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Analysis for Vinyl Chloride in PVC Powders by Head-Space Gas Chromatography

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Synopsis

At a temperature above the glass transition point of poly(vinyl chloride) (PVC), the solubility of vinyl chloride monomer (VCM) in PVC accurately follows Henry's law behavior for VCM contents up to 4000 ppm. This observation has lead to a rapid, simple gas-chromatographic method for the determination of VCM in PVC from the analysis of the vapor phase (head-space) over PVC powder samples in a sealed container. The basic experimental techniques, calculations, and examples of experimental data are given. The method can be used with any commercial gas chromatograph equipped with a flame ionization detector without instrument modification.

INTRODUCTION

Recent concern about the possible health hazard of exposure to vinyl chloride monomer (VCM)[1] has focused attention on the measurement of residual monomer contents of commercial PVC products. We report here a simple, rapid analysis for VCM in PVC through gas chromatography of the vapor phase over PVC powder samples.

The basis of our method is the observation[2] that at a temperature above the glass transition point of PVC, the solubility of VCM in PVC accurately follows Henry's law behavior up to a VCM content of at least 4000 ppm. The analytical procedure simply 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 phases, and analyzing a syringe sample of the "head-space" vapor for its VCM content. The original VCM content of the PVC is calculated as follows:

Let us say that the PVC sample of weight m grams originally contains W_t grams VCM. Upon equilibration at 90°C,

$$W_t = W_v + W_p \tag{1}$$

where W_v and W_p are the weights of VCM in the vapor and PVC phases, respectively. We may write Henry's law as

$$\frac{W_p}{m} = KP_v \tag{2}$$

where P_v is the partial pressure of VCM in mm, and K at 90° is 6.52 ppm/mm.[2] Combining eqs. (1) and (2) and assuming ideal gas behavior, it can be shown that

$$\frac{W_t}{m} = \frac{YRT_2}{M_vZ}\left(K + \frac{M_vV_g}{mRT_2}\right) \tag{3}$$

where R is the gas constant, $T_2 = 363°\text{K}$, M_v is the molecular weight of VCM, V_g is the volume of vapor phase (vial volume less volume of PVC sample), and Y is the weight of VCM in a syringe sample of vapor volume Z cc. After calibrating the GC response on known gas mixtures, Y may be obtained directly from the height or area of the VCM peak of the gas chromatogram. Thus, eq. (3) gives the VCM content of the PVC sample, W_t/m, directly from the GC analysis of the vapor phase.

The time required for equilibration of VCM between vapor and PVC phases can be estimated from recently reported diffusion data.[3] From the solution of Fick's diffusion equation for spherical geometry,[4] the time required for 99% of the original VCM dissolved in a PVC sample to diffuse out into a VCM-free environment is given by

$$t_{.99} = \frac{0.113d^2}{D} \tag{4}$$

where d is the particle diameter in cm and D is the diffusion coefficient in cm^2/sec. For VCM in PVC at 90°C, D is approximately 2×10^{-10} cm^2/sec; hence, $t_{.99}$ will be less than 1 hr for PVC particles of less than 25 microns effective diameter. In our experience, a 1-hr heating time at 90°C has proved satisfactory for the analysis of most commercial PVC resins in the as-polymerized powder form. Our analytical method is less satisfactory for molded, extruded, or otherwise fused PVC samples because of the very long equilibration times required.

EXPERIMENTAL

In developing the head-space method of analysis, we have used a Hewlett Packard 5710 gas chromatograph equipped with a flame ionization detector. Other commercially available gas chromatographs having suitable sensitivity and resolution can also be used. The chromatographic column used for the analysis is a 6 ft × ⅛ in. stainless steel column, packed with 80/100-mesh Porapak QS. The column oven is controlled at 140°C, the detector at 250°C, and the injection port at 150°C. Carrier gas (helium) flow is 30 cc/min. Under these conditions, vinyl chloride elutes from the chromatograph in approximately 280 sec.

Since numerous other organic vapors may also be present in the head space from commercial PVC resins (due to initiator fragments, solvents, trace monomer impurities, etc.), it is recommended that the identity of the VCM peak be verified by an initial analysis using a gas chromatograph–mass spectrometer tandem system or other suitable verification procedure. Our GC–MS analysis of a number of different types of commercial PVC resins has shown no significant interfering components. Methanol, if present, is not completely separated from VCM using the 80/100-mesh Porapak QS column, but can readily be seen as an interfering component in the trailing edge of the VCM peak.

A response factor for the chromatograph is determined by injecting known, standard mixtures of vinyl chloride and air.

Samples for analysis are prepared by weighing approximately 2 g PVC powder into a 12-cc vial and sealing the vial with a fold-over septum. The sample vials are then placed in an air oven or water bath controlled at 90°C and allowed to equilibrate.

After equilibrium is established, an aliquot of the vapor space in the vial is removed with a gas-tight syringe. The volume of this vapor sample at room temperature and pressure is noted, and the sample is injected into the chromatograph for analysis. As a convenient alternate to manual syringe-sampling of the head-space vapor, we have recently used an automated head-space analyzer (Perkin-Elmer Model F-40). Determination of the residual vinyl chloride in the sample is made using eq. (3) above.

RESULTS AND DISCUSSION

To verify the accuracy of the head-space analysis, a PVC resin was stripped of all residual vinyl chloride via vacuum-thermal techniques. Head-space analysis of this resin showed no detectable VCM. This "clean" resin was weighed into sample vials which were then septum sealed. Known amounts of vinyl chloride gas were injected into the vials and allowed to equilibrate for 1 hr at 90°C. The vial head-space was then analyzed as described. Table I compares the head-space analytical results with the calculated ppm vinyl chloride.

TABLE I

Head-Space Analysis of Known Samples

Resin Weight, gms	VCM Charged, cc	Calculated, ppm VCM	Head-space Analysis, ppm VCM
3.2	2.	1600	1586
3.2	1.	793	759
3.2	.5	397	379
3.2	.025	20	23.3

The head-space method has also been compared to a direct method of analysis in which residual vinyl chloride is determined without relying on establishment of polymer/vapor equilibrium. In this method, 20–30 mg PVC resin is weighed into a glass tube which fits into the injection port of the H-P 5710 chromatograph. The PVC powder is held in the heated section of the tube with a glass-wool plug. The injection-port septum is removed, the sample tube dropped into the injection port, and the septum replaced. The heat of the injection port (150°C) drives the volatiles out of the polymer into the carrier gas stream. To produce plug flow through the column, its first 2 or 3 in. are chilled with Dry Ice before the sample is introduced. After sample insertion, the column oven is programmed at 16°C/min to 200°C. Vinyl chloride elutes in approximately 6 min. The vinyl chloride peak area is a direct measure of the total VCM content of the PVC sample. While this method of

TABLE II

Comparison of Head-Space and Direct Methods

Sample	Head-space analysis, residual VCM	Direct method of analysis, ppm residual VCM
PVC Homopolymer "A"	30	30
	31	29
	31	20
	29	24
PVC Homopolymer "B"	46	47
	45	45
	43	48

analysis appears reliable, the small PVC sample size introduces a possible weighing error, and the need to chill and program the column temperature makes the method somewhat less convenient than the head-space method. Table II compares data from the two methods.

We have repeatedly verified the precision and sensitivity of the head-space analysis. For example, twenty samples of a single PVC homopolymer resin were analyzed over a ten-day period by our method, with manual sampling; the VCM content was found to be 7.1 ppm with a standard deviation of 1.0 ppm. In a series of PVC resins ranging from 0.5 to 750 ppm VCM content, the standard deviation between duplicate analyses by the head-space method with automated sampling was 4.6%.

The head-space analysis appears superior in precision and convenience to procedures in which the PVC is dissolved in a solvent and liquid samples of the solution then are analyzed for VCM by gas chromatography. We have found standard deviations of 16% in one laboratory, and greater than 20% in cross-checks between laboratories, using such a solvent method. The solvent method also requires lengthy purging, or a backflushing operation, to clear the solvent from the GC column between analyses; this inconvenience is avoided by the head-space, vapor-sampling method.

In closing, we suggest that a similar analytical method might be generally applicable for the determination of volatile components in polymers. To establish the method for a new polymer/penetrant system would require, first, the determination of conditions where Henry's law applies and of the Henry's law constant, and second, an estimate of the time required to establish vapor–polymer equilibrium.

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