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DETERMINATION OF VINYL CHLORIDE MONOMER RESIDUE IN POLY(VINYL CHLORIDE) AT THE PARTS-PER-BILLION LEVEL WITH AN AUTOMATIC PURGE-AND-TRAP TECHNIQUE

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SUMMARY

A method for the determination of vinyl chloride residue in poly(vinyl chloride) using a commercial purge-and-trap ancillary unit has been developed. Concentrations lower than 10 ppb (10^9) with relative standard deviations in the region of 10% in up to 24 samples are detectable with fully automatic operation without operator attendance. With multiple extraction of the same sample an external standard is used; the matrix does not have any influence on the recovery of vinyl chloride.

INTRODUCTION

Vinyl chloride monomer (VCM) has been proved to be a human carcinogen[1] even though a threshold toxicity level has not yet been established, stringent regulations for the use and handling of VCM have been promulgated by the Food and Drug Administration (FDA) in the U.S.A. This has necessitated sampling and analytical techniques able to detect VCM at low concentrations; a recent FDA proposal established a new limit in the range 5–50 ppb* of VCM, depending on the type of polymer and polymer resin will lead to a search for improved methods of detection and monitoring. Headspace gas chromatography (GC) has so far been the method of choice owing to its ease of manipulation and high sensitivity.

Two approaches to the headspace analysis of residual monomer in polymers have been used, the solid and the solution approach. The solid approach[2] involves the equilibration of a solid polymer sample at 90°C in a sealed system, followed by headspace analysis according to a single or multiple extraction technique[3]. The solution approach[4] involves the equilibration of a 10% solution of poly(vinyl chloride) (PVC) in dimethylacetamide in a sealed system, followed by analysis of the headspace gas. Although the solid method provides much higher sensitivity than the solution headspace method, it can be applied only to sample systems where equilibration with the headspace is rapid and complete. When the VCM concentration in PVC is lower than 0.1 ppm, determination by headspace sampling alone cannot be accurate; also, detection limits of a few ppb can be attained with both flame ionization and pho-

* Throughout this article, the American billion (10^9) is meant.

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toionization detectors if the solid approach is applied. The major drawback of this technique is that it cannot be considered to be universal and different samples need different equilibration times.

Another approach consisting in double concentration of the sample has been published[4]; it involves sparging of the solution to transfer the VCM to another solution in which VCM is present at higher concentration. The combination of the sparging step and the headspace sampling technique produces the desired sensitivity.

The approach described here consists in a dynamic headspace method involving a sparging and a focusing step before thermal desorption into the GC column. The method is automatic, and all operations are performed by means of a commercially available ancillary unit, which may be coupled to any GC system.

EXPERIMENTAL

Instrumentation

The dynamic headspace system used was a Dani SPT 37.50 purge-and-trap plus a dynamic headspace automatic sampler equipped with a Dani constant incubation time (CIT) device, in order to have the same equilibration time for each sample. The sampler was coupled to a Dani 84.00 gas chromatograph with a flame ionization detector.

The system, described in detail elsewhere[5], is shown schematically in Fig. 1. It consists of a constant-temperature bath and of a carousel into which up to 24 sealed glass vials containing the sample solution can be introduced. After a preconditioning

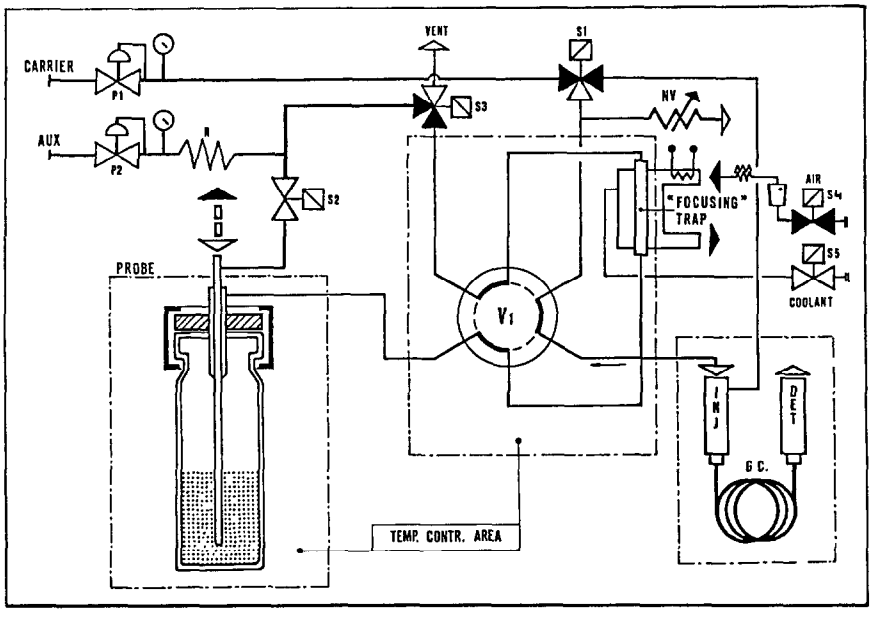

Fig. 1. Dani SPT 37.50 pneumatics scheme. P1, P2 = pressure regulators; S1–S5 = solenoid valves; NV = needle valve; R = calibrated restrictor; V1 = six-port pneumatic valve. INJ = Injection; DET = detection; TEMP. CONTR. = temperature-controlled.

time, the septum of a vial is penetrated by a twin two-port needle. Into the bottom of the vial is fed a sparging gas which also transfers the volatiles to a cold trap, mounted across a gas-sampling valve and filled with Tenax TA. When the purging and trapping steps are completed, the gas-sampling valve is rotated and the trap is connected with the gas chromatograph. The trap is then quickly heated and the VCM is desorbed by a stream of carrier gas and transferred to the GC column. Timing and temperature controls are provided by a microprocessor programming unit. Rapid heating of the trap is achieved by means of a stream of pre-heated, compressed air on the principle of programmed temperature desorption (PTD)[5]. A Shimadzu C-R3A integrator is used for peak-area determinations.

Reagents and materials

N,N-Dimethylacetamide (DMA) was sparged with a stream of nitrogen (30 ml/min) for up to 1 week at room temperature in order to remove chromatographic interferences. Glass vials and fluoropolymer-faced silicone rubber septa (Dani) were heated in an oven at 150°C for 2 h just before use.

Gas chromatographic conditions

A stainless-steel column (3 m × 3 mm I.D.), packed with 25% free fatty acid phase (FFAP) (Supelco, Bellefonte, PA, U.S.A.) on Chromosorb P (80–100 mesh), was programmed from 60°C (held for 4 min) at 20°C/min to 195°C (held for 16 min). The flow-rate was 30 ml/min and the detector sensitivity was given by an electrometer setting of $\times 1 \times 8$ ($8 \cdot 10^{-12}$ A f.s.).

Purge and trap conditions

The following conditions were used: constant-temperature bath, 90°C; switching valve and transfer lines, 150°C; sample, 10 ml of 10% solution in DMA in standard 23-ml vials, capped with fluoropolymer-faced silicone-rubber septa; incubation time, 1 h; flow-rate of purge gas (nitrogen) 30 ml/min; trap packing, 200 mg of Tenax TA (60–80 mesh); trap temperature, initial 30°C, final 200°C (heating rate 1200°C/min); purging time, 5 min; trap desorption time, 50 s; trap back-flushing time at final temperature (200°C), 10 min.

RESULTS AND DISCUSSION

Fig. 2 shows a typical chromatogram of a synthetic mixture of 10 ppb of VCM in DMA. Note the full-scale peak of DMA. Its complete elution and complete baseline recovery at the indicated sensitivity take about 35 min. The amount of DMA entering the chromatographic column is only a small part of the total amount retained in the focusing trap, the main part being back-flushed from the trap during the last step of the purge-and-trap cycle. The introduction of DMA into the chromatographic column could be avoided by using a short pre-column and a back-flushing valve. However, the analysis time is not substantially shortened, owing to the elution of substances not retained by the pre-column. Moreover, working at such a high sensitivity, the VCM would not be so clear because of baseline fluctuations due to the pneumatic switching.

The use of other stationary phases such as Porapak N[6], Porapak S+T[7] or

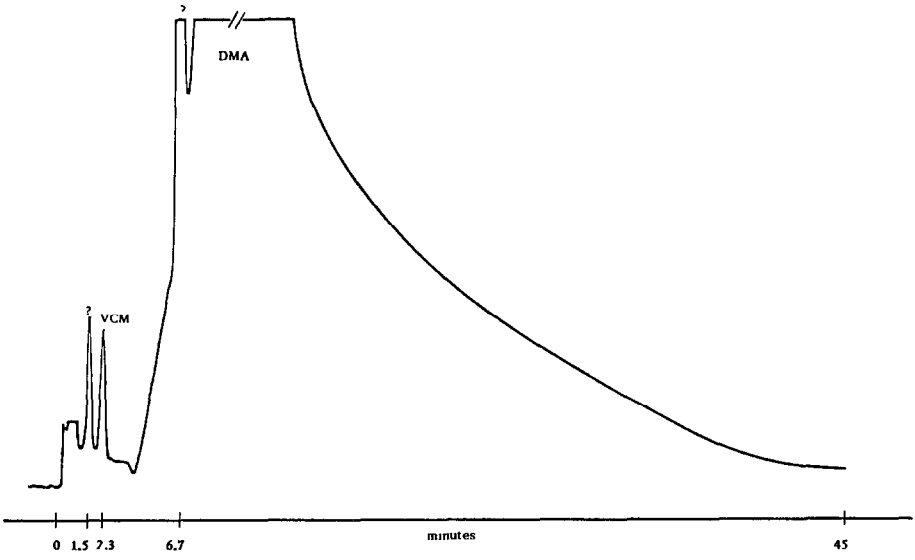

Fig. 2. Chromatogram of a calibration mixture of 10 ppb VCM in DMA. For experimental conditions, see text.

picric acid on Carbopack C^8, has been reported. With these phases, the retention time of DMA at the maximum allowable temperature is also too long. For this reason, FFAP was used in this investigation, allowing the elution of all hydrocarbons up to C_4 before VCM. There is an unidentified peak having a retention time of 1.5 min, close to VCM, but it does not overlap (Fig. 3). The nature of this peak has not been ascertained. A very small peak (1 ppb), having the same retention time as VCM,

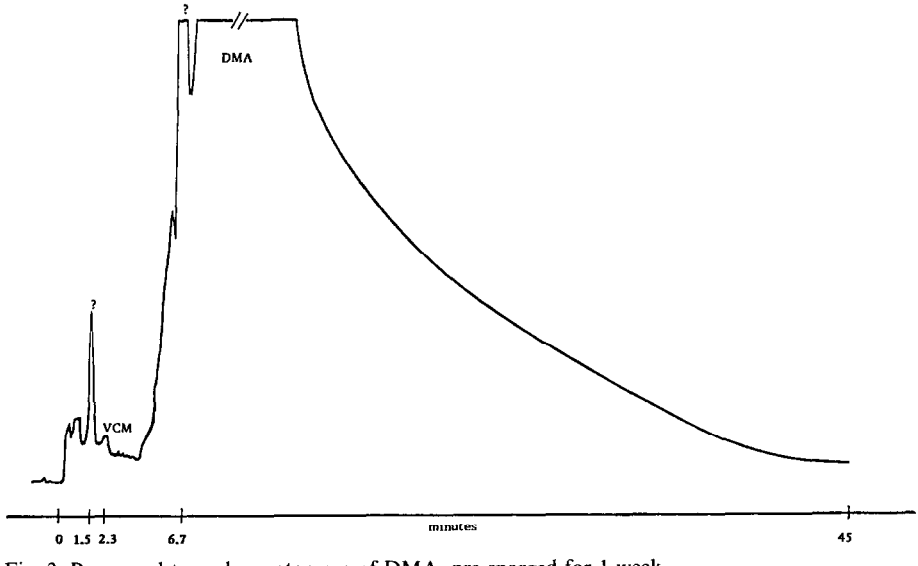

Fig. 3. Purge-and-trap chromatogram of DMA, pre-sparged for 1 week.

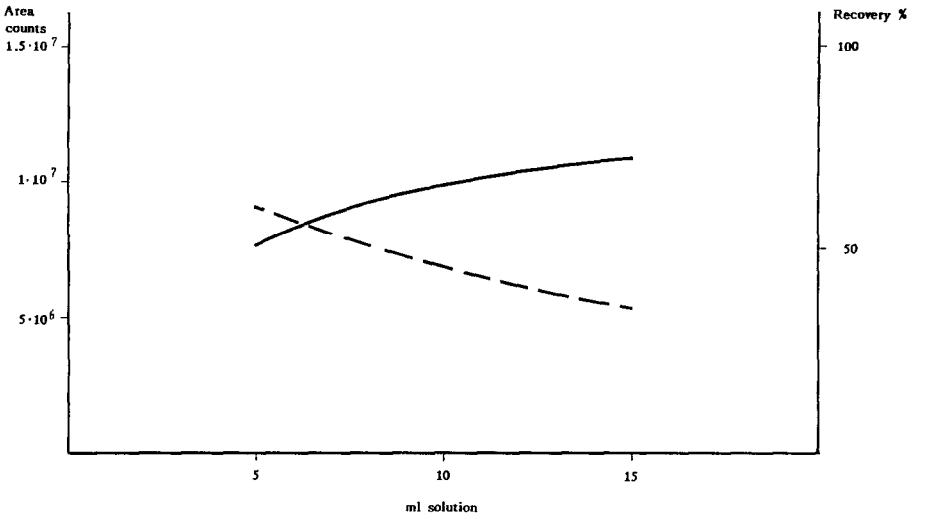

Fig. 4. Peak area (solid line) recovery (broken line) of VCM at the first extraction with different amounts of solution (100 ppb of VCM in DMA) in the vial.

could be an impurity or a trace of VCM present in DMA, either not perfectly purged or contaminated during the operation. A blank run is therefore suggested, the area of this interfering peak being subtracted.

The purge-and-trap conditions were optimized by changing the vial incubation temperature and the trap temperature in the desorption step, the flow-rate of the stripping gas and the time spent on sparging and trap desorption. For the volume of solution in the vial a compromise of 10 ml was chosen in order to have the highest response and safest purging conditions. Obviously, 15 ml of solution provides a larger peak are than 10 or 5 ml in absolute terms, but in relative terms the results are better with only 10 ml. Fig. 4 shows the VCM recovery behaviour with different amounts of solution. The gas flow-rate and purging time were also a compromise to avoid aerosol formation in the vial and possible losses of VCM at the trap level.

Two adsorbents were tested for the focusing trap packing: Tenax TA and Carbotrap (kindly supplied by Supelco). Tenax TA is preferred, because DMA is removed in a shorter time during the focusing trap back-flushing step. Both flame ionization and photoionization detectors were used; the latter did not show any advantages in terms of sensitivity and selectivity.

Quantitation

The advantage of the sample solution approach over the solid sample and headspace techniques is the simplification of the calibration procedure and the rapidity with which equilibrium is obtained between the liquid and gaseous phases. With the purge-and-trap approach, these advantages are even more evident. The availability of an automatic instrument, providing a means of following the multiple extraction, represents another advantage. This method[9,10] is based on performing multiple analyses of the same sample. The total amount of extracted VCM and the recovery can be determined without adding standards. The detector response factor

must still be determined, but any influence of the matrix on the recovery is eliminated. In the determination of VCM, only two extractions are necessary. Thereafter, some simple calculations provide the VCM concentration. In practice, the total VCM peak area is calculated after two extractions of the unknown sample and subtracting the blank areas according to the following equation:

$$T = \frac{(A - C)2}{(A - C) - (B - C)}$$

Then

$$T = \frac{(A - C)^2}{A - B} \tag{1}$$

where A is the VCM peak area in the first analysis, B is the VCM peak area in the second analysis, C is the blank peak area and T is the total VCM peak area.

The total VCM peak area is multiplied by the response factor calculated on

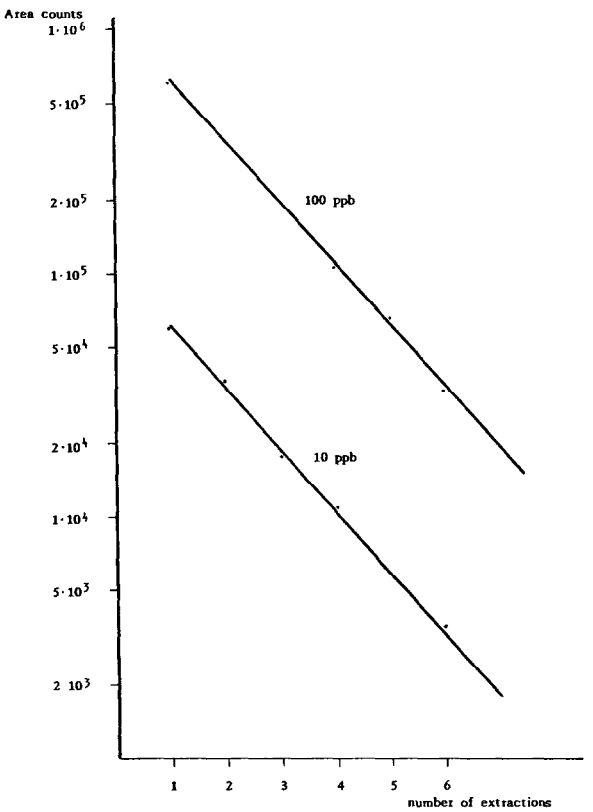

Fig. 5. Semi-logaritmic plot of peak area against the number of extractions obtained during a calibration run.

TABLE I

PEAK AREAS AND RECOVERIES OF 10 ng OF VCM OBTAINED WITH DIFFERENT INJECTION METHODS AND MODES OF CALCULATION

Mode of calculation	*Peak area (arbitrary units)**	*Recovery (%)*	*Injection*
Single peak area integration	126 200	Theoretical (100)	1 ml of gas containing 10 ng of VCM
Total peak areas, calculated from the sum of 8 injections	128 700	102	Purge and trap of 10 ml of DMA containing 10 ppb of VCM
Total peak areas, calculated from the value of the first two analyses according to eqn. 1.	130 200	103.2	Purge and trap of 10 ml of DMA containing 10 ppb of VCM

* Average of three determinations.

a sample containing a known weight of VCM in pure DMA. The weight of VCM is then divided by the weight of polymer in the vial to obtain the concentration in ppb (ng/g).

Fig. 5 is a semi-logarithmic plot of peak area against the number of extractions carried out during a calibration run. Table I shows the peak areas of 10 ng of VCM obtained with various modes of injection and calculations. The three sets of data are in good agreement, showing also a more than acceptable VCM recovery. Table II summarizes the results obtained during a series of calibration runs and Table III shows the results obtained in the determination of VCM residues in several PVC samples.

CONCLUSION

It has been confirmed that the determination of VCM residues in various PVC powders and fabricated materials is feasible by means of a purge-and-trap method which provides a pre-concentration step before the GC separation. The optimization of different operating parameters allows the determination of VCM at the low-ppb

TABLE II

CALIBRATION RUNS WITH THREE DIFFERENT AMOUNTS OF WEIGHED VCM IN DMA

Average for three vials with the same concentration. R.S.D. = Relative standard deviation.

VCM in DMA (ppb)	*Peak area (arbitrary units)*					
	1st extraction	*2nd extraction*	*Calculated from first 2 extractions*	*R.S.D. (%)*	*Calculated from sum of 6 extractions*	*R.S.D. (%)*
1000	6 107 740	3 695 465	15 464 442	2.2	13 758 330	2.5
100	601 866	352 786	1 453 422	3.5	1 324 647	4.2
10	58 533	32 227	130 242	5.5	128 702	8.8

TABLE III

CONCENTRATION OF VCM RESIDUE IN DIFFERENT PVC SAMPLES

Average for three vials of each sample.

Sample (10% solution in DMA)	*Peak area (arbitrary units)*						*Concentration (ppb)*	
	1st extraction	*2nd extraction*	*Calculated from first 2 extraction (A)*	*R.S.D. (%)*	*Calculated from sum of 6 extractions (B)*	*R.S.D. (%)*	*A*	*B*
Rigid water bottle	519 050	314 750	1 310 956	3	1 295 860	3.2	850	840
Thin plasticized food film	1771	967	3901	14.5	–	–	2.99	–
Monopolymer powder	5834	3195	12 659	8.3	–	–	9.73	–
Copolymer film	8779	4724	19 034	5	20 460*	6.5	15	16.2

* Five extractions.

level with an acceptable relative standard deviation. The use of a commercial ancillary unit provides full automation of the operations, involving sparging of the sample solution, trapping of VCM in a focusing trap, thermal desorption, transfer of VCM to the GC column and removal of the major part of the DMA. The quantitation of VCM is made very easily and independently of the type of matrix by means of the multiple extraction technique, followed by external calibration. The final results are obtained by performing only two extractions. The total VCM peak area is calculated by means of a mathematical extrapolation. Up to 15 samples per day can be processed without operator attendance.

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