CHROM. 10,786

Note

Analysis of trace amounts of dichloromethane in polycarbonates

GIOVANNI DI PASQUALE*, GIORDANO DI IORIO and TARCISIO CAPACCIOLI

ANIC S.p.A., Laboratorio Assistenza Tecnica e Sviluppo Applicazione Prodotti, 20097 S. Donato, Milan (Italy)

Dichloromethane (DCM) is used as a solvent in the manufacture of polycarbonates by polymerization[1], but small amounts of it remain in the resin, even after it has been made into pellets. The physical properties of the polycarbonates are improved if the level of the chlorinated solvent in the resin is reduced.

As polycarbonates are used for food packaging and containers, there is the possibility that the entrapped DCM may migrate into the foodstuffs. It is advisable to analyse for DCM in the resin down to the level permitted by the law on toxic substances[2–4]. Generally, gas chromatography (GC) is the best technique for this kind of analysis, but the usual procedure of dissolving the polymer and injecting part of the solution into the apparatus is not sufficiently sensitive to detect trace amounts of DCM.

Some authors have improved the procedure by enrichment of the solution to be analysed[5–7], *e.g.* by distillation.

The headspace technique, however, allows the direct determination of the content of DCM down to the necessary level. The technique offers several advantages over other GC techniques[8]: it prevents column contamination, reduces interference due to impurities in the solvent and improves the sensitivity. We have compared the headspace and direct injection techniques for the determination of trace amounts of DCM in polycarbonates.

EXPERIMENTAL

Apparatus

For the headspace technique:

Perkin-Elmer Multifract F 40 automated head-space analyzer, equipped with a flame ionization detector (FID).

Glass vials of 24 ml capacity equipped with rubber-septum covered with a PTFE membrane and an aluminium sealing ring.

Perkin-Elmer Minigrator M2 Integrator: to measure retention times and calculate the areas of the chromatographic peaks.

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* To whom correspondence should be addressed.

Perkin-Elmer Model 56 Recorder.

For direct injection technique:

Hewlett-Packard gas chromatograph Model 7624A with flame ionization detector, equipped with Model 7123A recorder and Model 3370B Integrator, to measure retention times and to calculate the areas of the chromatographic peaks.

Chemicals

The solvents used, dichloromethane (DCM), tetrahydrofuran (THF), chloroform and 1,4-dioxane, were analytical grade reagents. The 1,4-dioxane needed further vacuum distillation and the chloroform simple distillation to avoid interference due to impurities.

Preparation of calibration standards

Standard solutions were prepared by mixing a weighed portion of DCM with solvent (1,4-dioxane or chloroform) in the ratio $5:10^5$.

Internal standard solutions were prepared by mixing a weighed portion of THF with 1,4-dioxane or chloroform, in the ratio 1:100.

Calibration standard solutions were prepared by dissolving 2 g of DCM-free polycarbonate in septum-sealed vials containing 4 ml of solvent (1,4-dioxane or chloroform). The vials were heated at 60° until the polymer was dissolved, and then cooled to room temperature. A weighed portion of standard solution, corresponding to 0.1 or 5.0 ml, depending on the estimated percentage of DCM in the polymer, and 0.1 ml of internal standard solution were added to the polymer solution.

In the case of headspace sampling, the vials were equilibrated at 60° for 60 min.

Direct injection analysis procedure

2 g of polycarbonate were dissolved in a septum-sealed vial containing 10 ml of chloroform. The vial was heated at 60° for 60 min until the polymer was dissolved, and then cooled to room temperature; 0.1 ml of internal standard solution was then added.

3 μl of the polymer solution were injected into the Hewlett-Packard gas chromatograph Model 7624A, under the following operating conditions:

Column: 10 ft. × ⅛ in. stainless-steel tubing packed with 10% 2-ethylhexyl sebacate on Chromosorb W (60–80 mesh); carrier gas: nitrogen 30 ml/min; flame gases: hydrogen 30 ml/min, air 350 ml/min; temperatures: injection 80°, column 60°, detector 100°; sample size: 3 μl; chart speed: 30 in./h.

Headspace analysis procedure

2 g of polycarbonate were dissolved in a septum-sealed vial containing 9.9 ml of 1,4-dioxane. The vial was heated at 60° for 60 min until the polymer was dissolved, and then cooled to room temperature; 0.1 ml of internal standard solution was then added.

The vial was equilibrated at 60° for 60 min. The gas-chromatographic analysis was carried out under the following operating conditions:

Column: 10 ft. × ⅛ in. stainless-steel tubing packed with 10% 2-ethylhexyl sebacate on Chromosorb W (60–80 mesh); temperatures: thermostated sample tray 60°, injector/detector 125°, dosing line 145°, column 70°; injection time: 25 sec;

carrier gas: nitrogen 30 ml/min; flame gases: hydrogen 30 ml/min, air 350 ml/min; range: ×1; recorder: 1 mV full scale; chart speed: 5 mm/min.

RESULTS

The concentration of DCM in the sample, C_x, was determined from

$$C_x = \frac{A_d}{A_i} \cdot \frac{C_i}{R} \cdot \frac{10^6}{P} \tag{1}$$

where:

A_d, A_i = peak areas of DCM and THF, respectively; C_d, C_i = weight of DCM and THF, respectively; P = weight of dissolved polycarbonate; $R = (A_d \cdot C_i)/(A_i \cdot C_d)$ = response factor, determined in advance of every new run of analysis.

Figs. 1 and 2 show chromatograms related to different samples and different techniques. On comparing the direct injection and headspace techniques we found the latter to have a higher sensitivity, owing to the enrichment of the gaseous phase with DCM and to the possibility of injecting in the column a sample of higher volume and purity.
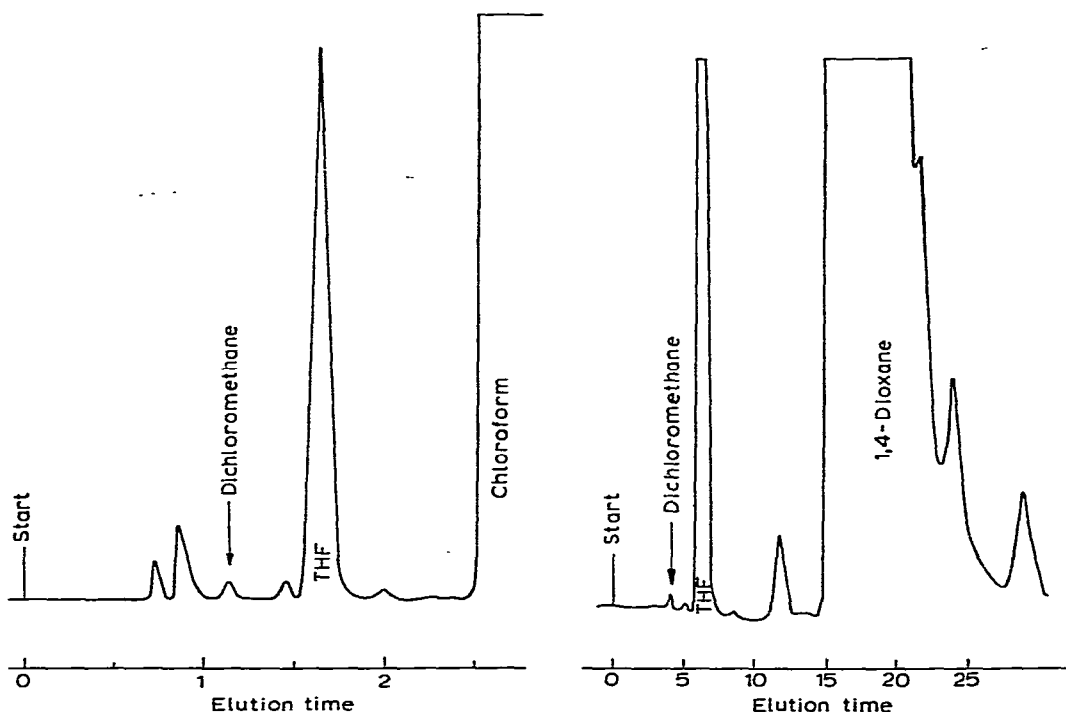

Fig. 1. Chromatogram of the direct injection of the solution of polycarbonates, containing 10 ppm of DCM, dissolved in chloroform solvent with the addition of THF internal standard.

Fig. 2. Chromatogram of the headspace above the solution of polycarbonates, containing 1 ppm of DCM, dissolved in 1,4-dioxane solvent with the addition of THF internal standard.

1,4-Dioxane was preferred to chloroform as solvent because, after distillation, it is degraded less on storage. Also, its higher boiling point means that the liquid and gaseous phases can be equilibrated at higher temperature.

The concentration range we examined was 1–100 ppm of DCM. In this range we found a linear relation, passing through the origin, between the areas of the chromatographic peaks and the concentration of DCM. The standard deviation, calculated for samples with *ca.* 100 ppm of DCM was 5%.

CONCLUSION

The headspace GC technique is the more suitable and practical method for the determination of small amounts of residual solvent in polymers that must be free from toxic products.

ACKNOWLEDGEMENT

The authors thank Dr. F. Montaguti for his helpful suggestions.

REFERENCES

1 L. Bottenbruch, in *Encyclopedia of Polymer Science and Technology —10*, Interscience, New York, 1969, p. 717.
2 Arrêté Royal - 25/8/1976 - Moniteur Belge, 24/6/1976 pag. 12035.
3 Decreto Minist. March 21, 1973, art. 10, *Gazzetta Uffic. Republica Italiana*, 104, April 20, 1973.
4 Decreto Minist. Nov. 19, 1974, *Gazzetta Uffic. Republica Italiana*, 319, Dec. 6, 1974, p. 8497.
5 P. Schilling and S. Gal, *Z. Lebensm.-Unters.-Forsch.*, 146 (1971) 255.
6 F. Dietz and J. Traud, *Vom Wasser*, 41 (1973) 137.
7 B. D. Page and B. P. C. Kennedy, *J. Ass. Off. Anal. Chem.*, 58 (1975) 1062.
8 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis*, Heyden, London, 1977.