

CHROM. 11,121

GAS CHROMATOGRAPHIC DETERMINATION OF 1,1,1-TRICHLOROETHANE IN VINYL CHLORIDE POLYMERS AND IN FOODS

J. GILBERT, J. R. STARTIN and M. A. WALLWORK

Ministry of Agriculture Fisheries and Food, Food Science Division, Haldin House, Queen Street, Norwich NR2 4SX (Great Britain)

(Received April 3rd, 1978)

SUMMARY

A gas chromatographic method is described for the quantification of levels of 1,1,1-trichloroethane in vinyl chloride polymer resins and in poly(vinyl chloride) (PVC) bottles used in the packaging of foods. By application of electron-capture detection the method can be extended to foods which have been stored in PVC bottles and 1,1,1-trichloroethane can be estimated with a limit of detection in the foodstuff of between 0.002 and 0.01 ppm depending on the food. The results of a small survey of the amounts of this compound in PVC bottles and foodstuffs purchased from retail outlets are reported.

INTRODUCTION

The need to assess the possibility of migration of minor constituents from plastic packaging materials into foodstuffs has become increasingly important in recent years. In particular, attention has centered on measuring levels of residual monomers *e.g.*, vinyl chloride in both plastic food containers^{1,2} and in foodstuffs packaged in poly(vinyl chloride) (PVC)^{3,4}, and on measuring the levels of migration of additives *e.g.*, heat stabilisers^{5,6} which might be incorporated by the fabricator during the course of manufacture of the finished article. However, residues of ingredients from the polymerisation process provide an alternative source of minor constituents in the polymer which are not often considered as potential migrants. Although methods based on the determination of functional groups have been reported⁷ for the estimation of residual peroxide initiator in the polymer, and for other residues of polymerisation ingredients in polymer migrates, these methods are generally non-specific and lack the necessary sensitivity. Polarography has been employed⁸ for the estimation down to 0.04 ppm of a mercaptan chain transfer agent used in the manufacture of Barex 210 but none could be detected in food simulant extracts of the bottles⁸.

In this paper we report the identification by gas chromatography-mass spectrometry (GC-MS) of 1,1,1-trichloroethane both in vinyl chloride polymer resin and in a selection of PVC bottles used in the packaging of foods. Halogen containing

organic compounds have been reported as effective chain transfer agents during the polymerisation of vinyl chloride⁹ but there are no published reports as to the levels remaining in the finished polymer. Using a modified solution-headspace chromatographic technique as described for styrene and 2-ethylhexyl acrylate determinations¹⁰ it was possible to quantify the amount of residual 1,1,1-trichloroethane in the polymer down to levels of 1 ppm. The technique involves dissolution of the polymer in a suitable solvent, dimethyl formamide (DMF), and addition of water to decrease the solubility of trichloroethane in the solvent and thereby effect a suitably high equilibrium concentration in the headspace prior to analysis. For the determination of trichloroethane in PVC-packaged foods a higher degree of sensitivity was required, and electron-capture detection was therefore employed which additionally gave a greater specificity against potential headspace interferences from the foods themselves. Quantification was possible down to levels of between 0.002 and 0.01 ppm depending on the food and the results of a small survey of PVC-packaged foods purchased from retail outlets are reported.

EXPERIMENTAL

Materials

PVC resin of a type commonly used for bottle manufacture was supplied by ICI Plastics (Welwyn Garden City, Great Britain), together with small sample bottles (100 ml capacity) blow moulded from the same resin and stabilised with either calcium-zinc stearate or an organotin compound incorporated in each case as part of a typical PVC-bottle formulation. Orange squash and groundnut oil which had not previously been in contact with the plastic were stored, respectively, in the calcium-zinc stearate-stabilised and organotin-stabilised bottles for a period of 10 days at 40°, representing accelerated storage. In addition a range of PVC bottles containing a variety of foods were purchased from a number of retail outlets.

Determination of trichloroethane in plastic containers

Gas chromatography. A Perkin-Elmer F 42 automated headspace analyser equipped with a flame-ionisation detector was used. This instrument, which is described elsewhere¹¹, is designed for automated headspace sampling of up to 30 vials contained in a thermostatted water bath. The operating conditions were as follows. Column, 3 m × $\frac{1}{8}$ in. O.D. stainless-steel tubing packed with 20% Apiezon L on Diatomite C (60-80 mesh); nitrogen carrier gas flow-rate, 25 ml/min, column temperature was kept isothermally at 70°; injection time, 9 sec; sample equilibration temperature, 70°; injector/detector temperature, 180°; dosing line temperature, 180°.

Sample preparation. A weighed portion (0.2 g) of the polymer sample was dissolved in DMF (4 ml) in a glass vial (24 ml capacity), sealed with a rubber septum and aluminium ring, with heating at 70° in a water bath to aid dissolution. The vials were then cooled and an aliquot of water (4 ml) was injected with shaking into the polymer solution. Vials were then returned to the water bath for 2 h prior to analysis. PVC resin which was free of trichloroethane was employed for the standards which were prepared in a manner similar to that described above. However, prior to precipitation of the polymer, microlitre quantities of trichloroethane in DMF (standard solutions prepared by weighing and dilution) were added to the vials to enable

calibration in the range 0–150 ppm. Quantification of the trichloroethane in each case was based on the measurement of peak heights.

Gas chromatography-mass spectrometry. For each of the plastic samples the identity of the component was confirmed as 1,1,1-trichloroethane by combined GC-MS. Spectra were obtained on a DuPont Model 21-490 B mass spectrometer interfaced with an all glass jet separator to a Pye 104 chromatograph. Vapour samples (1 ml) from above finely ground solid polymer samples (mesh size less than 1 mm) heated at 120° for 1 h, were injected manually onto a 7 ft. \times $\frac{1}{8}$ in. I.D. glass column packed with Spherosil XOB 015, operated isothermally at 70°, with a helium carrier gas flow-rate of 30 ml/min. Mass spectra were obtained at 70 eV, scanning over the mass range m/e 20–700 at 2 sec/decade. Data was acquired and processed on a VG 2020F data system. Confirmation of identification was taken as proven on the basis of good spectral agreement and coincidence of retention time with that of the authentic compound.

Determination of trichloroethane in food products

Gas chromatography. The apparatus used consisted of a Pye 104 chromatograph equipped with a ^{63}Ni electron-capture detector. The column (5 ft. \times $\frac{1}{4}$ in. O.D. packed with 10% Apiezon L on Diatomite C) operated at a gas flow-rate of 55 ml/min and with a nitrogen make-up gas employed to give a total flow-rate of 65 ml/min through the detector. The column temperature was 70° and the detector was operated at 200° in a pulsed mode with a spacing of 150 μsec .

Sample preparation. Empty glass vials (24 ml capacity) were sealed with rubber septa, evacuated with a vacuum pump and nitrogen filled at atmospheric pressure. This procedure was repeated, before injecting samples of the foods (2 g) into the vials and weighing. Equilibration took 1 h at 70° and vapour injections (1 ml) were made manually using a Hamilton 2.5-ml gas tight syringe. Using foods which had not been in contact with plastics, calibrations were made by adding standard solutions of trichloroethane in ethanol to give final concentrations in the range 0.002–0.05 ppm in foodstuff.

RESULTS AND DISCUSSION

The headspace technique described for the determination of trichloroethane in PVC polymers was adequate for quantification down to a level of 1 ppm. No interference peaks were experienced either from the DMF solvent or from other additives in the PVC. However for the estimation of trichloroethane in the foodstuffs by electron-capture detection, in order to achieve sensitivity of the order of a few ppb it was necessary to exclude laboratory atmosphere from the headspace of the vial, which otherwise contained interfering components. Evacuation and nitrogen flushing of the vials prior to filling with the foods ensured exclusion of contaminants.

Trichloroethane cannot be determined in PVC polymers by conventional headspace-above-solution techniques which have been employed for the determination of vinyl chloride monomer^{12,13}. This is because of the unfavourable partition and low volatility of trichloroethane in organic solvents compared to that of vinyl chloride. However, trichloroethane can be detected in the headspace above the heated solid polymer and this was the preferred method for confirmation of the identity by MS

due to the comparatively higher headspace sample concentration. For the purposes of quantification the method may be applied to solid systems only where equilibration with the headspace is rapid and complete, and hence the particle size of the ground polymer exerts a significant effect on the final equilibrium headspace concentration¹⁴; this requirement makes sample preparation difficult. Furthermore, even if equilibrium between solid and headspace is obtained, the partition coefficient for trichloroethane in PVC under the prescribed conditions must also be known in order to make quantitative calculations. For these reasons the solid-polymer method was used only for the MS identification experiments; quantitative measurements were made by headspace analysis over aqueous DMF suspension of PVC prepared in the manner described.

TABLE I

OBSERVED LEVELS OF TRICHLOROETHANE IN A VARIETY OF PVC CONTAINERS AND FOOD PRODUCTS

	Type	Level in bottle (ppm)	Level in food (ppm)
<i>Storage of food products for 10 days at 40°</i>			
	PVC base resin	126	—
	Ca-Zn stearate-stabilised orange squash bottles*	29	0.005
	Organotin-stabilised cooking oil bottles*	37	—**
<i>Samples purchased from retail outlets</i>			
	Orange squash bottles	10	—***
	Cooking oil bottles	80	—**
	Mineral water bottles	153	—***
	Beer bottles	42	—***

* Bottles blown from base resin.

** Not detectable at 0.01 ppm.

*** Not detectable at 0.002 ppm.

Table I shows the results for the levels of trichloroethane in a range of PVC bottles, and a typical chromatogram is shown in Fig. 1 for a PVC beer bottle. A number of bottles (minimum of 3 of each type) were examined, samples being analysed in triplicate of which the mean levels are reported in Table I. In addition to the samples analysed a number of further different brands of the same type of foods in PVC bottles were examined and found not to contain any trichloroethane. The calcium-zinc stearate and organotin-stabilised PVC bottles showed 29 and 37 ppm, respectively, of trichloroethane, being blown from PVC resin with an initial content of 126 ppm. This reduction during blowing would probably be caused by volatilisation during processing and possibly by further reaction of the trichloroethane in the polymer system.

By spiking of aqueous foods with trichloroethane the electron capture technique was shown capable of detection at a level of 0.002 ppm. Typical chromatograms

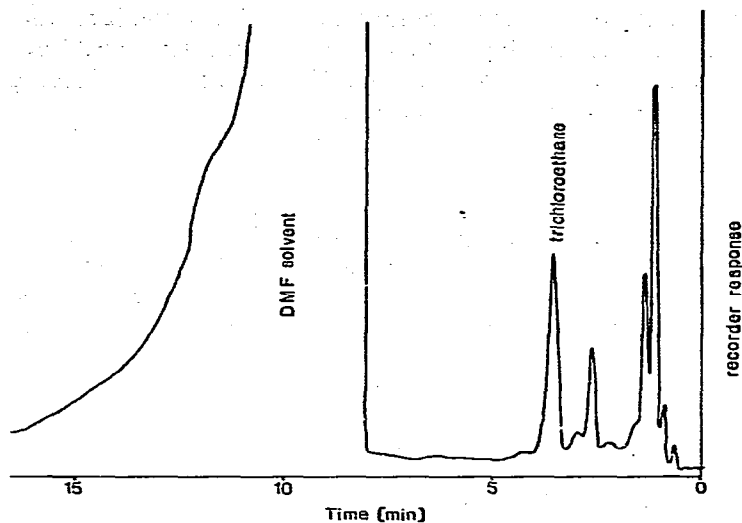


Fig. 1. Headspace chromatogram from above PVC beer bottle dissolved in DMF, water precipitated. Column 3 m \times $\frac{1}{8}$ in., packed with 20% Apiezon L on Diatomite C; flow-rate, 25 ml/min; temperature, isothermal at 70° (attenuation \times 10).

for orange squash in the presence and absence of trichloroethane are shown in Fig. 2. For the orange squash, mineral water and beer purchased from retail outlets trichloroethane could not be detected in the foodstuffs at a detection level of 0.002 ppm. For the orange squash which had been stored for 10 days at 40° in the calcium-zinc-stearate bottles a mean level of 0.0049 ppm trichloroethane was recorded.

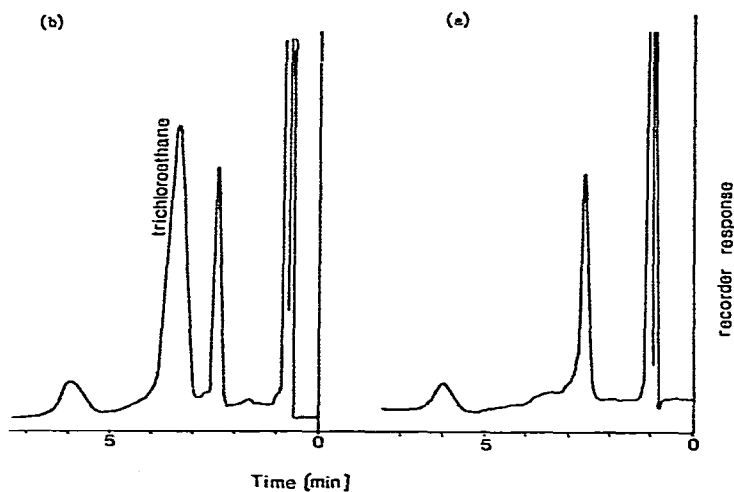


Fig. 2. Headspace chromatogram from above orange squash. a, Control containing no trichloroethane; b, spiked with 0.015 ppm trichloroethane. Column 7 ft. \times $\frac{1}{8}$ in., packed with 10% Apiezon L on Diatomite C; flow-rate, 55 ml/min; temperature isothermal at 70° (attenuation 2×10^2).

Partition of trichloroethane above heated cooking oil was less favourable and the method was only capable of a detection limit of 0.01 ppm. At this level trichloroethane could not be detected in either cooking oil from retail bottles or from oil stored for 10 days at 40° in the organotin-stabilised PVC bottles.

ACKNOWLEDGEMENTS

The authors wish to acknowledge ICI Plastics Division for the provision of PVC samples and to Fibrenyl of Beccles for the blowing of PVC bottles. Since the provision of the samples employed in this work, ICI Plastics Division have disclosed that 1,1,1-trichloroethane is no longer present in their food packaging grades of PVC.

REFERENCES

- 1 C. V. Breder, J. L. Dennison and M. E. Brown, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 1214.
- 2 D. A. Tester, *J. Soc. Cosmet. Chem., Br. Edn.*, 49 (1976) 459.
- 3 A. F. M. Ehtesham-Ud Din, E. Nordbo and B. Underdale, *Lebensm.-Wiss. Technol.*, 10 (1977) 33.
- 4 D. T. Williams and W. F. Miles, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 272.
- 5 J.-C. Meranger, *J. Ass. Offic. Anal. Chem.*, 58 (1975) 1143.
- 6 J. Koch and K. Figge, *Zlufar*, 147 (1971) 8.
- 7 H. Ostromow, *Ann. Ist. Sup. Sanita*, 8 (1972) 474.
- 8 V. F. Gaylor, B. F. Vincent and J. F. Jones, Paper presented at the 166th National Meeting of the American Chemical Soc., 1973.
- 9 G. A. R. Matthews, *Vinyl and Allied Polymers*, Vol. II, Iliffe Books, London, 1972, p. 20.
- 10 R. J. Steichen, *Anal. Chem.*, 48 (1976) 1398.
- 11 D. Jentzsch, H. Kruger, G. Lebricht, G. Denchks and I. Gut, *Z. Anal. Chem.*, 236 (1968) 96.
- 12 J. Puschmann, *Angew. Makromol. Chem.*, 47 (1975) 29.
- 13 W. R. Eckert, *Fette, Seifen, Anstrichm.*, 77 (1975) 319.
- 14 J. R. Startin, unpublished results.