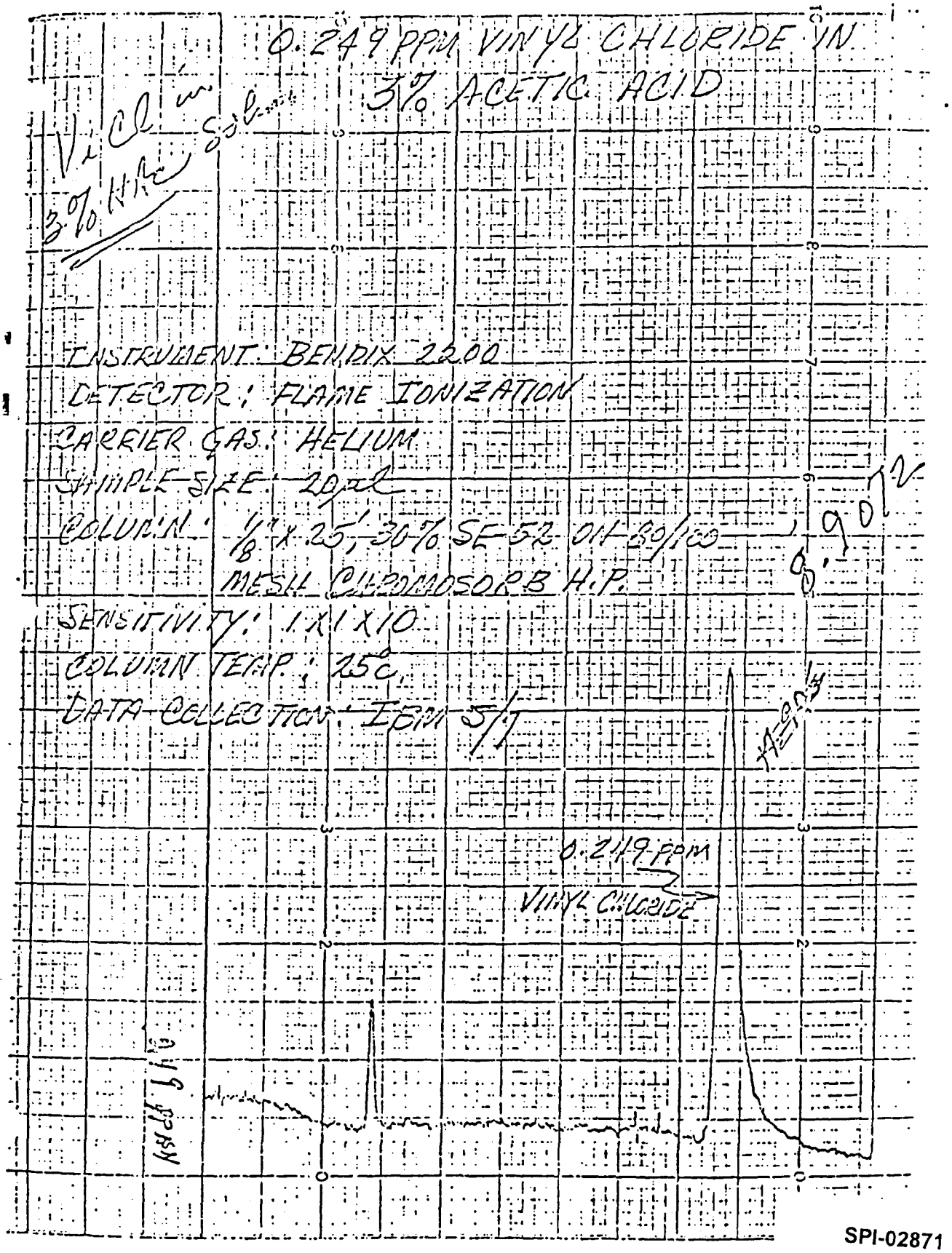
SPI-02868


BLANK ON 50-50 ETHANOL-WATER
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20ul
COLUMN: 1/8" X 25' 30% SE-52 ON 80/100
MESH, CHROMOSORB A.W.
SENSITIVITY: 1 X 1 X 10
COLUMN TEMP.: 25°C
Blank, 50-50 Ethanol-Water
VCM
Retention Time
0
1
2
3
4
5
6

SPI-02869


2.49 PPM VINYL CHLORIDE
IN 3% ACETIC ACID
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20 µL
COLUMN: 1/8" X 25' 3% SE-52 ON
80/100 MESH CHROMOSORB W.
SENSITIVITY: 1X1 X10
COLUMN TEMP: 25°C
DATA COLLECTION: IBM S/7
2.49 PPM
VINYL CHLORIDE
0.79
0
1
2
3
4
5

SPI-02870


0.249 PPM VINYL CHLORIDE IN 3% ACETIC ACID
INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20µL
COLUMN: 1/8" x 25', 30% SE-52 ON 80/100 MESH CHROMOSORB H.P.
SENSITIVITY: 1 X 1 X 10
COLUMN TEMP: 25°C
DATA COLLECTION: EDM 5/1
0.249 PPM
0.249 FROM VINYL CHLORIDE

SPI-02871

Heptane

3.55 / 113.23 = .031

3.55 PPM VINYL CHLORIDE IN HEPTANE

REPORT FOR GC 09 08/24/73 08:10 METHOD 9001 NOR RUN

COMPONENT NAME	ELUTION TIME	PEAK HEIGHT	AREA FRACTION	FACTOR	ANALYSIS
<<?>>	93.9	0.05	0.007586	0.00000	0.000000
UNKNOWN	113.3	0.00	0.004868	1.00000	0.572290
UNKNOWN	158.9	0.06	0.012816	1.00000	1.506400
UNKNOWN	235.3	0.05	0.011329	1.00000	1.331600
VINYL - CL	278.9	4.00	0.963370	1.00000	113.230000

INSTRUMENT: BENDIX 2200

DETECTOR: FLAME IONIZATION

CARRIER GAS: HELIUM

SAMPLE SIZE: 20µL

COLUMN: 1/8" X 25', 30% SE-52 ON 80/100 MESH CHROMOSORB G H.P.

SENSITIVITY: 1X1X10

COLUMN TEMP. 25°C

DATA COLLECTION: IBM

1X1X10

8/24/73

3.55 PPM VINYL CHLORIDE

3.55 FP

VINYL CHLO

2

0

SPI-02872

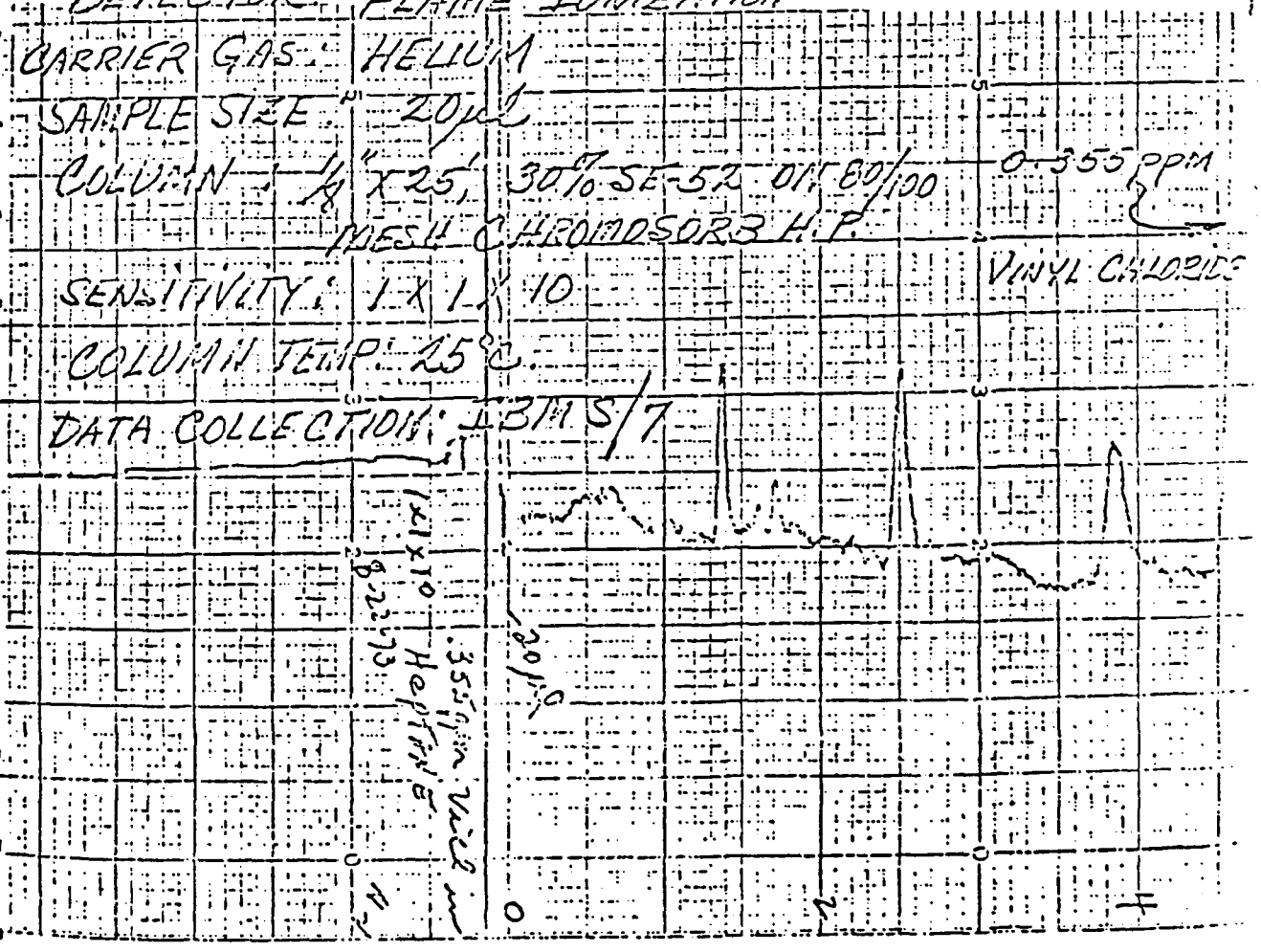
Heptane

$\frac{.355}{11.137} = .032$ ppm/area

REPORT FOR GC 09 08/22/73 13:50 METHOD 9001 NOR RUN

COMPONENT NAME	ELUTION TIME	PEAK HEIGHT	AREA FRACTION	FACTOR	ANALYSIS
<<?>>	95.5	0.05	0.105750	0.00000	0.000000
UNKNOWN	116.1	0.01	0.081302	1.00000	1.607300
UNKNOWN	164.9	0.08	0.129270	1.00000	2.555700
UNKNOWN	245.1	0.06	0.120300	1.00000	2.378200
VINYL - CL	293.5	0.40	0.563350	1.00000	11.137000

INSTRUMENT: BENDIX 2200
DETECTOR: FLAME IONIZATION
CARRIER GAS: HELIUM
SAMPLE SIZE: 20µl
COLUMN: ⅛" X 25' 30% SE-52 ON 80/100 MESH CHROMOSORB H.P.
SENSITIVITY: 1 X 1 X 10
COLUMN TEMP: 25°C.
DATA COLLECTION: ABM S/T



SPI-02873

PROCEDURE

Method used

The Determination of Vinyl Chloride Monomer in Various Solvents or Liquors

SCOPE

1. This method is designed to determine as little as 0.01 ppm vinyl chloride monomer in various solvents or liquors that have been stored in polyvinylchloride containers.

OUTLINE OF METHOD

2. The solvent or liquor is taken up in a microliter syringe and injected directly into a gas chromatograph equipped with a flame ionization detector.

Calibration is done on an absolute basis by obtaining the peak area for VCM in fixed aliquots of standard solutions.

APPARATUS

3. (a) Gas Chromatograph - Bendix Model 2200, or the equivalent, equipped with a flame ionization detector.

(b) Gas Chromatographic Column - 1/8" x 25', 30% SE-52 on 80/100 mesh Chromosorb HP.

(c) Microliter Syringe - A 50 µl Hamilton gas chromatography syringe No. 705-N or the equivalent.

(d) High Purity Nitrogen, Hydrogen and Compressed Air -

(e) Volumetric Flasks - 50, 100 and 1000 ml capacity.

(f) Rubber Stoppers, Serum Type -

(g) "Gastight" Syringe - a 2.5 ml Hamilton "gastight" syringe #1002 or the equivalent fitted with a 4" No. 25 needle.

(h) Data Processing Equipment - IBM System/7 or the equivalent, if desired.

REAGENTS

4. (a) Vinyl Chloride - High purity, available from Ethyl Corporation, Baton Rouge, La.

(b) Ethyl Alcohol - 95% alcohol (190 proof).

(c) 3% Acetic Acid Solution -

(d) Heptane - Phillips 99 mole % or the equivalent.

GAS CHROMATOGRAPHIC CONDITIONS

5. (a) Carrier Gas: 40 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 Port Temperature: 200°C

(f) Detector Temperature: 300°C

(g) Oven Temperature: Ambient during the run until the vinyl chloride elutes from the column, then the oven temperature is programmed @ 15°/min to 155°C and held for 12 minutes to clear the column prior to injection of the next sample.

CALIBRATION

6. (a) Prepare a standard mixture of vinyl chloride in the solvent by dissolving 1.0 cc of vinyl chloride gas (approx. 2540 µg Vic) in enough solvent to fill a 1000 ml volumetric flask. (The flask should be weighed empty and then filled with the solvent and re-weighed so that the actual weight of solvent can be determined).

A serum cap is then placed over the mouth of the volumetric flask and the flask inverted. In this position 1.0 cc of vinyl chloride gas is injected via the gas tight syringe into the solvent and the flask shaken for several minutes in this inverted position to allow the vinyl chloride to go into solution.

This standard solution will contain from 2.5 to 3.5 ppm vinyl chloride depending upon the weight of solvent.

Further dilutions of this standard may be made by pipeting known volumes of the standard into volumetric flasks and diluting with additional solvent. For example, a convenient way of obtaining 0.05 ppm vinyl chloride in 50-50 ethanol-water is to prepare the standard as described, using about 940 g of the 50-50 mix, then 1.0 cc of vinyl chloride gas (2540 µg ViCl) is injected. This will result in a stock mixture containing 2.70 ppm vinyl chloride. A 10 ml aliquot of this stock mixture is then diluted to 100 ml with fresh 50-50 solution giving an intermediate standard of 0.27 ppm vinyl chloride. A 10 ml aliquot is then taken of this 0.27 ppm mixture and diluted to 50 ml with additional 50-50 solution. This will result in a standard containing 0.054 ppm vinyl chloride.

(b) Exactly 20 µl of the 0.27 ppm vinyl chloride standard mixture is injected into the gas chromatograph via the system inlet and the area of the vinyl chloride peak is obtained via the System/7 or by hand calculating. The factor is then calculated by dividing the concentration (0.27 ppm) by the peak area thus giving an absolute response in terms of ppm/peak area unit.

This procedure is repeated several times, preferably including a duplicate preparation of the 0.27 ppm standard solution.

PROCEDURE

7. (a) Inject exactly 20 µl of the sample solution into the gas chromatograph. This solution can be either 50-50 ethanol-water, 3% acetic acid, heptane or liquor.

Obtain the peak area on an IBM System/7 or other suitable integrator. If the concentration of VCM is below 0.05, hand calculation from the recorder chart is recommended.

CALCULATIONS

8. (a) Calculate the ppm vinyl chloride monomer in the sample as follows:

ppm ViCl = A x B

where:

A = ViCl peak area for sample. (20 µl)

B = ppm ViCl/unit area obtained from absolute calibration of the instrument. (20 µl of std.) (see Calibration Section)

The detection limit for this method is approx. 0.01 ppm ViCl. The sensitivity is ±0.01 at the 0.05 ppm level and the accuracy is ±13% at 0.05 ppm level.

/ss
10-3-73

Revised 11-15-7[illegible]

GAS CHROMATOGRAPHIC METHOD FOR THE ANALYSIS OF VINYL CHLORIDE MONOMER IN POLYVINYL CHLORIDE

INTRODUCTION

This method includes the dissolution of polymer in tetrahydrofuran, which contains ethyl bromide standard, and the analysis of the solution via gas chromatography.

MATERIALS

1. Gases: All must be high purity, water pumped where applicable, and suitable for use with a gas chromatograph.

   Hydrogen
   Air
   Helium

2. Chemicals (Reagent Grade):

   Ethyl Bromide
   Tetrahydrofuran (THF)

3. Magnetic stirrers
4. Stirring bars
5. 125 ml Erlenmeyer flasks
6. 100 ml Volumetric flask
7. Syringers, 50 µℓ, 10 µℓ
8. 50 ml Pipette
9. No. 268 Sani-Tab caps
10. Gas Driers (Tek Lab Cat. No. 235)

INSTRUMENTS

1. Gas Chromatograph

   Varian 1740 or equivalent equipped with dual flame ionization detectors. Columns: 16 feet by 1/8 inch thin wall (.012 in.) stainless steel tubing packed with 16.7% 1, 2, 3, tris(2-cyanoethyl)propane, (TCEP), on Chromosorb W, AW, 70/80 mesh. Columns are to be arranged for on-column injection.

2. Strip Chart Recorder

   0 - 1 millivolt full scale
   1 inch per minute chart speed

PROCEDURE

1. Standard Solution: Fill to the mark, a 1000 ml volumetric flask with THF and add to it exactly 40 µℓ of ethyl bromide. This provides a 65 ppm solution of ethyl bromide.

2. Weigh exactly 2.50 g of PVC sample into an Erlenmeyer flask and pipette 50 ml of standard solution into the same flask. Add a stirring bar, cover with a Sani-Tab cap, and magnetically stir the mixture until the sample is dissolved or gives a homogeneous suspension.

3. Inject 5 µℓ of solution into the gas chromatograph under the following conditions:

Injection Temp.	100°C
Detector Temp.	250°C
Oven Temp.	75°C
Helium Flow	40 cc/min. (60 lb)
Electrometer Range =	10^{-11}amps/mv
Attenuator =	2

4. The attenuation may need switching from sample to sample in an effort to keep the vinyl chloride peak and ethyl bromide peak on scale. If at any time, the peaks exceed the limit of the chart paper, the sample must be rerun.

5. After the peaks of interest are collected, the analyst must wait for complete elution of THF solvent before the next sample is injected.

6. At the end of a series of samples, elevate oven temperature to 150° for approximately one hour.

7. Measure the areas of the peaks representing vinyl chloride and ethyl bromide and calculate the ppm vinyl chloride using the following arithmetic:

$$\frac{Av}{As} \times 0.573 \times 65 \times 17.6 = C$$

Av = area of vinyl chloride peak
As = area of ethyl bromide peak
C = ppm, by weight, of vinyl chloride in the sample.

PRECISION AND ACCURACY

The precision and accuracy of the method has been shown to be ± 10-20% relative at the 1 ppm level.