Journal of Chromatography, 198 (1980) 337–346
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,022

DETERMINATION OF RESIDUAL VINYL CHLORIDE IN POLY(VINYL CHLORIDE) RESINS

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(First received October 4th, 1979; revised manuscript received June 10th, 1980)

SUMMARY

The determination of residual vinyl chloride (VC) in poly(vinyl chloride) (PVC) powders based on thermal desorbtion in a carrier gas stream and trapping of the VC is described. A trap is installed in the heated injection port of a gas chromatograph and desorbed volatiles are chromatographed by a two-stage chromatographic system. While VC is purged through an analytical column, the first column is cleaned by back-flushing. The method has been tested on various types of PVC powders and has no limit of sensitivity.

INTRODUCTION

Owing to the carcinogenic properties of vinyl chloride (VC)[1,2], it must be analysed both in poly(vinyl chloride) (PVC) and in PVC materials. Modern requirements for the purity of PVC range from a few parts per million downwards[2,3]. These severe requirements for the purity of PVC are conditioned by wide fluctuations in VC content in PVC resins and products depending on the technology of PVC production and processing.

Purity is especially important for foodstuffs packing materials, as foodstuffs should not contain more than 50 ppb of VC[4,5], and there is a linear relationship between the VC concentration in packing materials and that subsequently found in packed foodstuffs[6] and cosmetics[7]. Different foodstuffs extract VC to different extents[8].

The determination of VC in foodstuffs is difficult; the direct injection method is unsatisfactory[9], and the headspace method is generally used[6,8,9], frequently combined with mass spectrometry for greater reliability[10,11]. Conversion of VC into dibromochloroethane[12] and combustion of VC combined with electrochemical detection of hydrogen chloride[13] are selective methods used in VC trace analysis.

Various methods have been described for the determination of residual VC in PVC. In one method[14,15] the polymer is dissolved in a suitable solvent and a portion of the polymer solution is chromatographed. However, possible clogging of the

0021-9673/80/0000–0000/$02.25

chromatograph evaporator by the polymer is a serious inconvenience in this method. The sensitivity is *ca.* 10 ppm.

Gaseous contaminants in PVC may be trapped on heating the polymer in a vacuum, measuring the liberated gas and analysing it by gas chromatography or IR or mass spectrometry[16,17].

The solution mode of the headspace method that is generally used is inconvenient as it requires time for dissolving the sample and equilibration, and the purity of the solvent must be high with only very low contents of impurities that may be chromatographed simultaneously with VC[6,18,19]. Analysis of the gas phase above the solid PVC is a labourious and slow procedure, demanding precautions against possible loss of VC[20].

Owing to these difficulties we preferred a dynamic method to static methods for removal of VC from PVC powder.

The principle and possibilities of the mode have been described briefly[20,21], but no routine analysis has been suggested so far.

EXPERIMENTAL

Auxiliary equipment

The system for the separation and trapping of volatiles from PVC is installed in the cover of the detector oven of a Tsvett-104 chromatograph (OCBA, U.S.S.R.). The system is shown schematically in Fig. 1. The system for feeding the gas into the device includes a pressure-reducing valve, a pressure gauge and a needle valve to adjust the carrier gas flow-rate in the tube containing PVC and in the trap. For cooling the trap should be dipped half its height into a Dewar vacuum flask containing liquid nitrogen.

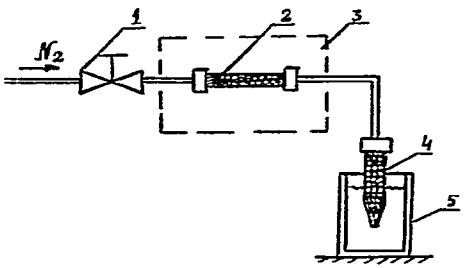

Fig. 1. System for trapping volatiles from PVC powder. 1 = Needle valve; 2 = tube with PVC; 3 = oven; 4 = trap containing sorbent; 5 = Dewar flask containing liquid nitrogen.

Preliminary procedures

The system should be assembled as shown in Fig. 2. The system consists of two columns (pre-column and analytical column) connected to the instrument through a six-port switching valve. Depending on the position of the switching valve, the columns may work under conditions of direct purging (solid line) or back flushing (dotted line). For observing the back-flushing the pre-column may be connected to the second flame-ionization detector (FID).

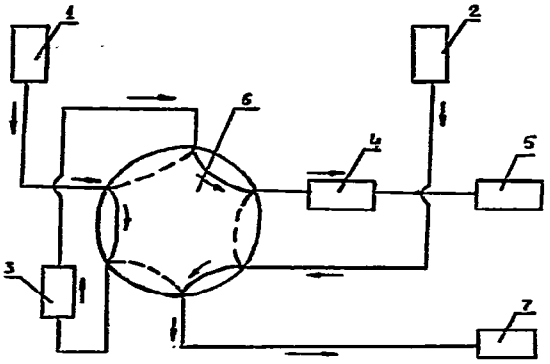

Fig. 2. Schematic flow diagram with six-port switching valve. 1,2 = First and second channels of injection port; 3 = pre-column; 4 = analytical column; 5,7 = detectors; 6 = six-port switching valve. Arrows show carrier gas flow in direct purging.

Fig. 3 shows the installation of the trap in the injection port. As there is a ground-glass joint at the end of the trap, the trap enters into the corresponding connection with the ground-glass joint, connected to the evaporator in the same manner as the glass column.

The traps are removed from the evaporator with tweezers that have narrow tips with cuts.

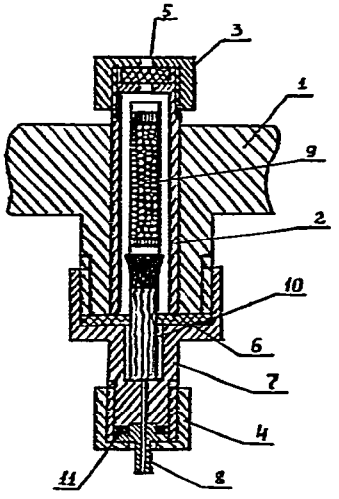

Fig. 3. Installation of trap in evaporator. 1 = Oven body; 2 = evaporator body; 3,4 = nuts; 5,6 = silicone-rubber seals; 7 = union; 8 = stainless-steel capillary tube; 9 = trap filled with sorbent; 10 = ground-glass joint coupling, filled with glass-wool; 11 = aluminium gasket.

Column preparation

The pre-column is filled with a sorbent consisting of 15% Apiezon L on Chezasorb AW, with particle dimensions of 0.210–0.360 mm (Chemapol, Prague,

Czechoslovakia). The sorbent for the analytical column is Polysorb 1 (0.125–0.250 mm fraction) or Chromosorb 104. The pre-column and analytical column are made of glass, with dimensions 100 × 0.4 cm I.D.

The column system is assembled and conditioned for 24 h at 150°C in the back-flushing mode.

Chromatographic conditions

The carrier gas is nitrogen at flow-rates, measured at ambient temperature in the analytical column exit, of 8.5 ml/min during direct purging, 50 ml/min during back flushing and 10 ml/min at the trap exit during desorption of volatiles from PVC. The desorption time is 15 min. The following temperatures are used: column oven, 80°C; evaporator, 230°C; and detector oven, 110°C. The flow-rates of hydrogen and air are 40 and 400 ml/min, respectively. The scale is from $5 \cdot 10^{-7}$ to $5 \cdot 10^{-11}$ a.u.f.s., depending on the VC concentration. The amount of polymer taken is 20–200 mg.

Determination of efficiency of analytical column

It is necessary to establish the efficiency of the analytical column by using a model mixture of methyl chloride, VC and ethyl chloride and determining the selectivity coefficient (K_S), separation factor (K) and number of theoretical plates (N):

$$K_S = \frac{t_{R_2} - t_{R_1}}{b_2 + b_1}$$

$$K = \frac{t_{R_2} - t_{R_1}}{t_{R_2} + t_{R_1}}$$

$$N = 5.54 \cdot \left(\frac{t_{R_2}}{b_2}\right)^2$$

where t_{R_1} is the retention time of VC (sec), t_{R_2} is the retention time of ethyl chloride (sec) and b_1 and b_2 are the peak widths of VC and ethyl chloride, respectively, measured at half the peak height.

The determination is carried out in the back-flushing mode, introducing the mixture through the injection port.

The analytical column should satisfy the following requirements: $K_{\text{methyl chloride–VC}} > 0.8$, $K_{\text{VC–ethyl chloride}} > 2.0$, $K_{S\ \text{VC–ethyl chloride}} > 0.30$ and $N_{\text{ethyl chloride}} > 500$.

Determination of vinyl chloride zone cut-off time

To determine the time required for the VC zone to pass through the pre-column, it is necessary to install a T-joint before the analytical column so that the greater portion of the flow enters the analytical column and lesser portion arrives at the detector. The resulting VC peak in the chromatogram is used for a rough estimation of the time required for the PVC zone to pass through the pre-column and enter the analytical column. The final VC zone cut-off time is determined from the VC and ethyl chloride peak areas, depending on the valve switching time. To accom-

plish this the system is assembled as shown in Fig. 2 (without a T-joint). A mixture of VC and ethyl chloride is introduced through the sample loop. By varying the cut-off time of the VC zone it is feasible to make the final determination. If the exclusion time is properly selected (*i.e.*, if the time of switching the valve from direct purging to back-flushing is determined correctly), the VC peak areas show good reproducibility when replicate measurements are carried out. The results demonstrate that the VC zone entered the analytical column completely.

Calibration regression equation

The relationship between peak area and VC content is interpreted by the least-squares method. Coefficients (a, B) for the regression equation are found:

$$y = a + Bx$$

where y is the VC peak area in mm² (S) and x is the absolute VC content in mg (P); or

$$S = a + BP$$

Hence,

$$P = \frac{S - a}{B} \tag{1}$$

The VC concentration in the sample being analyzed in parts per million (Q) would be given by

$$Q = \frac{P \cdot 10^6}{\text{weighed amount of sample (mg)}}$$

Substituting from eqn. 1 instead of P we obtain

$$Q = \frac{(Sf - a) \cdot 10^6}{B \cdot \text{weighed amount of sample (mg)}} \tag{2}$$

where f is a scale conversion coefficient, *i.e.*, a coefficient that equals in current units (A) the ratio of the scale used for analysis to the scale used for calibration.

The sensitivity by the method of Freed and Mujsce[22], A_1 (= B in eqn. 1), correlates well with the sensitivity, A_2, taken from the method of absolute calibration, *i.e.*,

$$A_2 = \frac{\sum_{n=1}^{10} S/10 \text{ (mm}^2\text{)}}{\text{VC in sample (mg)}}$$

where $\sum_{n=1}^{10} S$ is the sum of the areas of ten VC peaks obtained on its introduction into the evaporator through the sample loop.

Good agreement between the sensitivities A_1 and A_2 (to within 5%) permits absolute calibration to be employed for the calculation of the residual VC levels in the range from hundredths to thousands parts per million.

Sequence of analysis

A weighed portion of PVC from 20 to 200 mg is held in the glass tube between two glass-wool plugs and is located in the detector oven with the help of nuts, after which the trap is adjusted. The oven cover is closed and the oven is heated.

The trap is immersed in the Dewar flask containing liquid nitrogen, then the flow of carrier gas is started. After the trapping, the trap is disconnected and fitted into the chromatograph evaporator, and simultaneously a stop-watch is started. The switching valve is in the direct purging position but, after the cut-off time, the valve is switched into the back-flushing position.

During the time interval from purging to back-flushing the next tube, filled with a weighed portion of polymer for desorption, is installed in the detector oven. Fig. 4 shows a chromatogram of a VC zone obtained under the above conditions. The analysis time is about 20 min.

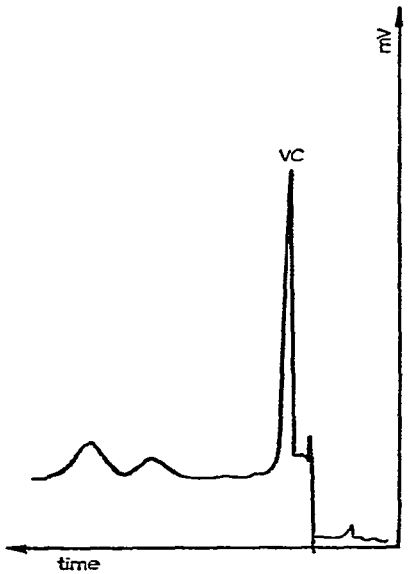

Fig. 4. Chromatogram obtained during separation of VC band on analytical column.

RESULTS AND DISCUSSION

According to the literature, the specific surface area of PVC powder is less than 10 m^2/g, and it is doubtful whether PVC powder can retain VC by adsorption[23]. Hence the major proportion of VC is absorbed in the polymer particles. Owing to the small diffusion coefficients, it is difficult to carry out the removal of VC quantitatively. An abrupt increase in the diffusion coefficient occurs above the glass transition point, so VC can be removed quantitatively from small polymer particles in the chromatographic regime, *i.e.*, by continuous purging a stream of carrier gas through the polymer layer. The only limitation is the narrow temperature range between the glass transition point at 80°C and decomposition at 130°C, so it is necessary to maintain the operating temperature carefully.

The polymer was placed in a small glass tube and heated to 110°C, with simultaneously the stream of nitrogen purging through it. Such a technique, combined with chromatography and on-line mass spectrometry, facilitates the investigation of polymer volatiles[24].

To concentrate stripped volatiles, they were transferred into a trap cooled by liquid nitrogen, after which the trap was placed in the injection port of the chromatograph for further analysis[25,26].

However, it must be noted that there are no data on PVC impurities, except for residual VC. The first analysis of volatiles removed from PVC shows that they have a complex composition, containing many components at different concentrations, complete analysis of which was possible only with a high-efficiency column and mass spectrometry.

Together with VC, methyl and ethyl chlorides were found among PVC contaminants with a relatively high vapour pressure[27]. This mixture was used as a model for the examination of the analytical column. The behaviour of these compounds when chromatographed on polymer sorbents is well known[28].

The complex composition of the volatiles demands a very careful chromatographic separation, as constant control by mass spectrometry is difficult. That is why a double column system for chromatographic separation was suggested. A narrow fraction containing VC was transferred from the first column (pre-column) to the second column (analytical), then the pre-column was purged with carrier gas in the reverse direction (back-flushing) to clean the column from other components and to prepare it for further analysis[29]. The choice of the analytical column and the separation conditions was made very carefully as a complete VC separation was needed.

Both of the columns should be operated in one oven, otherwise the instrumentation required for analysis would be too complex.

For maximal sensitivity it was preferred to use the device at a high sensitivity ($2 \cdot 10^{-11}$–$5 \cdot 10^{-11}$ a.u.f.s.), so the background signal should be minimal. Columns with polymeric sorbents are preferable. Chromosorb 104 (one of the most polar polymeric sorbents) or Polysorb 1 are the best.

The time of the valve switching for transferring the VC band from the pre-column to the analytical column was selected so that the VC passed through the pre-column completely, as indicated by an alteration of the ethyl chloride peak area eluted after VC.

Determination of vinyl chloride in PVC of different types

Berens[23] showed that VC stripping depends on sample morphology, and this gave rise to doubts during the investigation. The diffusion time for spherical particles depends on the square of the diameter of a particle, so this method can be applied to polymer powders consisting of loose particles, which in turn consist of smaller subparticles with diameters of a few microns. In this case the diffusion time is several minutes at temperatures near 100°C. Glassy particles of larger diameter in the polymer retard the removal of VC. In order to study this aspect, some types of polymers with different glassy particles contents were investigated (Table I).

Samples of different types were analysed by our method and the solution method; the results of the latter do not depend on the type of polymer used. Table II shows the good agreement obtained.

TABLE I
CHARACTERISTICS OF DIFFERENT TYPES OF PVC

PVC type	*Specific surface area (m^2/g)*	*Homogeneity* (glassy particle content)*
C-58	0.34	Very low
C-70	1.20	$\frac{1.2}{6}$; $\frac{1.66}{8.8}$
C-63M	0.66	Many fiine particles
PVC filler	0.35	$\frac{3}{15}$; $\frac{3}{15}$
Microsuspension	3.7	High

* PVC homogeneity was measured according to the U.S.S.R. State Standard. The numerator is the average number of glassy particles in a square 10 × 10 cm; the denominator is the number of glassy particles in the film of the same square and volume of 0.1 cm^3.

TABLE II
COMPARISON OF RESULTS FOR THE ANALYSIS OF PVC SAMPLES

PVC	*Sample No.**	*VC content (ppm)***	
		Solution method	*Proposed method*
C-70	1	330	315
	2	120	127
C-63M	1	130	148
	2	87	97
C-58	1	88	93
	2	347	356
C-66	1	416	450
	2	65	49

* Different VC removal conditions used in polymerization process.
** Average of two results.

Control experiments

Control experiments showed the complete desorption of VC from the polymer and its quantitative transfer into the chromatographic column by the cooled trap. To verify the complete removal of VC, the VC liberated was trapped for 15 min, as described under Experimental. For trapping VC the trap was packed with sorbent (15% Apiezon L on Chezasorb AW, particle size 0.210–0.360 mm) and cooled by liquid nitrogen. The first trap was replaced with a new one for a further 15 min. The traps were analysed for their VC contents and the second trap was tested on the most sensitive scale ($5 \cdot 10^{-12}$ a.u.f.s.). There was no VC from any type of PVC in the second trap.

The completeness of VC trapping and desorption from the trap in the injection port was tested in the following way. The VC sample was injected either in the cooled trap by a sample valve or without a trap directly on to the column. The VC peak areas (average of 10 measurements) were 863.1 and 859.7 mm^2, respectively.

It is known that a considerable amount of water is adsorbed on the PVC powder surface. According to the literature[30], the sensitivity of the FID is decreased by water which is eluted together with other components; consequently, it was necessary to check whether the bands of VC and water overlap. A glass tube con-

taining calcium carbide was placed before the FID and a water sample was injected into the evaporator. The detector recorded the signal of acetylene. The retention time for water is 5 min 56 sec., whereas that for VC under the same conditions is 1 min 43 sec. Hence it is evident that water elutes later and is removed by back-flushing.

Calibration

For VC calibration we used the method proposed by Freed and Mujsce[22]. This consists in the dehydrochlorination of 1,2-dichloroethane to VC in a pre-column packed with anhydrous potassium carbonate at 300°C, and gives a linear calibration graph of amount of VC *versus* peak area in the range 1–125 ng. We investigated amounts of VC in the range 10–400 ng and have obtained a linear calibration graph in the range 10–200 ng. In attempts to prepare higher VC levels, we observed the non-linear character of the dependence, probably because of the tube dimensions and the amount of potassium carbonate used the large amount of sample has insufficient time to react.

The sensitivity of the method obtained from the calibration graph interpreted by the least-squares method was compared with absolute calibration of detector by injection of VC through the inlet sample valve. The results were in good agreement, the discrepancy being about 5%.

Statistics

It was interesting to find how the relative standard deviation changes in relation to VC content. Table III shows the results for the analysis of five PVC samples with different VC contents. Obviously the relative standard deviation increases with decreasing VC content.

TABLE III

VARIATION OF RELATIVE STANDARD DEVIATION WITH VC CONTENT*

Sample No.	$\bar{x} = \frac{\Sigma x_i}{n}$ (ppm)	n	$S = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x)^2}{n-1}}$ (ppm)	$S_r = \frac{S}{\bar{x}} \cdot 100$ (%)
1	1118.0	4	53.4	4.8
2	710.6	4	51.9	7.3
3	72.32	4	5.46	7.5
4	2.46	4	0.25	10.2
5	0.24	4	0.034	14.1

* x_i = VC content; $\bar{x}$ = arithmetic mean; n = number of samples; S = root-mean square; S_r = relative standard deviation.

It should be noted that PVC resin loses noticeable amounts of VC on storage. Thus in one sample the VC content decreased from 2230 to 70 ppm after storage for 1 week. Owing to this the root-mean-square deviation and the relative standard deviation were measured not by special experiments, involving multiple analysis of one sample (not less than 20 measurements), but by current data[31]. The VC content varied from 70 to 350 ppm and all measurements were duplicated. S and S_r were measured according to the equations

$$S = \sqrt{\frac{1}{2m} \sum_{i=1}^{m} d_i^2}$$

$$S_r = \frac{1}{2m} \sqrt{\sum_{i=1}^{m} \frac{(d_i)^2}{\bar{x}}}$$

where d_t is the difference between duplicate measurements and m is the number of samples. It was found that S_r was 5%.

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