BUSINESS CONFIDENTIAL **PROJECT REPORT**

VINYL RESINS

ANALYSIS OF RESIDUAL VINYL CHLORIDE MONOMER BY HEAD-SPACE GAS CHROMATOGRAPHY AND COMPARISON TO THE EXISTING SOLUTION POLYMER GAS CHROMATOGRAPHIC METHOD

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SUMMARY A head-space gas chromatographic analysis has been r ported for measurements of low levels of residual vinyl chlorid monomer in vinyl resins. The method is not applicable for polym rs in fused form, such as sheets or cubes. Likewise, the method was not designed to accommodate latex samples.

The results when compared to those obtained by the existing tetrahydrofuran solution polymer technique-gas chromatographic m thod indicate that the method has good potential. However, the head spac method consistently gave lower results for both homopolymers and copolymers than the solution polymer method.

Although the method is a good viable technique for measuring vinyl chloride monomer, it is not recommended at this time as a r placement for our solution polymer technique-gas chromatographic method.

The vinyl chloride monomer results obtained on various types of vinyl resins produced at Texas City are tabulated.

INTRODUCTION The Environmental Protection Agency (EPA) issued proposed standards for the determination of vinyl chloride monomer (VCM) in in-process waste water samples and polyvinyl chloride (PVC) resin, slurry, wet cake and latex samples in the Federal Regist r of D cember 24, 1975. They have recommended for the analytical method of analysis a relatively new technique, head space gas chromatography.

The basis for the method relates to the vapor equilibrium which is established between VCM, PVC, resin, water, and air in a closed system. Supposedly, it has been demonstrated that the VCM in a PVC resin will equilibrate in a closed vessel quite rapidly, provided that the temp rature of the PVC resin is maintained above the glass transition temperatur of that specific resin.

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Presently Perkin-Elmer Corporation markets a Model F-40 Head Space Analyzer for approximately $14,000-$16,000 which supposedly will do the required analysis, and this instrument is mentioned in the proposal. However, it is stated in the proposed method that the m ntion of trade names on specific products does not constitute endorsement by the EPA. Furthermore, the proposed method of analysis is essentially that of B. F. Goodrich Chemical Company's Standart Test Procedure No. 1005-T-1.

In light of the supposedly firm direction in which the EPA apparently is heading, Dr. J. J. Brezinski proposed that we investigat head space gas chromatography for the analysis of VCM in Union Carbide's various vinyl resin products and compare the data with that obtained from polymer solution gas chromatography. These products would include not only PVC homopolymers but also various copolymers each of which is prepared by a separate process. To this end Mr. R. M. Arnold, Texas City, provided us with samples of the various types of vinyl resins produced at the Texas City Plant.

DISCUSSION The most widely accepted procedure for determining r sidual vinyl chloride monomer in vinyl resins, powders, films and latexes is to dissolve the sample in a solvent and anaylze the solution by gas chromatography[1]. Recently, however, there has been a noted effort emerging which would change the analysis technique form solution-gas chromatography to head space-gas chromatography. The basis of the method relates to the vapor equilibrium which is established betw en the sample and the atmosphere in a closed system. Furthermore, it has been observed[2] that at a temperature above the glass transition point of polyvinyl chloride (PVC), the solubility of vinyl chloride monom r (VCM) in PVC accurately follows Henry's law up to a VCM content of at l ast 4000 ppm. The analytical procedure involves sealing a weighed PVC sample containing VCM in a suitable vial at room temperature, heating the vial to 90°C to establish VCM equilibrium between PVC and vapor phas s, and analyzing a syringe sample of the "head space" vapor for its VCM cont nt.

As one might expect, this procedure has been automated. The Perkin-Elmer Corporation is marketing a Model F-40 Head Space Analyz r. The package includes a gas chromatograph and a thermostated constant temperature bath which has an approximate range of 10°-95°C. A sampling turntable which holds 30 sealed sample vials (~20 ml each) is low red into the preset constant temperature bath and equilibrium is established. After reaching equilibrium, about 1 hour at 90°C, the "head space" above the sample is automatically sampled and injected into the attached gas chromatograph.

Needless to say, we do not have a F-40 Head Space Analyz r; therefore, we have used a Hewlett-Packard 5750 gas chromatograph equipped with a flame ionization detector. The chromatographic column used for the analysis was a 6-ft. x 1/4-in. stainless steel column packed with 80/100 mesh Porapak QS. The column oven was maintained at 140°C isothermal,

the detector at 250°C and the injection port at 150°C. Carrier gas (helium) flow was 30 cc/min. A retangular water bath filled with silicone oil and maintained at 90°C±5°C, with constant stirring, was used in the absence of a good constant temperature bath.

In Table I are tabulated the results of the "head space" analyses obtained on various samples of vinyl resins produced at T xas City. The three different production processes as well as examples of both homopolymer and copolymer are included. In all of the gas chromatograms obtained for these samples, there was an unidentified peak which eluted just prior to the VCM peak. The presence of this peak did not particularly interfere with the measurement of the VCM peak except for the VYHH sample. In this case the VCM peak appeared as a shoulder on the tailing side of the unknown peak, thereby ruling out even a r asonable estimate of its size. Possibly the selection of another column could eliminate this for future analysis.

From the data in Table II it is apparent that the "head spac " analyses are lower than the "solution" results obtained in our laboratory and the Texas City laboratory. It is possible that recalibration could correct the situation. But when the data are examined closely, it becomes apparent that the differences range from a low of 6 p rcent to a high of 38 percent and probably it is not due to calibration. Mor than likely, the data spread is a reflection of the poor temperature control in the silicone bath.

The discrepancy between the South Charleston and Texas City data for QSAN-7 is thus far unexplained. It can, however, be assumed that the sample lost its VCM in transit.

Since we are analyzing these samples by a manual technique, there are other factors which could effect the data. The loading of the sample vails, the sampling of the "head space" with a microsyring , and the injection of the sample into the chromatograph are just a f w of points to be considered.

The sample vials we used were the same as Perkin-Elmer uses with their F-40 instrument. They are 23.5-ml Hypo-vials sealed with Teflon faced Tuf-Bond disks. The sample, approximately 2 gm, was quickly loaded into the tared vial and subsequently capped using a vial capper. After calculating the weight of the sample, the vial was then placed in the temperature bath and allowed to equilibrate at 90°C±5°C for 1 hour. The "head space" was sampled using a 500-ml Hamilton gas tight syring and injected into the gas chromatograph. Vinyl chloride eluted at 4.2 minutes. The system was calibrated using a 100-ppm VCM in air sample prepared and checked by members of the Environmental Health Group.

Two additional pieces of data are required for "head spac " analysis which are not encountered in solution-gas chromatographic methods. The complex equation used for calculating VCM requires both

the barometric pressure and air temperature at the time of the measurement. Certain other values must also be known, such as Henry's Law Constant for VCM in PVC at 90°C and the gas constant. Both of these values are known and become constants if the equilibrium temperatur is maintained at 90°C. The equation for calculating VCM is as follows:

$$\text{ppm VCM} = \frac{A_s P_a}{R_f T_1}\left[\frac{M_v V_g}{MR} + KT_2\right]$$

where A_s = Area counts for sample VCM peak
P_a = Atmospheric pressure, mm Hg
R_f = Response factor for VCM standard (counts per ppm)
T_1 = Room temperature, °K
M_v = Molecular weight VCM (62.5)
V_g = Total vial volume less volume of PVC, cc's
M = Sample weight, gms
R = Gas constant (62,400)
K = Henry's Law Constant for VCM in PVC at 90°C
T_2 = Equilibration temperature, 363°K (90°C) ✓

An example calculation would be as follows:

$A_s = 21{,}200$
$P_a = 745$
$R_f = 119.93$
$T_1 = 297$
$M_v = 62.5$
$V_g = \left(23.5 - \frac{2.6233}{1.4}\right)$
$M = 2.6233$
$R = 62{,}400$
$K = 6.52 \times 10^{-6}$
$T_2 = 363$

$$\text{ppm VCM} = \frac{(21{,}200)(745)}{(119.93)(297)}\left[\frac{62.5\left(23.5 - \frac{2.6233}{1.4}\right)}{2.6233(62{,}400)} + (6.52 \times 10^{-6})(363)\right] = 4.70$$

Notebook Reference 6HTB1

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2) Berens, A. R., et al, "Analysis for Vinyl Chloride in PVC Powd rs by Head-Space Gas Chromatography", Journal of Applied Polymer Sci nce, Vol. 19, 3169-3172, 1972.

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TABLE I

RESIDUAL VINYL CHLORIDE ANALYSIS OF VINYL RESINS BY HEAD-SPACE GAS CHROMATOGRAPHY

Resin Type	Process	Composition	Residual VCM, ppm
QYNL	Non-Solvent	PVC	2.9
VYNW	"	VCl-VA	2.9
VYHH	Solvent	VCl-VA	0
VSKK-10	Suspension	VCl-VA	197.1
QSQH-7	"	VCl-Ethylene	11.5
QSAN-7	"	PVC	10.6
QSAL	"	PVC	4.7

TABLE II

COMPARISON OF RESIDUAL VINYL CHLORIDE ANALYSIS
BY HEAD-SPACE-GAS CHROMATOGRAPHY WITH
SOLUTION-GAS CHROMATOGRAPHY

	Residual VCM, ppm		
Resin Type	Head Space	Solution	
		S. C. Tech Center	T xas City
QYNL	2.9	4.3	5.1
VYNW	2.9	3.7	3.6
VYHH	0	0.13	0.2
VSKK-10	197.1	241	237
QSQH-7	11.5	18.7	20.2
QSAN-7	10.6	11.3	40.2
QSAL	4.7	5.3	6.6

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