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Note

Direct headspace gas chromatographic determination of dichloromethane in decaffeinated green and roasted coffee

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Gas chromatographic (GC) analysis of chlorinated solvents in foods and in coffee, has in recent years been the object of several investigations, and attention has been paid to the determination of dichloromethane since its content is regulated in several countries. Most methods used distillation[1–5] to isolate the solvent followed by GC with an electron-capture or electrolytic conductivity detector for quantitation.

Headspace gas chromatography (HSGC) is at present extensively used for the determination of volatile compounds in liquid and solid matrices[6–18]. Recently a procedure for the determination of dichloromethane in decaffeinated tea and coffee has been reported which uses a packed column and an electrolytic conductivity detector[19].

The present investigation has been carried out to develop a simple procedure for the analysis of dichloromethane in decaffeinated coffee by use of a capillary column and a temperature programmed vaporizer injection system (PTV) and electron-capture detection (ECD). These devices have been applied because a variety of volatile compounds are present in green and roasted coffee and an efficient fractionation of them is required to isolate and detect dichloromethane.

EXPERIMENTAL

HSGC was carried out on a glass capillary column, 50 m × 0.30 mm I.D., precoated with Carbopack A, coated with FFAP (free fatty acid phase) and stabilized with DCUP (dicumylperoxide)[20]. The procedure used to prepare the column is briefly as follows: 50 mg of Carbopack A were added to 25 ml of dichloromethane and 25 ml of tetrachloromethane and placed in an ultrasonic bath to obtain an uniform suspension. The suspension was made to flow four times in the capillary each time reversing the flow direction. A flow of nitrogen was then passed through the column to remove the solvents. On the carbopack layer a stationary phase consisting of 4% FFAP and 0.15% dicumylperoxide was coated by using a dynamic procedure.

The column was conditioned by a flow of hydrogen for 1 h at 250°C and is thereafter ready for use. The number of theoretical plates was 150 000 for 2,6-dimethylanaline ($k' = 4.5$) at 150°C.

A DANI (Monza, Italy) gas chromatograph Model 6500 equipped with a temperature-programmed vaporizer (PTV) injector and an electron-capture detector con-

nected with a Shimadzu integrator Model CR 3A was used. Operating conditions used for HSGC of dichloromethane: column temperature, 70°C for 5 min then programmed at 1°C/min to the end of the analysis; PTV programmed from 50 to 70°C and with the valve closed.

RESULTS AND DISCUSSION

Headspace analysis of roasted coffee yields a gas chromatogram with several peaks and in order to determine dichloromethane it has been found convenient to operate with a coffee suspension in water and to perform the headspace analysis by using an high-resolution capillary column allowing equilibrium among the three phases.

The solubility of dichloromethane and equilibrium conditions are affected by several factors (temperature, shaking time, salt concentration). In Fig. 1 are shown the results of HSGC of a decaffeinated coffee sample in water and in saline solution (0.5 M sodium suplhate) obtained with the capillary column described. With the saline solution an higher peak than with the aqueous solutions was measured and the interference from a compound frequently found in roasted coffe was less.

The gas-phase concentration measured by HSGC depends upon equilibria occurring among the solid; the liquid and the gas phases. In order to obtain information on the time required to reach equilibrium, a set of experiments has been carried out on roasted coffee samples to which 1.4 μg dichloromethane were added. The samples were either shaken by hand or subjected to ultrasonic vibrations: with the former
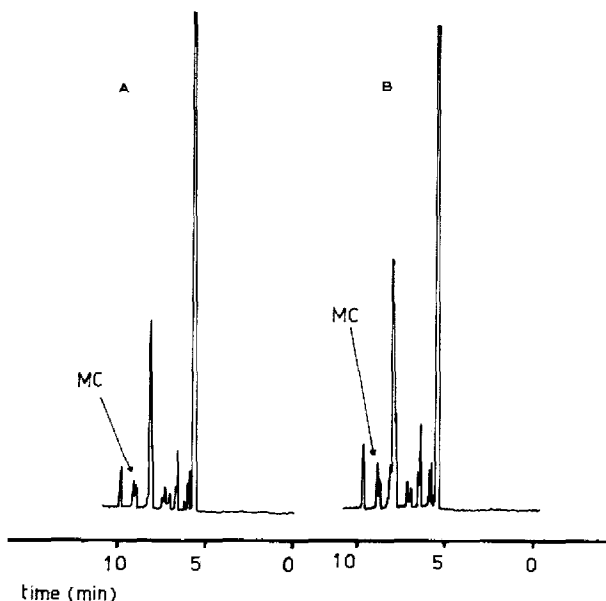

Fig. 1. Headspace gas chromatograms of a decaffeinated roasted coffee. (A) In distilled water suspension; (B) in saline solution.
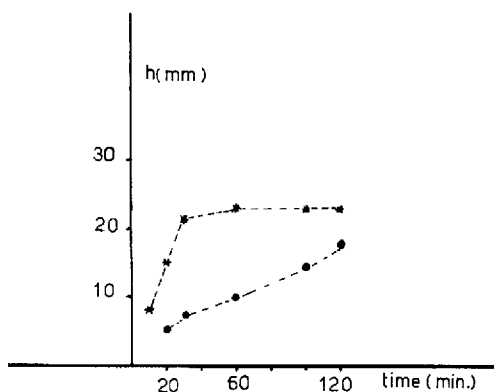
Fig. 2. Dichloromethane peak height *vs.* conditioning time for coffee samples containing 1.4 ppm dichloro-methane (∗) subjected to ultrasonic vibration; (●) shaken manually.

procedure no equilibrium is reached after mixing for 2 h, whereas with the latter a constant value is obtained after about 30 min as shown in Fig. 2.

The following procedure has been developed for the sample preparation: for each coffee sample, three 20-ml vials are taken to which 1 g of roasted or green coffee, previously dried, is transferred with 10 ml 0.5 M sodium suplhate solution. To each vial known amounts are added of standard dichloromethane in xylene solution (1–10 μl dichloromethane, 1 mg ml^{-1}). The vials are closed with an aluminium capsule with a rubber septum coated with PTFE and placed in an ultrasonic bath for 10 min to obtain an uniform homogenisation. The samples are conditioned at 30°C for 60 min to obtain equilibrium among the solid, liquid and gas phases; 0.5 ml of the gas phase are injected for GC.

By operating with the PTV system set at low temperature the injection of less volatile compounds is prevented. In Fig. 3 is shown the plot of peak height *versus* concentration of dichloromethane added expressed in terms of ppm. Extrapolation of the straight line to the abscissa axis yields the dichloromethane concentration of the sample.
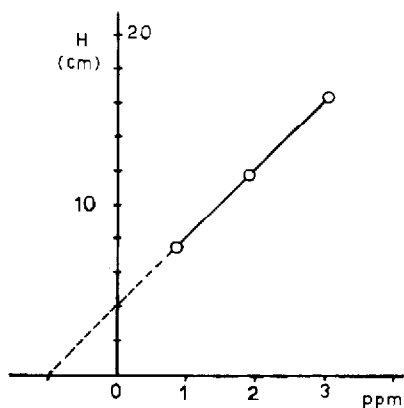

Fig. 3. Dichloromethane determination in decaffeinated samples according to the procedure described.

TABLE I

MEASUREMENT OF DICHLOROMETHANE IN GREEN AND ROASTED COFFEE SAMPLES

	Dichloromethane (ppm)	n (measurements)	S*	C.V. (%)
Roasted coffee	2.5	30	0.1	4.0
Green coffee	2.5	20	0.02	0.9
Decaffeinated roasted coffee				
A	0.9	4	0.07	7.8
B	0.6	3	0.08	13.3
C	0.5	3	0.07	14.0
D	1.1	5	0.05	4.5
E	8.7	4	0.07	0.8
Decaffeinated green coffee				
A	1.5	3	0.03	2.0
B	1.0	5	0.02	2.0
C	2.0	3	0.04	2.0
D	1.8	6	0.04	1.8

By performing the same determination on various days and by subjecting the sample under investigation to ultrasonic vibration to homogenize the suspension, the same analytical results for dichloromethane concentration is obtained though the line slope may be different.

In order to evaluate the reliability of the procedure, samples of roasted and green coffee to which 2.5 ppm of dichloromethane has been added were analyzed and the repeatability ($S^* \cdot 100/\bar{x}$) was calculated, where S^* = standard deviation. In Table I are collected also the results obtained on various samples with different dichloromethane concentrations. The coefficient of variation (C.V.) is lower for green coffee and for the sample with an higher dichloromethane concentration in the roasted coffee; it is rather high for low values of dichloromethane in roasted coffee because of the presence of a peak present in small concentration with a retention time close to that of dichloromethane.

The results indicate that the analytical procedure described permits the reliable determination of dichloromethane in decaffeinated coffee; it is rapid and simple and needs only minor manipulations, no internal standard is used and the calibration of the detector is carried out with all measurements. It requires however an high-resolution capillary column and the use of standard additions to the sample under examination.

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