

LATEX AND VINYL RESINS
GAS CHROMATOGRAPHIC DETERMINATION OF RESIDUAL
VINYL CHLORIDE MONOMER

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SUMMARY A gas chromatographic analysis has been developed for the measurement of low levels of vinyl chloride monomer in vinyl latexes. A TERGITOL E-35 column capable of separating vinyl chloride from acetaldehyde is defined which offers an improved definition of vinyl chloride in vinyl chloride-vinyl acetate containing polymer latexes and resins.

Due to interferences from seemingly inherent trace impurities found in tetrahydrofuran, this method has an apparent 1-ppm minimum limit of detection for residual vinyl chloride monomer in latexes and resins.

The gas chromatographic method of analysis is attached as Appendix A.

INTRODUCTION Residual vinyl chloride monomer in vinyl resins and films is currently being analyzed by gas chromatography using a method developed by Messrs. H. T. Bias and R. A. Bleidt (1). As is generally the case with most good analytical methods of analysis, requests are soon entertained to analyze similar products not designed for the analysis. The case in point was the analysis of residual vinyl chloride monomer in vinyl chloride based polymer latexes containing vinyl acetate monomer and to a lesser extent vinyl chloride-vinyl acetate copolymer solution resins. From the outset, the analysis appeared reasonable; however, these products consistently had higher vinyl chloride results than anticipated. Even after various chemical treatments designed to react or remove the monomer were applied, the results remained high.

At this point Mr. T. R. Smith of the Latex Program Group began questioning the results concerning the integrity of the observed vinyl chloride chromatographic peak. From this inquiry it was soon determined that acetaldehyde, a hydrolysis by-product from vinyl acetate, was the culprit.

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The gas chromatographic column being used was unable to separate vinyl chloride from acetaldehyde and therefore both were being reported as vinyl chloride.

Needless to say a revision of the existing gas chromatographic procedure was initiated. The tedious and diligent search was begun for a column which would separate vinyl chloride from acetaldehyde and yet be amenable to the samples. Eventually, a TERGITOL E-35 column emerged as the most successful candidate.

This report summarizes our findings in determining vinyl chloride in vinyl chloride-vinyl acetate containing polymers, latexes and resins. The final method of analysis is included.

DISCUSSION As previously stated, we are currently analyzing residual vinyl chloride monomer in vinyl resins and films by the gas chromatographic method of Messrs. H. T. Bias and R. A. Bleidt (1). This method was designed to handle vinyl resins, powders and films by dissolving each in a solvent prior to a gas chromatographic analysis. Tetrahydrofuran was chosen as the solvent not only for its superior dissolution but also because it was supposedly free of trace impurities which might interfere with low vinyl chloride detection.

When we were first approached to analyze vinyl latex suspensions for vinyl chloride monomer, it seemed a natural that we try the existing method. It appeared superficially that all of the details had been worked out and supposedly, no new problems should arise. This was later shown to have been wishful thinking as we were soon confronted with an interference from acetaldehyde. The existing column was not capable of separating acetaldehyde from vinyl chloride and as a result, we were reporting erroneously high vinyl chloride results.

The choice of a column which would give the necessary separation of vinyl chloride and acetaldehyde was 20-ft x 1/8-in 20 percent TERGITOL E-35 on 60/80 mesh Chromosorb-W AW. This column permitted a lower column temperature, 70°C, to achieve maximum separation and yet allowed the components to elute as reasonably sharp symmetrical peaks with a minimum of tailing (See Figure 3 for a typical scan).

Another criterion for the final accepted method concerns the limit of detection or sensitivity. The current method has a minimum detectable limit for vinyl chloride of 1.5 ppm. Ideally a new method should meet or surpass that which is already available. However, to improve on a method at these levels, inherent problems associated with the gas chromatographic method begin to emerge.

First, the method is limited with respect to the amount of sample injected into the chromatograph. The current method uses 2 microliters of a 10 percent solution in tetrahydrofuran. This could probably be increased to 20 percent; however, this would in all likelihood be limited to certain samples. Also the injected sample could be increased to approximately 10 microliters; however, saturation of the detector could occur.

Secondly, these latex samples are approximately 50 percent water. Even though the flame ionization detector is non-responsive to water, there is an unbalance noted on the recorder when water enters the flame. The column must be tailored to selectively elute water either before or after the desired component depending on the complexity of the analysis.

Thirdly, there is always inherent trace impurities associated with the solvent. To date we have not located a supply of tetrahydrofuran which is free of these trace impurities. Attempts have been made to "clean-up" the solvent with relatively little success. Generally with this approach new impurities are introduced which are more detrimental than the original. Another method having ~~some~~ limited utility is the introduction of scrubber columns connected in series with the analytical column. In this manner the impurities are absorbed by the scrubber column or reacted in a manner to alter their affinity for the analytical column.

Fourthly, comes the assignment of the observed peak. The assumption that a peak of a certain retention time on the gas chromatogram is a specific material is risky. In the ppm level the actual confirmation by conventional techniques is essentially nonexistent. Mass spectrometer-gas chromatograph interfaced techniques are being examined however at the present time a reliable procedure has not been worked out. With the gas chromatographic analysis suffice it to say that the minimum detectable limit is the maximum ~~level~~ present if the peak is correctly assigned. The final method adopted for the low ppm vinyl chloride determination in polymer latexes and resins was designed with full consideration of these points.

The sample size was increased 10-fold; however a modification was made in the helium carrier gas route during the analysis. A Bendix 8-port sliding plate valve was installed to provide a column backflush mode. Shown in Figure 1 is the flow schematic adopted. In this manner, the carrier flow gas can be reversed in the column at any time to backflush those components still in the column of which there is no interest of detecting. Consequently the large volume of solvent injected into the column never reaches the detector. The backflush valve is switched just after vinyl chloride is detected

and is allowed to remain in that position for 10 minutes to purge the column. Returning the valve to its original position prepares the instrument for the injection of another sample. Acetaldehyde, which elutes approximately one minute after vinyl chloride, can be determined by delaying the valve switching until after acetaldehyde is detected on the recorder.

Various attempts were made to remove certain inherent trace impurities in the tetrahydrofuran solvent but to no avail. Finally it was decided that the method could not be tailored to detect less than a 1-ppm vinyl chloride. If a "clean" solvent is obtained the method should provide data to "tenths" of a ppm vinyl chloride. Shown in Figure 4 are scans of the solvent impurities along with a latex sample which calculated to contain 1.8 ppm vinyl chloride. Notice that certain other unidentified peaks are also present in the sample which intensify the solvent impurities.

Shown in Table I are some typical results obtained on samples of UCAR 1000, UCAR 508, MILT 29, and MILT 31.

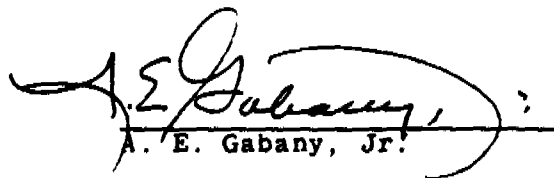
CONCLUSIONS A TERGITOL E-35 column capable of separating vinyl chloride from acetaldehyde has been used in a gas chromatographic method to improve the definition of vinyl chloride in vinyl chloride-vinyl acetate containing polymer latexes and resins. The method also uses a Bendix 8-port sliding plate valve to allow a backflush mode in the system.

ACKNOWLEDGMENT Messrs. J. L. Marchio and A. L. Monday contributed to this project with their advice and installation of the Bendix 8-port sliding plate valve.

BIBLIOGRAPHY

- 1) Bias, H. T. and Bleidt, R. A., Vinyl Resins, Gas Chromatographic Method for the Determination of Low Levels of Vinyl Chloride Monomer, Project Report, R and D, South Charleston, W. Va., File No. 19072, January 2, 1974.

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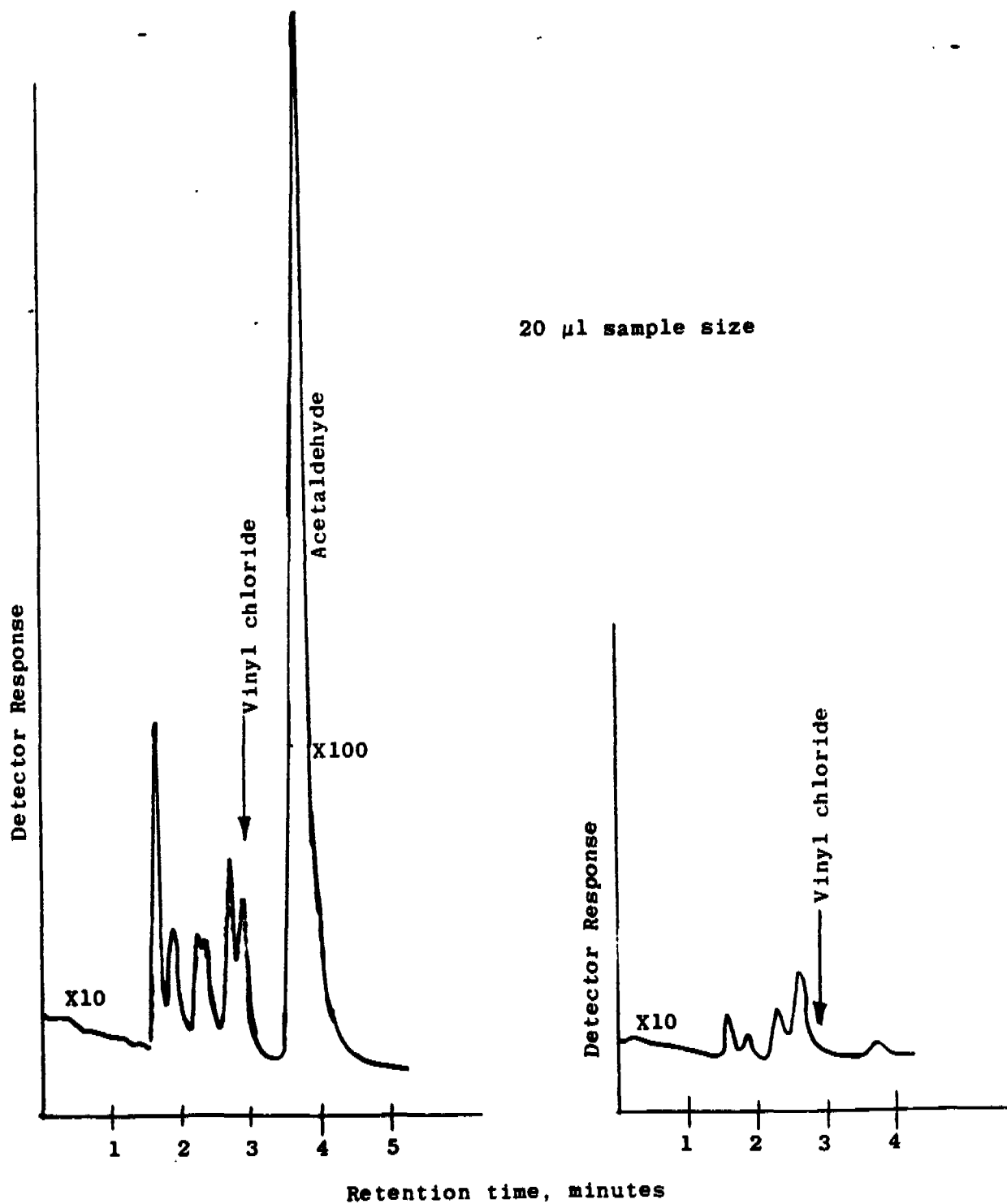
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Attachments:

- 1 Appendix A
- 1 Table
- 4 Figures

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FIGURE 4
GAS CHROMATOGRAM OF TRACE IMPURITIES IN
TETRAHYDROFURAN AS RELATED TO LOW PPM
VINYL CHLORIDE IN LATEXES



APPENDIX A
DETERMINATION OF RESIDUAL VINYL CHLORIDE
MONOMER IN VINYL LATEXES

- 1 PURPOSE A procedure for determining small amounts of residual vinyl chloride monomer in vinyl latex is described. The latex suspension is dissolved in a suitable solvent and is analyzed using a gas chromatographic technique utilizing a backflush mode. The method is applicable for use with vinyl chloride-vinyl acetate copolymer latexes and resins, vinyl chloride-vinyl acetate-ethylene terpolymer latexes and other vinyl latexes and resins in which there are no volatiles which interfere in the determination. The method resolves acetaldehyde from vinyl chloride and can be quantitated with proper calibrations.
2. EQUIPMENT AND REAGENTS
- Gas Chromatograph, Hewlett-Packard (F and M) Model 5750 or equivalent, equipped with a hydrogen flame ionization detector.
 - Backflush valve, Bendix 8-port sliding plate valve, or equivalent.
 - Tetrahydrofuran, reagent grade.
 - Balance with accuracy to 0.10 gram.
- 3 INSTRUMENT PARAMETERS
- | | |
|--------------------|---|
| Instrument | Hewlett-Packard (F and M) Mod 1 5750 or equivalent, equipped with hydrogen flame ionization detector |
| Column | 20 feet x 1/8-inch stainless steel tubing packed with 20 percent TERGITOL E-35 on Chromosorb W AW, 60/80 mesh |
| Backflush valve | Bendix, 8 port sliding plate valve or equivalent (Figure 1) |
| Temperatures | |
| Column | 70°C isothermal |
| Injection port | 100°C (maximum) |
| Detector | 300°C |
| Carrier gas | helium |
| Flows | |
| Helium carrier gas | |
| a) inject | 40 cc/minute |
| b) backflush | 40 cc/minute |
| Hydrogen | 20 psi at cylinder head |
| Compressed air | 40 psi at cylinder head |
| Sample size | 2 microliters (20 microliters if the expected monomer is less than 10 ppm) |

Approximate elution times

Vinyl chloride	2.8 minutes
Acetaldehyde	3.7 minutes

- 4 SCHEMATIC OF FLOW SYSTEM A schematic of the flow system utilizing the Bendix 8-port sliding valve is attached as Figure 1.
- 5 PROCEDURE Accurately weigh one gram of the latex to be analyzed into a 6-dram vial containing 9 grams of tetrahydrofuran (THF). Cap the vial and shake to effect solution. Inject 2 microliters of the test solution (20 microliters if the expected monomer content is less than 10 ppm) into the gas chromatograph using the parameters listed in Section 3. A backflush valve has been incorporated into the system to facilitate the analysis. After the vinyl chloride monomer and or acetaldehyde have eluted from the chromatographic column, the column is backflushed and vented to the atmosphere thus preventing the solvents from reaching the detector. In this manner the analysis time per sample is drastically shortened.

<u>Component</u>	<u>Backflush time</u>
vinyl chloride	10 minutes
acetaldehyde	10 minutes

After the prescribed backflush period, return the valve to its original position. The baseline should be allowed to equilibrate before injecting another sample.

Measure the area of the vinyl chloride peak using an acceptable technique (e.g. planimeter, automatic integrator, computer, etc.).

- 6 CALIBRATION Prepare solution mixtures in THF of varying amounts of vinyl chloride to cover the expected ppm range of concentration. Obtain the gas chromatogram for each sample using the parameters listed in Section 3. NOTE: Use 2-microliter sample size. Prepare a chart plotting the area obtained from the chromatogram of each sample versus the known concentration to establish a relative detector response. See Figure 2 for typical calibration curve.
- 7 CALCULATIONS Determine the monomer content in the test solution from the calibration chart. Apply the area of the monomer obtained from the chromatographic scan of the test solution to the calibration curve and read the the corresponding concentration in parts per million (ppm). [If the sample size of the test solution injected into the gas chromatograph was 20 microliters, multiply the ppm concentration by a 0.1 dilution factor]

The concentration value obtained from the calibration curve is total monomer in the solution. In order to convert the data to monomer concentration based on total latex the value must be multiplied by a factor of 10.

8 TYPICAL CHROMATOGRAM A typical chromatogram is attached as Figure 3.

TABLE I
TYPICAL ANALYSES OF VINYL CHLORIDE-
VINYL ACETATE LATEX SUSPENSIONS

<u>Sample</u>	<u>ppm Vinyl Chlorid</u>
UCAR 1000 ^(a)	
Reading, Pa.	50
San Francisco, Calif.	113
Carrollton, Texas	88
Atlanta, Ga.	63
Huron, Ohio	88
Chicago, Ill.	50
UCAR 508	
Somerset Storage	90
UCAR 508 B-1857 (21HOC53)	75
UCAR 508 B-2599 (21HOC105-C)	37
UCAR 508 B-2441 (21HOC94-A)	2.8
UCAR 508 B-2597 (21HOC105-A)	50
UCAR 508 B-1859 (21HOC55)	9.6
UCAR 508 (21HOC127-A)	1.8
UCAR 508 B-2290 (21HOC90-A)	7
VACA B-1107	6
MILT 29 B-4489	38
MILT 29 B-4630	100
MILT 31 B-4564 (19HOC136B)	250
MILT 31 B-5072	188
MILT 31 B-4901	38

(a) Samples shipped to Glidden Paint

FIGURE 1
SCHEMATIC OF FLOW SYSTEM UTILIZING THE
BENDIX 8-PORT SLIDING PLATE VALVE

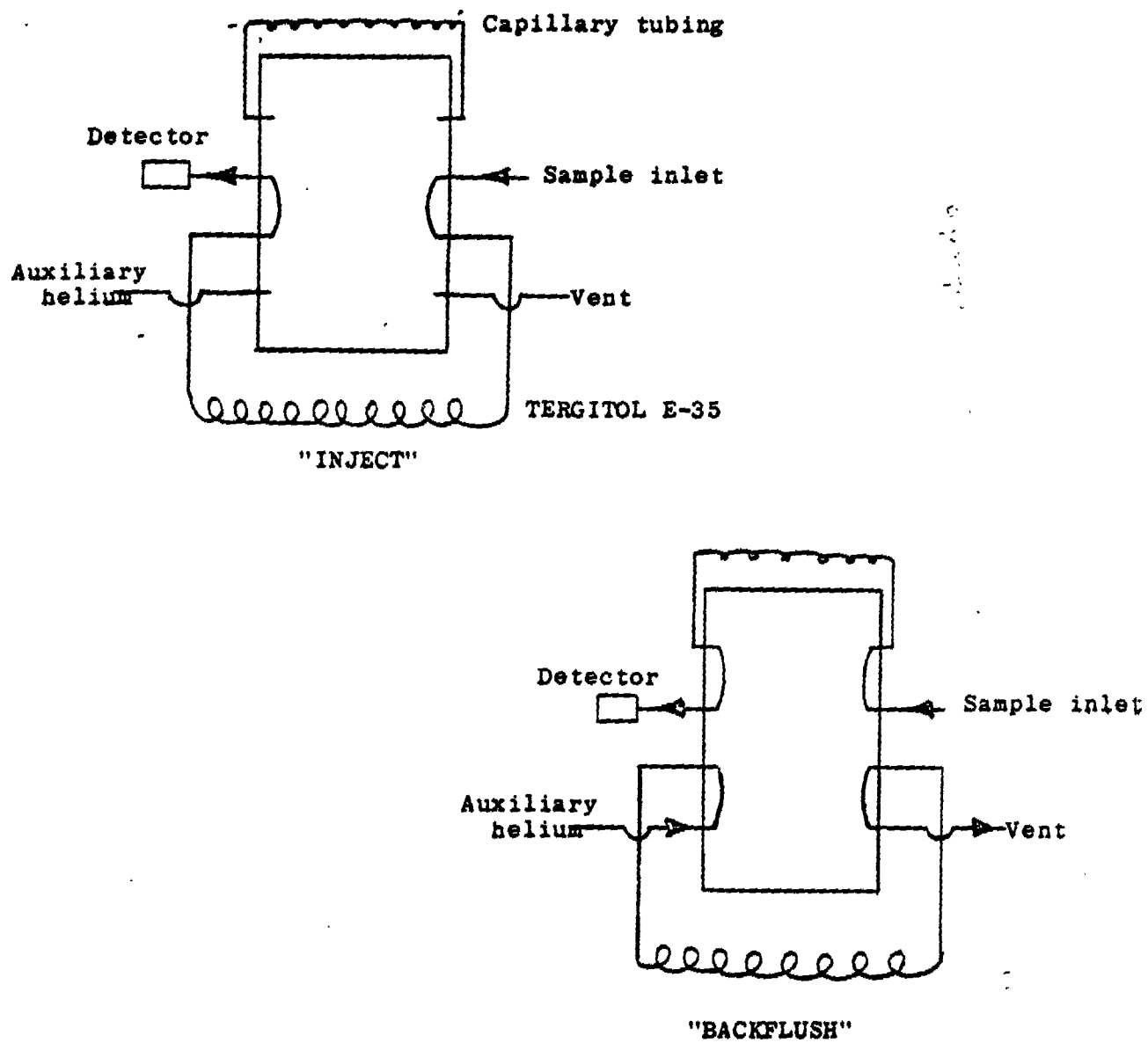
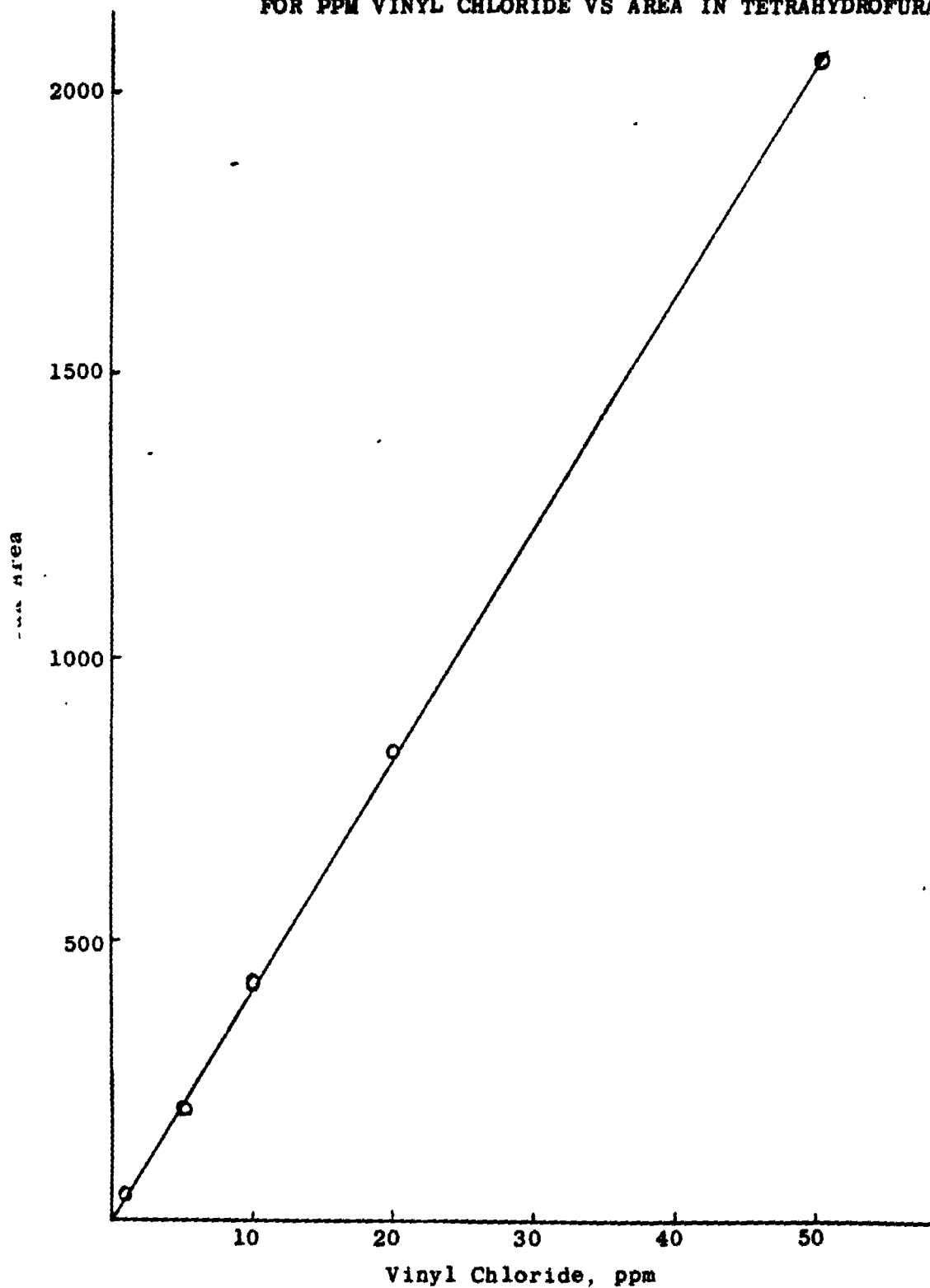
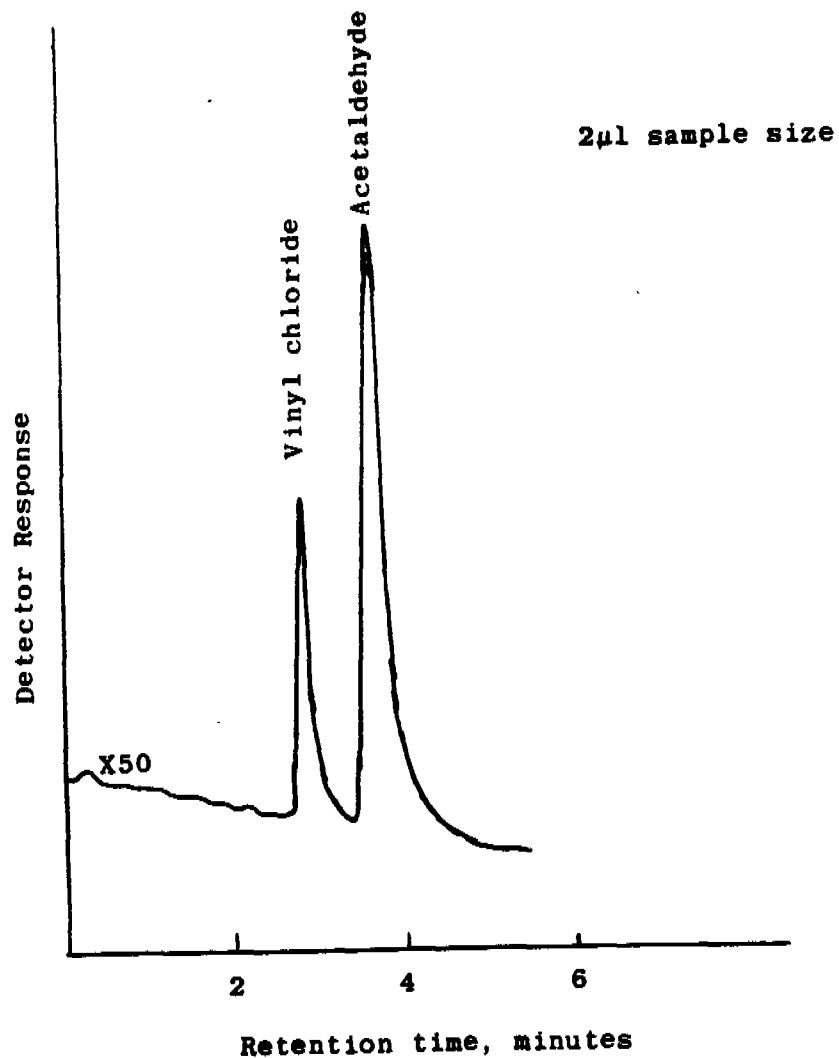


FIGURE 2
TYPICAL GAS CHROMATOGRAPHIC CALIBRATION CURVE
FOR PPM VINYL CHLORIDE VS AREA IN TETRAHYDROFURAN



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FIGURE 3
TYPICAL GAS CHROMATOGRAM OF VINYL LATEXES
FOR RESIDUAL VINYL CHLORIDE MONOMER



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