

CHROM. 13,456

Note

Oxygen doping of carrier gas in the determination of dichloromethane in liquid foodstuffs by headspace gas chromatography with electron-capture detection

G. DI PASQUALE* and T. CAPACCIOLI

ANIC, Divisione Materie Plastiche, Centro Tecnologico, 20097 San Donato Milanese (Italy)

(Received October 24th, 1980)

In a previous paper¹, we described the advantages of the determination of trace amounts of dichloromethane in polycarbonates by headspace gas chromatography (HSGC). As analyses of trace amounts of solvents and monomers in simulated liquid foodstuffs²⁻⁴ are often required and the detection limits are very low, highly sensitive methods have to be developed^{2,5,6}.

We have used HSGC to determine dichloromethane in liquid foodstuffs such as sunflower oil, water and water containing 3% of acetic acid, because this technique can detect trace amounts of volatile compounds^{7,8}.

The determination of dichloromethane in sunflower oil with a flame-ionization detector (FID) showed that the volatile compounds of the oil interfere with the dichloromethane peak also when columns of different polarity were used. The use of a ⁶³Ni electron-capture detector (ECD) did not allow us to obtain positive results. On the other hand, we obtained good results and a dramatic increase in the detection sensitivity by doping the carrier gas with oxygen and using a ⁶³Ni ECD, as reported by Grimsrud and co-workers⁹⁻¹¹.

EXPERIMENTAL

Apparatus

A Carlo Erba Fractovap Model 4200 gas chromatograph, equipped with an automatic head-space accessory (HS Model 250, modified) (Fig. 1), an FID and an ECD (Model HT25), was used. The HS 250 sample syringe holder was slightly modified (see Fig. 1) so as to prevent contamination by interfering components present in the ambient air used to flush the syringe between the samples.

The detector cell was polarised with negative voltage pulses of amplitude 50 V and width 5 μ sec. Integration of peak areas was accomplished with a Hewlett-Packard Model 3370B integrator. A Leeds and Northrup (North Wales, PA, U.S.A.) Model FB Mark II recorder and glass vials (10 ml) with PTFE-laminated rubber septa were also used.

Chemicals

Distilled water, sunflower oil, acetic acid, trichloroethylene and dichloromethane (analytical-reagent grade, Carlo Erba, Milan, Italy) were used.

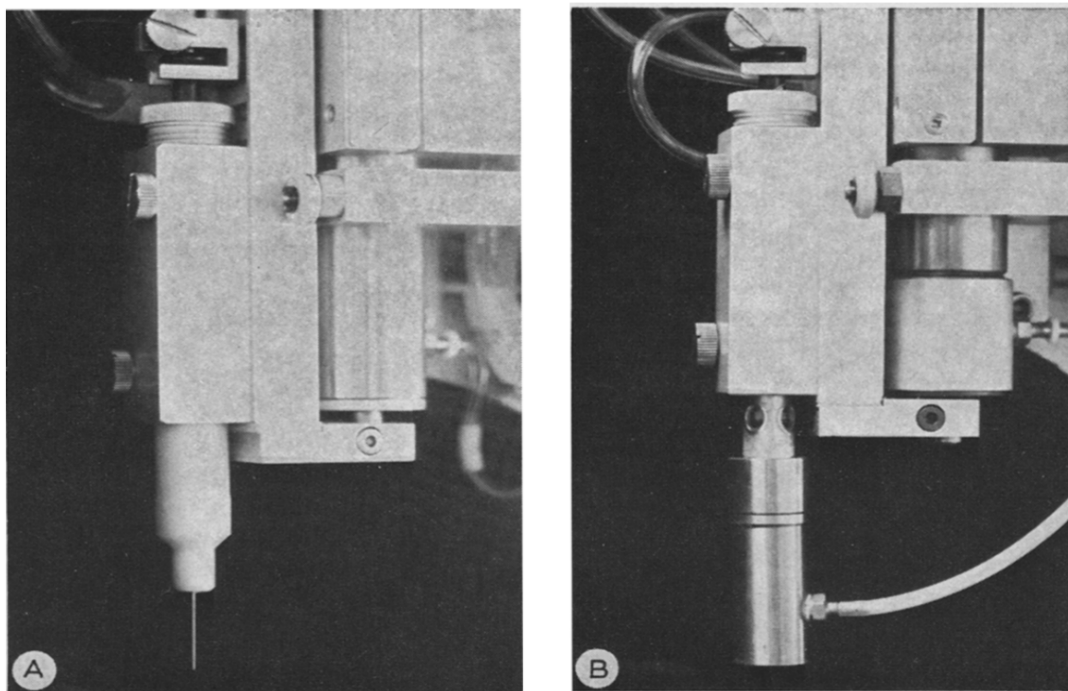


Fig. 1. (A) Syringe holder of the HS Model 250 headspace sampler (Carlo Erba); (B) modified syringe holder.

Methods

For each sample, a 5-ml volume was placed in a 10-ml vial, which was then tightly sealed and equilibrated at 70°C for 60 min.

The analyses were carried out on a 4 m × 2 mm I.D. stainless-steel column packed with 10% Carbowax 1500 on Chromosorb W AW (60–80 mesh) (Supelco, Bellefonte, PA, U.S.A.). The thermostatted sample turntable was maintained at 70°C, the syringe at 80°C, the injector and detector at 100°C and the column at 60°C. The sample size was 2 ml. The syringe was flushed seven times with nitrogen. The carrier gas was high-purity nitrogen at a flow-rate of 30 ml/min. An auxiliary flow (50 ml/min) of doped carrier gas (nitrogen containing 2000 ppm of oxygen), passing through the make-up line of the gas chromatograph, on the ⁶³Ni source was used.

Figs. 2 and 3 show the chromatograms obtained under these conditions.

RESULTS AND DISCUSSION

As legislation specifies very low limits of dichloromethane (in some instances 0.05 µg/ml), sophisticated analytical control methods are essential. The classical use of the FID and ECD, operated under normal conditions, does not provide satisfactory results for the determination of dichloromethane because of interfering peaks released by, *e.g.*, sunflower or olive oil.

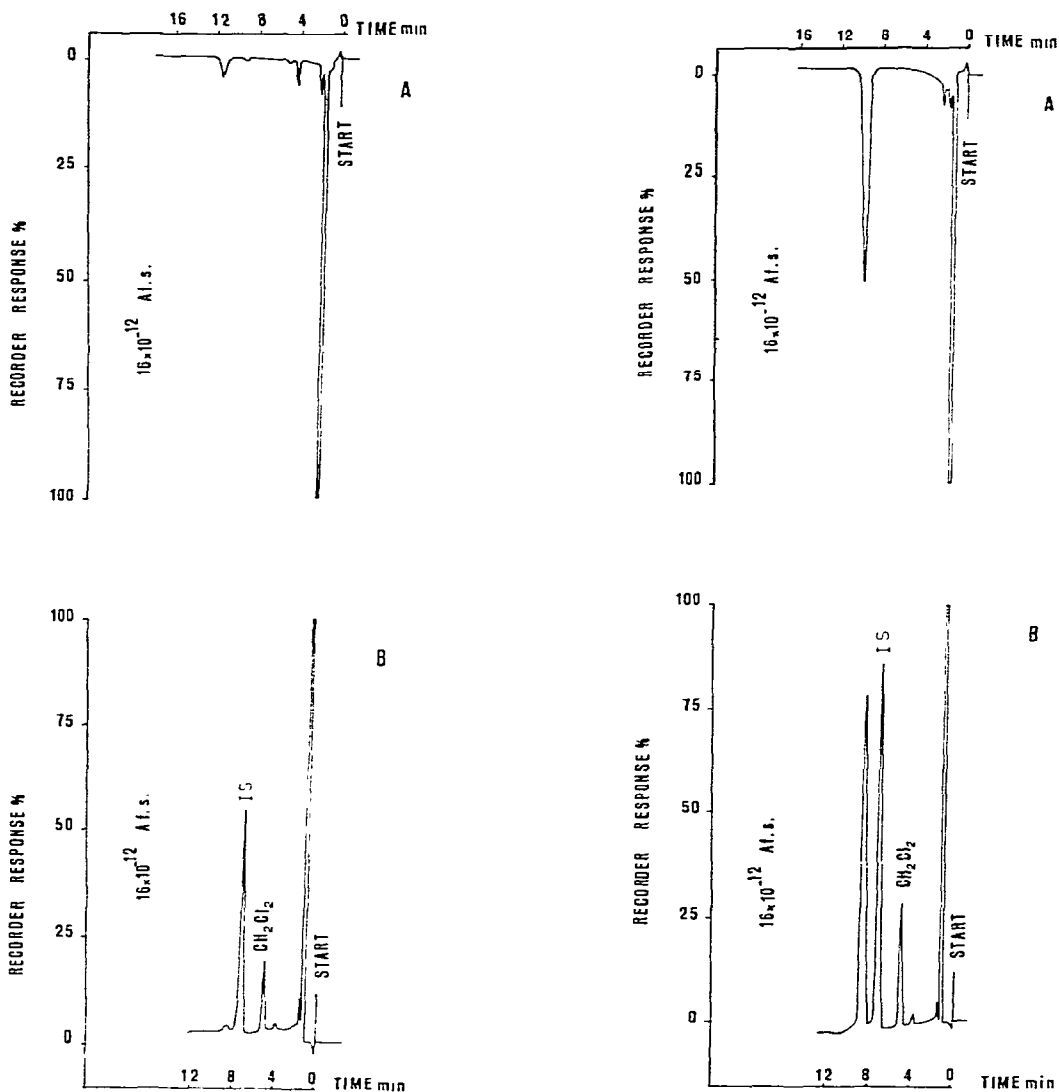


Fig. 2. Chromatograms of (A) blank oil and (B) headspace above oil containing $1.7 \mu\text{g/ml}$ of dichloromethane (internal standard, I.S., trichloroethylene) with electron-capture detection and doping of the carrier gas with oxygen.

Fig. 3. Chromatograms of (A) blank water and (B) headspace above water containing $0.72 \mu\text{g/ml}$ of dichloromethane (internal standard, I.S., trichloroethylene) with electron-capture detection and doping of the carrier gas with oxygen.

Fig. 4 shows the chromatograms obtained with both detectors for a blank oil showing the peaks interfering with the dichloromethane peak when a high sensitivity is required.

The use of columns with different polarities and lengths did not give any improvement.

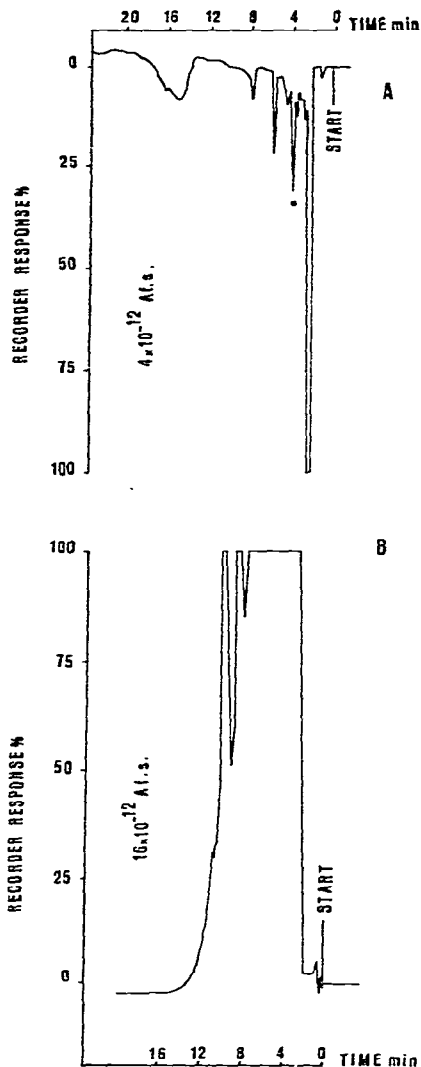


Fig. 4. Chromatograms of headspace above oil with (A) flame-ionization detection and (B) electron-capture detection. * = impurity from the matrix interfering with dichloromethane.

The best results, as shown in Figs. 2 and 3, were obtained by using an ECD with the carrier gas doped with oxygen.

Under these conditions, the analysis of sunflower oil was made possible and the sensitivity to dichloromethane in water and in water +3% acetic acid was ten times higher than that achievable with an FID.

Doping of the carrier gas with oxygen was effected downstream the column by means of a built-in-make-up line in the gas chromatograph. This permitted the flow-rate through the chromatographic column to be kept low for optimal resolution whilst preventing oxygen from reducing the column efficiency.

The determination of dichloromethane was carried out using the internal standard method because this gave better results than standard calibration; trichloroethylene was used as the internal standard.

The standard deviation for ten replicate determinations was 8% in the range 10 ppb*–5 ppm. The detection limits achieved were 30 ppb of dichloromethane in sunflower oil and 10 ppb in water and in water containing 3% of acetic acid.

ACKNOWLEDGEMENTS

We thank A. Sironi, G. R. Verga and P. Gagliardi (Carlo Erba Strumentazione, Milan, Italy) for their valuable advice.

REFERENCES

- 1 G. Di Pasquale, G. Di Iorio and T. Capaccioli, *J. Chromatogr.*, 152 (1978) 538.
- 2 Arrêté Royal 25/8/1976, *Monit. Belge*, Sept. 25th (1976) 12035.
- 3 L. Rossi, *Second International Symposium on Migration, Hamburg, November 1976*.
- 4 D.M. 19/11/1974, *Gazz. Uff. Repub. Ital.*, (1974) 319.
- 5 G. Di Pasquale, G. Di Iorio, T. Capaccioli, P. Gagliardi and G. R. Verga, *J. Chromatogr.*, 160 (1978) 133.
- 6 G. Di Pasquale, G. Di Iorio and T. Capaccioli, *Ann. Chim. (Rome)*, 68 (1978) 719.
- 7 H. Hachenberg and A. P. Schmidt, *Gas Chromatographic Headspace Analysis*, Heyden, London, 1977.
- 8 B. Kolb, *Applied Headspace Gas Chromatography*, Heyden, London, 1980.
- 9 E. P. Grimsrud and R. G. Stebbins, *J. Chromatogr.*, 155 (1978) 19.
- 10 E. P. Grimsrud and D. A. Miller, *Anal. Chem.*, 50 (1978) 1141.
- 11 D. A. Miller and E. P. Grimsrud, *Anal. Chem.*, 51 (1979) 851.

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