



Flynt Kennedy
Manager
Chemicals Research Division
Research & Development

Continental Oil Company
P.O. Box 1267
Ponca City, Oklahoma 74601
405-762-3456

May 24, 1974

Air Mail - Certified Mail

Hearing Clerk
Food and Drug Administration
Room 6-86
5600 Fishers Lane
Rockville, Maryland 20852

Dear Sir:

Mr. Jerome H. Heckman has indicated that information related to residual vinyl chloride monomer (VCM) in typical polyvinyl chloride (PVC) materials, including potable water pipe, should be sent to your attention per the request in the April 22, 1974 Federal Register, p. 14215. You will find enclosed in quintuplicate the following information:

- Enclosure I Analysis of Polyvinyl Chloride (PVC) Resin for Residual Vinyl Chloride Monomer (VCM)
- Enclosure II Extractability of Vinyl Chloride Monomer in Polyvinyl Chloride Pipe
- Enclosure III Gas Chromatogram of VCM in Water
- Enclosure IV Gas Chromatogram - Water Blank
- Table I Residual VCM in PVC Pipe
- Table II Residual VCM in Flexible PVC Compound Pellets
- Table III Residual VCM in Miscellaneous PVC Items
- Table IV Water Extraction of Residual VCM in PVC Pipe

74P-0001

C 3

Summary

The samples of commercial PVC pipe analyzed by Enclosure I of the attached procedures generally contain zero to 90 parts per million (ppm) of residual VCM.

When the pipe is subjected to water extraction at 25°C or 50°C for 72 hours per Enclosure II of the attached procedures, less than 50 parts per billion (ppb) of VCM is normally found in the extract. The exceptions to the latter occurred when pipe was extracted for periods of 18 days and 3 years. These lengthy extractions under stagnant conditions are thought to be very unrealistic representations of normal piping system usage.

We believe the data submitted clearly show that PVC pipe can be used for potable water and not cause any problem related to extraction of the residual VCM.

The analysis of various other finished PVC items, including compound pellets used in extrusion of finished items, shows that in most cases there is either no detectable VCM present or very low levels. However, a value of 150 ppm in one compound pellet sample was found and is indicative of random scatter.

Determination of Residual VCM in PVC Materials

The intention was to examine a variety of fabricated products for residual VCM levels. A significant variable is the time lapse following fabrication, on the assumption that VCM will diffuse from the structure with time. Therefore, an effort was made to sample materials with a variety of elapsed times since production; emphasis was on VCM content as soon after production as possible to better assess the highest VCM levels that could possibly be encountered in product use.

Another variable is the amount of residual VCM in the PVC resin from which the object is made. Where possible, the resin was analyzed for VCM, although a certainty that a given resin sample corresponds to a subsequently produced section of product is clearly not possible.

The data presented in Table I indicate that PVC pipe may contain up to 100 ppm of VCM, with a general trend to lower levels of VCM with increasing time. The data do show some random scatter; it is believed that additional samples will show the scatter to be statistically expected.

The data found in Table II show that very low quantities of VCM are present in compound pellets with the exception of one value of 150 ppm. We have no explanation for the high value other than of random scatter in data.

Hearing Clerk
Food and Drug Administration
May 24, 1974
Page 3

In Table III, various miscellaneous items were analyzed for residual VCM. In all cases, less than one ppm of VCM was found.

Extractability of Residual VCM in PVC Pipe

Data are presented in Table IV related to extraction of residual VCM from PVC water pipe. The data, except for the last two samples, are derived from an extraction method (Enclosure II) essentially identical to that used by the National Sanitation Foundation (NSF). The only difference is that deionized water was used in the present test method; NSF uses water at pH 5 to facilitate the extraction of heavy metal ions which are of concern to NSF. For the current purpose, it was judged that the use of neutral, deionized water would not affect the extraction of VCM. The last two samples (Ref. No. 26 and 27) represent analyses of water which was contained in a two-foot length of two-inch diameter sealed pipe for the period indicated. Since the pipe had been set aside, neither the temperature nor the ratio of surface to water was controlled. The temperature probably varied from 5° to 35°C. It is believed that lengthy exposure of stagnant water in a piping system, as in these samples, is an unrealistic representation of exposure under practical circumstances. We plan to do additional work on this point.

Future Plans

Additional data will be collected regarding residual VCM in PVC pipe, compound pellets, and miscellaneous items, along with the continuing work related to extractability of residual VCM from PVC pipe. Since the method for determining residual VCM in PVC will probably be a required plant function, it is advisable to adapt the methods (Enclosures I and II) of detection to flame ionization. Flame ionization detection (FID) is potentially equally as sensitive as coulometry but requires more attention to chromatography since FID is not selective. Impurities which could come from the solvent and/or the resin must be separated chromatographically from the VCM before entering the detector. We have made good progress in adapting the method for FID but much more work must be completed before the method becomes routine.

Should you require additional information or believe a meeting would aid your evaluation of these data, please advise me.

Yours very truly,



lm

enc

Copy w/enc to:

Mr. Jerome H. Heckman
1150 17th Street N.W.
Washington, D.C. 20036

ENCLOSURE I

ANALYSIS OF POLYVINYL CHLORIDE (PVC) RESIN FOR RESIDUAL VINYL CHLORIDE MONOMER (VCM)

Various PVC resins have been analyzed for residual VCM by first dissolving the resin in tetrahydrofuran (THF) and then chromatographing the headspace gas for quantitative analysis of VCM present in the resin. Micro-coulometry is used for detection because this detector is specific for the chlorinated species. Compounds other than halogenated materials will not be detected; consequently, separation of components via the chromatographic column is not nearly so critical as with other types of detection.

EXPERIMENTAL

Samples. The samples of resin are dissolved using 5 grams of resin in 50 milliliters of THF. This mixture must be stirred or shaken to dissolve the resin. Using either a roller-mixer or magnetic stirring, it can take up to two hours to complete solution. The mixture is dissolved in a 4-oz bottle equipped with a Teflon-lined septum cap. Before sampling, shake the solution vigorously and withdraw 5 milliliters of the headspace gas. When sampling, inject the same volume of air equal to the volume of headspace gas to be taken for injection. This prevents depletion of the headspace volume. The sample is injected into a chromatograph equipped with a Dohrmann model C-200 coulometer as a detector. The sample is converted to HCl in an oxidation furnace; the resultant HCl is then titrated in an Ag-AgCl coulometric cell.

Standards. Into a 4-oz bottle put 50 milliliters of THF. Close the bottle with a Teflon-backed septum cap. Inject one milliliter of VCM into the liquid and mix thoroughly. Let stand for 10 minutes and inject sample. Inject into the bottle a volume of air equal to the volume of headspace gas to be taken for the injection. This amount of VCM in 50 milliliters of THF is the equivalent of 280 ppm by weight of a 5-gram portion of PVC dissolved in 50 ml of THF, uncorrected for pressure and temperature. Standard temperature and pressure corrections should be made when actually running the standards. Various concentrations are prepared and a calibration graph plotted. This graph is then used when analyzing the samples to determine concentration.

Chromatographic Conditions. The column used is a 5' x 1/4" O.D. aluminum tube packed with 8 percent SE-30 (silicon oil from General Electric Company) on 80/100 mesh Chromosorb G (Johns-Manville). The column is not critical when using the coulometer for detection since the detector is specific for halogenated compounds. The sample is injected using a gas syringe. The oxidation furnace is maintained at 850°C with a flow rate of ~20 cc/min of oxygen. Load resistors are chosen dependent on sample concentration and sample size, varying from 50Ω to 300Ω. Carrier gas is helium at a flow rate of 35 cc/min.

DISCUSSION

The method as set forth above gives accurate, reproducible results. Linearity of response is maintained from one ppm to 18,000 ppm. Accuracy at the 100 ppm level or less is \pm three percent at the 99% confidence level. At higher concentrations the deviation approximates $\pm 10\%$. In theory the coulometer is straightforward and permits absolute determinations of concentration. However, in practice the detector requires considerable technique and careful control of operating parameters. Its major advantage is the fact that it is selective for only halogenated species, thus eliminating numerous possible interferences.

May 24, 1974

ENCLOSURE II

EXTRACTABILITY OF VINYL CHLORIDE MONOMER IN POLYVINYL CHLORIDE PIPE

Polyvinyl chloride (PVC) pipe can be safely used for potable water providing significant amounts of vinyl chloride monomer (VCM) are not extracted with water when treated at either room temperature (25 degrees Centigrade) or at elevated temperature (50 degrees Centigrade). Significant amounts are those in excess of 50 ppb. The tests are made under static conditions using an appropriate ratio of one thousand square inches of pipe to four thousand milliliters of water.

APPARATUS

Glass Syringes. Fifty-milliliter, glass syringes are used for preparation of standards and as equilibration chambers for sample preparation.

Sample Container. A 4-liter Mariotte bottle is used to hold the sample (PVC pipe) and the water. The bottle outlet is equipped with a short length of Latex tubing and a clamp. This provides a means for withdrawing a sample. A stopper is affixed with a short length of Saran tubing to permit degassing of the water as well as allowing for filling of the bottle completely with water.

Gas Chromatograph. The gas chromatograph (F&M Company Model 810 or equivalent) is equipped with a suitable column, a gas sampling valve and a specific detector, i.e., a microcoulometer. The specificity of the detector, in this case specific for halogenated materials, eliminates interference from other non-halogenated species which may be present. The instrument is operated using conditions adequate to separate VCM from the halogenated species with a sensitivity capable of detecting vinyl chloride when present in concentrations of 50 parts per billion or greater.

Gases. Helium is used as the carrier gas for transport of the sample through the column and into the microcoulometric detector. High-purity-grade helium is used with the appropriate regulator. Extra-dry-grade oxygen, with the appropriate regulator, is used as a supply to the combustion furnace of the microcoulometer.

PROCEDURE

Standardization. Forty milliliters of deionized water is added to a fifty-milliliter syringe equipped with a syringe valve. All of the air is expelled from the syringe and ten microliters of VCM is discharged into the center portion of the water. This is accomplished using a ten-microliter syringe, inserting it through the syringe valve and discharging the contents into the water. The syringe containing the

water is in an inverted position for this operation. The ten-microliter syringe is withdrawn after discharge of its contents, the valve closed and the water-VCM mixture shaken until the VCM bubble is dissolved. Ten milliliters of air is drawn into the syringe and the syringe is shaken vigorously for fifteen minutes. The air is injected into a one-milliliter, flow-through sample loop and injected into the chromatograph. The gas sampling loop is maintained at 50 degrees Centigrade. The peak area obtained is ratioed to the peak area obtained from the sample. A ten-microliter sample of VCM in 40 milliliters of water corresponds to 625 ppb VCM by weight using a calculated density for gaseous VCM of 2.49 mg/ml at 25°C and 740 Torr.

Sample Analysis. A sample of PVC pipe is cut so as to obtain approximately 1000 square inches of surface area. This material is placed in the 4-liter Mariotte bottle and the bottle filled with deionized water. Water is added one liter at a time. After each water addition the bottle is connected to house vacuum and agitated slightly until all visible air bubbles are removed. The second, one-liter portion of water is added and the same procedure followed. This is repeated after each water addition until the bottle is full to the lip of the bottle. A rubber stopper equipped with a short length of Saran tubing is forced into the neck of the bottle until water overflows through the tube. The tube is then stoppered with a microstopper. The volume of water is recorded as well as the surface area of the pipe. The bottle plus sample is immersed in a thermostated water bath and controlled at the temperature of choice. Samples can be taken at time intervals selected. A typical series of sampling times is zero, 24 hours, 48 hours, and 72 hours. When a sample is to be withdrawn, the bottle is removed from the water bath and a syringe equipped with a three-way valve is affixed to rubber tubing at the outlet. The microstopper is removed and 40 milliliters of water is drawn into the syringe. The syringe is withdrawn from the outlet and 10 milliliters of air is drawn into the syringe. The valve is closed and the syringe is shaken vigorously for 15 minutes. The syringe is then attached to the heated, one-milliliter, flow-through gas sampling valve and the air sample injected. The peak area obtained is ratioed to the peak area of the standard to determine the concentration of vinyl chloride.

Operating Conditions. The gas chromatograph is equipped with a column consisting of a 6-foot by 1/4-inch O.D. aluminum tube packed with SE-30 (silicon oil from General Electric Company) on 80/100 mesh Chromosorb G (Johns-Manville). The helium carrier gas rate is 45 milliliters per minute. The transfer line from the chromatographic column is maintained at 200°C and the column temperature is maintained at ambient. The furnace temperature of the combustion oven is 850°C with a 20-milliliter-per-minute flow of oxygen. The load resistor is maintained at 300 ohms for

the sample and 50 ohms for the standard. Under these conditions, 50 parts per billion of VCM gives a peak height consistently ten times the average noise level, and substantially better (up to 40 times noise) when the instrument is prepped for maximum performance.

May 24, 1974

ENCLOSURE III

GAS CHROMATOGRAM OF VCM IN WATER

INSTRUMENT

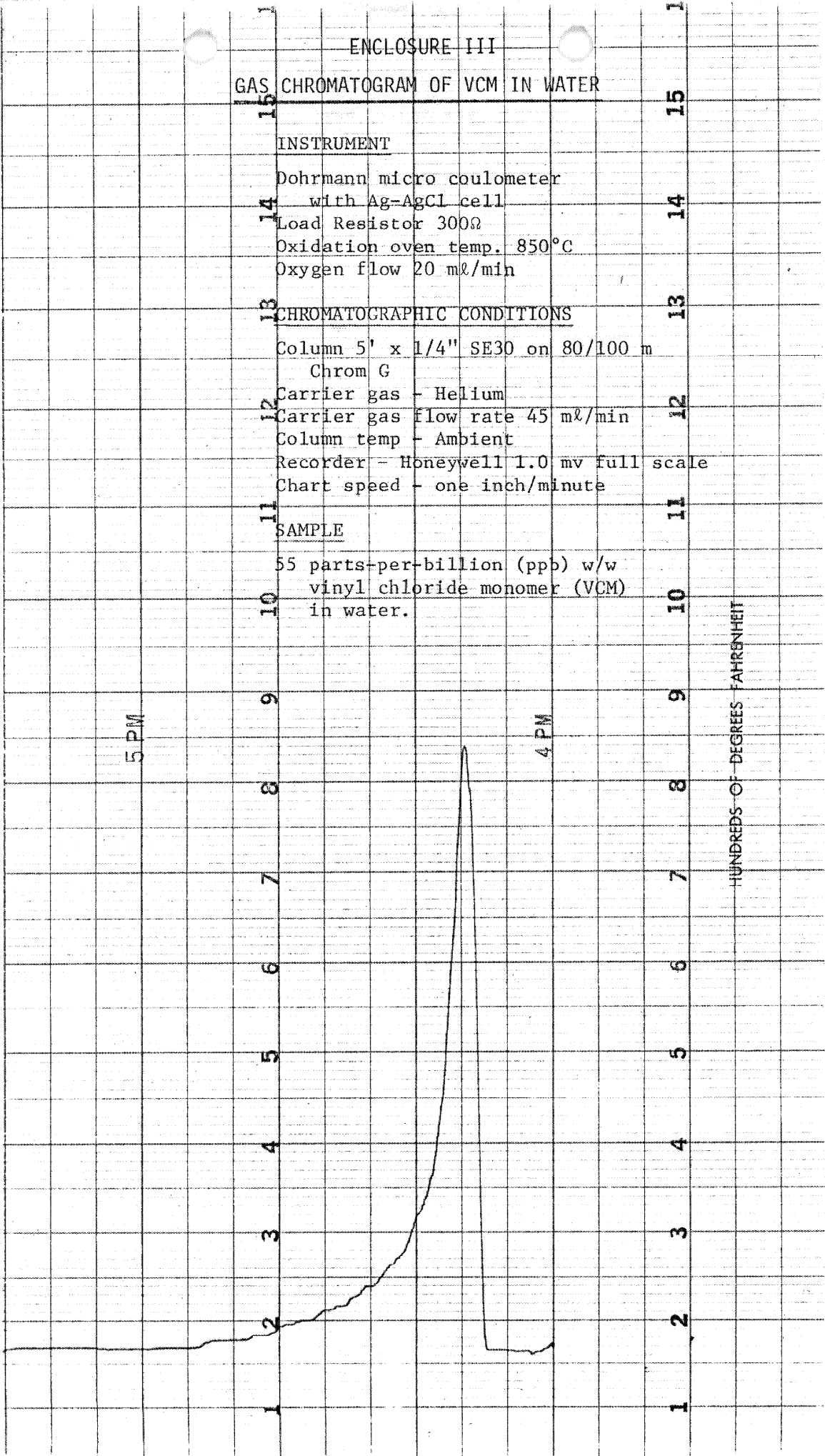
Dohrmann micro coulometer
with Ag-AgCl cell
Load Resistor 300Ω
Oxidation oven temp. 850°C
Oxygen flow 20 ml/min

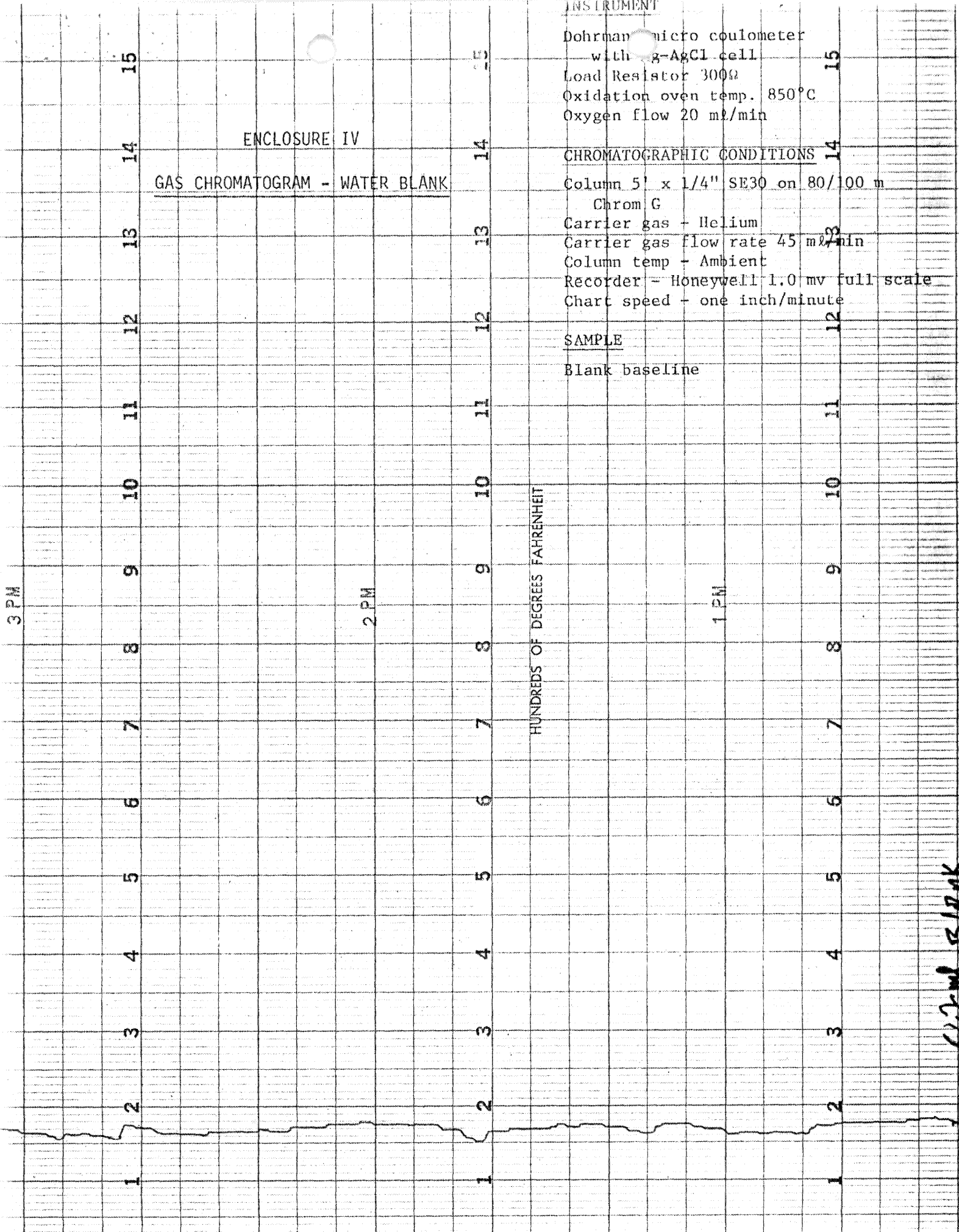
CHROMATOGRAPHIC CONDITIONS

Column 5' x 1/4" SE30 on 80/100 m
Chrom G
Carrier gas - Helium
Carrier gas flow rate 45 ml/min
Column temp - Ambient
Recorder - Honeywell 1.0 mv full scale
Chart speed - one inch/minute

SAMPLE

55 parts-per-billion (ppb) w/w
vinyl chloride monomer (VCM)
in water.





ENCLOSURE IV

GAS CHROMATOGRAM - WATER BLANK

INSTRUMENT

Dohrman micro coulometer
 with Ag-Cl cell
 Load Resistor 300Ω
 Oxidation oven temp. 850°C
 Oxygen flow 20 ml/min

CHROMATOGRAPHIC CONDITIONS

Column 5' x 1/4" SE30 on 80/100 m
 Chrom G
 Carrier gas - Helium
 Carrier gas flow rate 45 ml/min
 Column temp - Ambient
 Recorder - Honeywell 1.0 mv full scale
 Chart speed - one inch/minute

SAMPLE

Blank baseline

HUNDREDS OF DEGREES FAHRENHEIT

G. J. M. BLANK

TABLE I
RESIDUAL VCM IN PVC PIPE

<u>Sample*</u> <u>Reference</u>	<u>Estimated Time</u> <u>from Production</u> <u>Until Analysis</u>	<u>Estimate of VCM (ppm)</u> <u>in Resin</u> <u>Used in Fabrication</u>	<u>Residual VCM</u> <u>in Pipe (ppm)</u>
1	7 days	120	67
2	5 "	150	15
3	5 "	530	18
4	4 months	-	91
5	5 "	-	<1
6	12 "	-	7
7	13 "	-	4
8	20 "	-	3
9	30 "	-	23
10	36 "	-	<1

*See attached Bibliography

TABLE II

RESIDUAL VCM IN FLEXIBLE PVC COMPOUND PELLETS

<u>Sample* Reference</u>	<u>Estimated Time from Production Until Analysis</u>	<u>Estimate of VCM (ppm) in Resin Used in Fabrication</u>	<u>Residual VCM in Article (ppm)</u>
11	7 days	5,000	54
11	7 "	2,500	150
12	<3 months	-	<1
13	<3 "	-	<1
14	3 days	7	<1
15	7 "	230	6

*See attached Bibliography

TABLE III
RESIDUAL VCM IN MISCELLANEOUS PVC ITEMS

<u>Sample*</u> <u>Reference</u>	<u>Item and Estimated Time</u> <u>from Production Until Analysis</u>	<u>Estimate of</u> <u>VCM (ppm) in Resin</u> <u>Used in Fabrication</u>	<u>Residual VCM</u> <u>in Article (ppm)</u>
16	Laboratory Tubing, 1/2-in. Unknown Production Date	-	<1
17	Electrical Cable Coating, 7 days	-	<1
18	Calendered Sheet, 0.010-in. Thickness, 3 days	1,400	<1
19	Calendered Sheet, 0.015-in. Thickness, 3 days	1,800	<1
20	Medical Tubing, 3 mm., 2-4 weeks	-	<1

*See attached Bibliography

TABLE IV

WATER EXTRACTION OF RESIDUAL VCM IN PVC PIPE

<u>Sample* Reference</u>	<u>Estimated Time from Production Until Extraction</u>	<u>Extraction Temperature °C/Time</u>	<u>Extracted VCM (ppb)</u>
21	9 months	25/72 hours 50/72 "	<50 <50
22	<2 weeks	25/24 hours 25/48 " 25/72 "	<50 <50 <50
23	6 weeks	50/72 hours	<50
24	<4 weeks	25/15½ hours	<50
25	6 weeks	25/72 hours 25/432 "	<50 370
26	10 weeks	-/10 weeks**	730
27	10 weeks	-/108 weeks**	1,560

*See attached Bibliography

**Temperature ranged from 5° to 35°C.

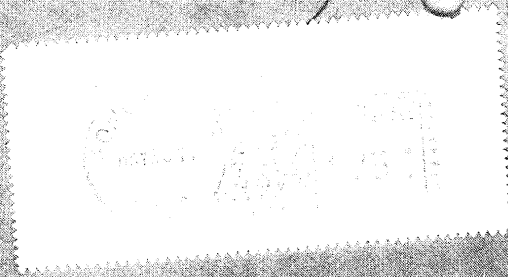
BIBLIOGRAPHY

Sample References

1. IOC, W. R. Sorenson to F. Kennedy, April 11, 1974, "VCM in Resin and Downstream Materials," item A-1.
2. Ref. 1, item A-2
3. Ref. 1, item A-3
4. Notebook No. 1, W. R. Sorenson, p. 141-1
5. Ref. 4, p. 141-6
6. Ref. 4, p. 141-5
7. Ref. 4, p. 141-4
8. Ref. 4, p. 141-3
9. Ref. 4, p. 141-2
10. Ref. 4, p. 141-1
11. Ref. 1, item B-1 ab, -1cd
12. Ref. 1, item B-2
13. Ref. 1, item B-3
14. IOC, W. R. Sorenson to F. Kennedy, April 17, 1974, "VCM in Resin and Downstream Materials II," items B-1, -2.
15. Ref. 14, items B-3, -4
16. Ref. 1, item B-3a
17. Ref. 4, p. 139-5
18. Ref. 14, items B-1, -2
19. Ref. 14, items B-3, -4
20. Ref. 1, item C-8

Sample References (Continued)

21. IOC, E. A. Setzkorn to F. Kennedy, "Analysis for VCM in PVC Pipe," June 29, 1973.
22. IOC, R. E. Laramy to F. Kennedy, "Analysis for VCM in PVC Pipe by Water Leaching," April 9, 1974, item 5.
23. Research Notebook L2923, pp. 126-130, Continental Oil Company.
24. Research Notebook L3190, pp. 164, 168, Continental Oil Company.
25. Research Notebook L2960, p. 152, Continental Oil Company.
26. Ref. 4, p. 141-6a
27. Ref. 4, p. 141-2a



AIR MAIL

CERTIFIED MAIL

30
30
15



F. Kennedy
Continental Oil Company
P.O. Box 1267
Ponca City, Oklahoma 74601

First Class

Hearing Clerk
Food and Drug Administration
Room 6-86
5600 Fishers Lane
Rockville, Maryland 20852

RETURN RECEIPT REQUESTED

CERTIFIED
NO. 39564