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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

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

90° is 0.52 ppm ... eharior, it can be

(3)

r weight of VCM, of PVC sample), lume *Z* cc. After y be obtained di- s chromatogram. *m*, directly from

r and PVC phas- From the solu- he time required diffuse out into a

(4)

ion coefficient is × 10⁻¹⁰ cm²/sec; an 25 microns of- 90°C has proved is in the analysis ctory for molded, y long equilibra-

e used a Hewlett ization detector, itable sensitivity mn used for the 80/100-mesh Po- tector at 250°C, w is 30 cc/min. atograph in ap-

n the head space vents, trace mo- f the VCM peak mass spectrome- e. Our GC-MS resins has shown is not complete 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

[illegible] Head-Space Analysis [illegible] Samples [illegible]

[illegible]	[illegible]	[illegible] ppm VCM	Head-space Analysis, ppm VCM
[illegible]	[illegible]	[illegible]	1556
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	22.3

The head-space [illegible] has also been [illegible] method of anal- [illegible] vinyl chloride is determined without relying on estab- [illegible] equilibrium. In this method, 20–30 mg PVC [illegible] is weighed into [illegible] the injection port of the H-P 5710 [illegible] is held in the heated section of the tube [illegible] is removed, the sample [illegible] replaced. The heat of [illegible] the vinyl chloride out of the polymer into the car- [illegible] column, [illegible] the first 2 or 3 [illegible] the sample is introduced. After sample inser- tion, the column [illegible] °C/min to 200°C. Vinyl chloride [illegible] The vinyl chloride peak [illegible] a direct mea- [illegible] of the PVC sample. While this method of

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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
	[illegible]	29
	31	28
	29	24
PVC Homopolymer "B"	46	47
	46	45
	46	48

analysis [illegible], 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 [illegible] data from the two methods.

We have [illegible] verified the precision and sensitivity of the head-space analysis. For example, twenty samples of a single PVC homopolymer resin were analyzed over a [illegible]-day period by our method, with manual sampling; the VCM content was found to be [illegible] ppm with a standard deviation of 1.0 ppm. In [illegible] of PVC [illegible] ranging from [illegible] to [illegible] ppm VCM content, [illegible] analysis by the head-space method [illegible]

[illegible]

In closing, we suggest that [illegible] analytical method might be generally [illegible] in polymers. [illegible] would require, first, the determination of conditions where Henry's law applies and of the Henry's law constants, [illegible]

[illegible]

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