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Note

Analysis of vinyl chloride in food simulants at low parts per billion levels by mass fragmentography

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Poly(vinyl chloride) (PVC) is used as packaging material for many food and drink products, such as wine, olive oil, soft drinks and margarine. From this material vinyl chloride monomer may migrate into the food product. Since vinyl chloride is carcinogenic, there are already strict regulations regarding the amount of VC which may be present in the air in factories[1], and the preliminary results of oral administration of olive oil, containing vinyl chloride, to rats resulted in a proposed ban on the use of vinyl chloride plastics in rigid and semi-rigid packaging in the United States of America[2]. In the European Community a maximum limit of 50 ppb of vinyl chloride in food and drinks is proposed, also due in part to the lack of more sensitive methods of analysis. The present methods[3–5] are mainly based on the use of gas chromatography with flame ionization detection to determine the amount of vinyl chloride, migrated into food and simulants, as salad oil, acetic acid–water and alcohol–water mixtures. The sensitivity of these methods is limited and identification of the vinyl chloride may be difficult. A specific halogen detector according to Hall enables identification, but little gain in sensitivity is obtained[6].

Since the need for more sensitive methods of analysis is imminent, mass fragmentography seemed to be a promising technique to use, although reported detection levels in food and food simulants were still in the 50 ppb range[7]. We report here the determination of vinyl chloride in food simulants at the 1 ppb level by use of mass fragmentography[8].

EXPERIMENTAL

Materials

The following materials were employed: vinyl chloride (Matheson, East Rutherford, N.J., U.S.A.); pure salad oil packed in cans, 96% alcohol and acetic acid (E. Merck, Darmstadt, G.F.R.); and tap water.

Preparation of samples

Liquid vinyl chloride, obtained by condensing the gas in solid carbon dioxide–

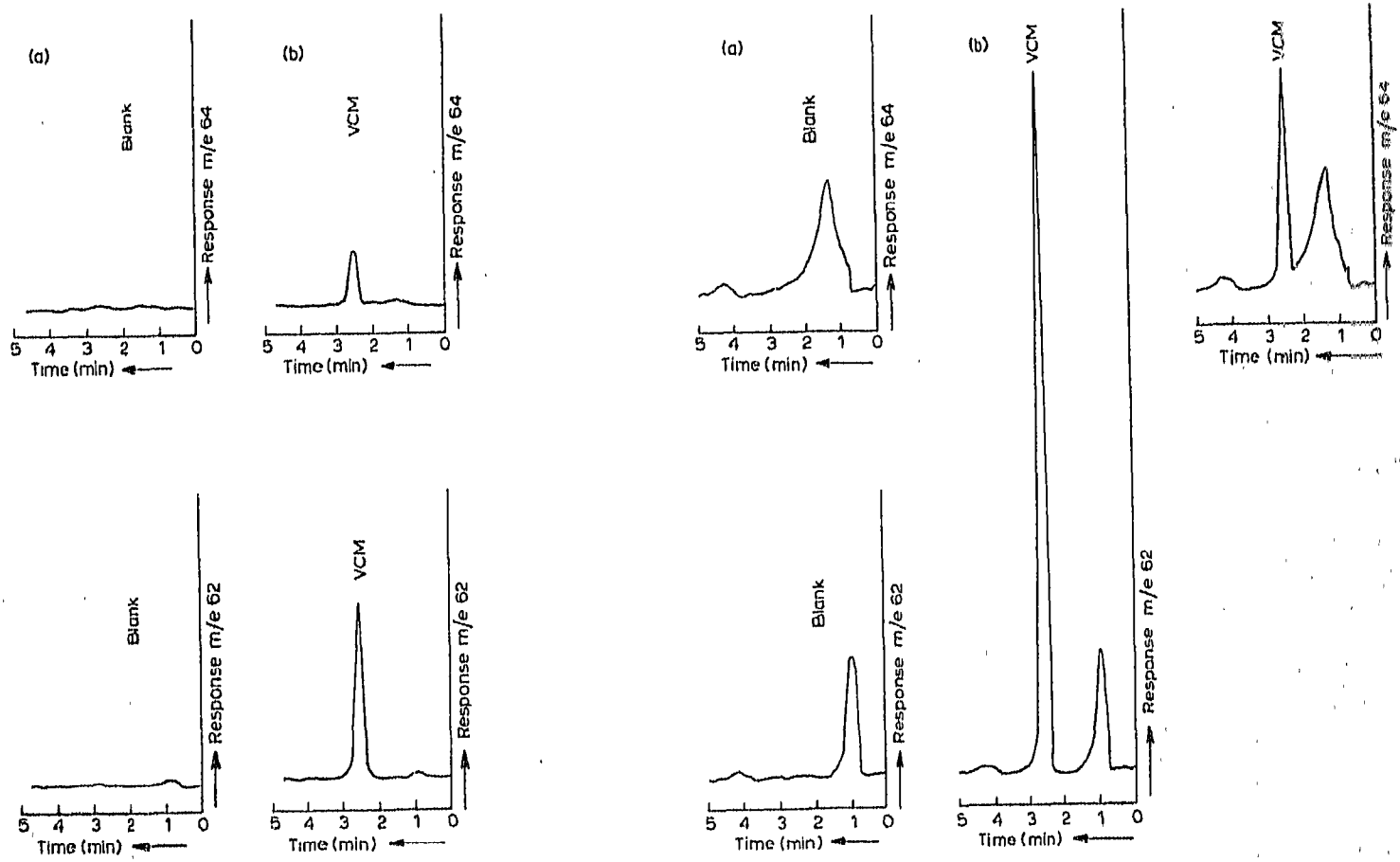

Fig. 1. Fragmentograms of salad oil (blank) (a) and of salad oil containing 98.6 ppb of vinyl chloride (VCM) (b).

Fig. 2. Fragmentograms of salad oil (blank, amplification 20 times higher than in Fig. 1) (a) and of salad oil containing 7.6 ppb of vinyl chloride (VCM) (b).

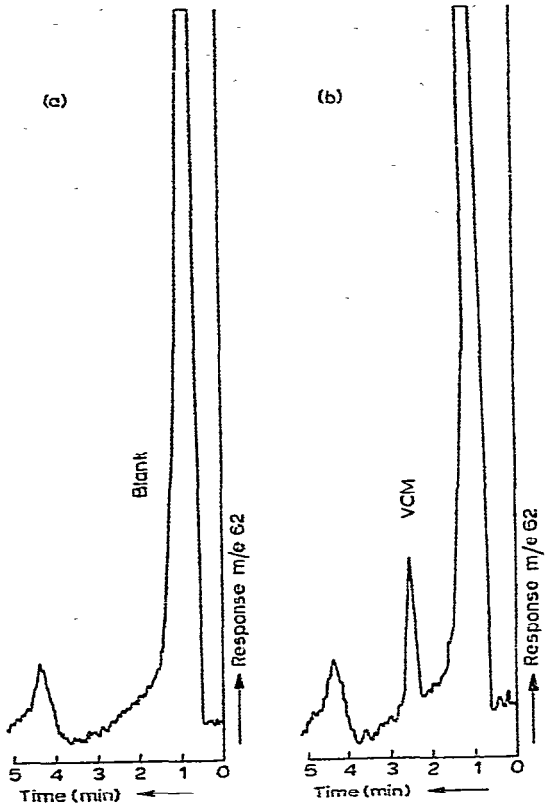

Fig. 3. Fragmentograms of salad oil (blank, amplification 10 times higher than in Fig. 2) (a) and of salad oil containing 0.3 ppb of vinyl chloride (VCM) (b).

acetone, was added to a known amount of simulant and the amount of vinyl chloride added was determined by weight. 100 g of the sample were placed in a 320-ml infusion flask which was then closed with an aluminium screw cap and silicone rubber septum. This flask was conditioned in a water-bath at 50° for at least 1 h before injection.

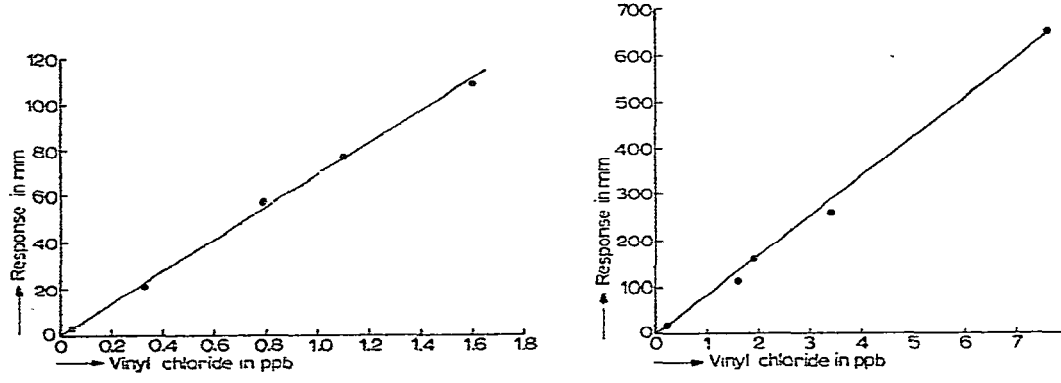

Fig. 4. Graphs of the response of the *m/e* 62 signal against the contents of vinyl chloride in salad oil.

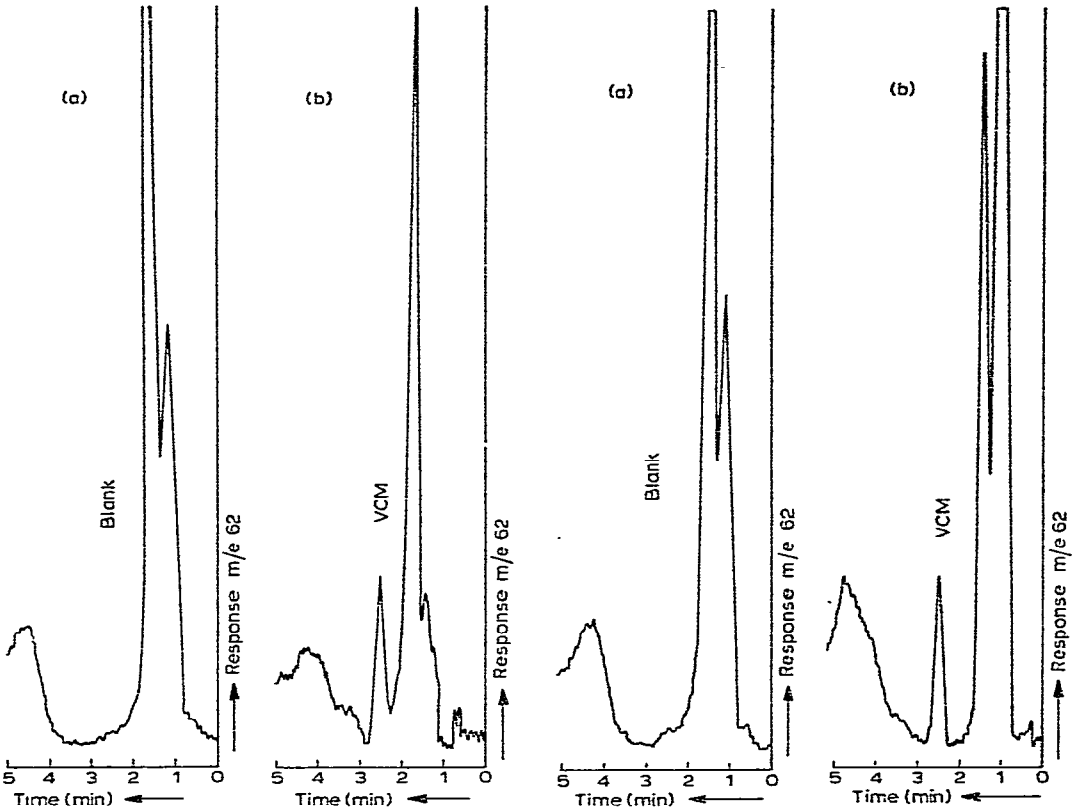

Fig. 5. Fragmentograms of 10% alcohol–water (blank) (a) and of 10% alcohol–water containing 0.1 ppb of vinyl chloride (VCM) (b).

Fig. 6. Fragmentograms of 3% acetic acid–water (blank) (a) and of 3% acetic acid–water containing 0.1 ppb of vinyl chloride (VCM) (b).

Gas chromatography–mass spectrometry (GC–MS) system

The analyses were carried out on a Finnigan 3200 GC–MS system, equipped with a multiple-ion detection (MID) unit and used in the electron-impact mode. The MID unit was tuned to the *m/e* 62 and 64 ions of vinyl chloride and the integrated signals were simultaneously recorded. 3-ml headspace samples were injected by means of a pre-warmed (50°) gas-tight syringe into a U-shaped glass column (1.5 m × 2 mm I.D.) which was loaded with Carbopack C (80–100 mesh) coated with 0.2% Carbowax 1500 (Supelco). The column was operated isothermally at 50°; injection block temperature, 180° .The carrier gas (helium) flow-rate was 20 ml/min. After elution of the vinyl chloride, the other components of the sample were vented to the atmosphere.

RESULTS AND DISCUSSION

In Figs. 1–3 we give some examples of mass fragmentograms for 98.6, 7.6 and 0.3 ppb of vinyl chloride in salad oil and the blanks. Although the influence of the air peak on the elution of lower concentrations of vinyl chloride is clear, the interference

is small due to the good separation of the Carbopack column. Other column fillings such as OV-1, SE-30, OV-17 and OV-207 on Chromosorb gave satisfactory results at the 50 ppb level, but at lower levels the better separation of the Carbopack column is essential.

Graphs of the peak heights of the *m/e* 62 response against the known vinyl chloride content in salad oil are given in Fig. 4, showing the good linearity of the method. Figs. 5 and 6 show the *m/e* 62 response for 0.1 ppb of vinyl chloride in the food simulants 10% alcohol–water and 3% acetic acid–water respectively.

On the basis of these results we can say that amounts of 1 ppb of vinyl chloride in food simulants can be easily detected and quantitated since we used food simulants of technical grade without further purification. We expect to have indicated a sensitive and specific method for the direct analysis of vinyl chloride in food and drink samples. Although definite conclusions can only be made after thorough evaluation of large series of analyses of various foods and drinks, so far this method is superior to existing ones using gas chromatography and flame ionization detection. Further experiments on food simulants and analyses of food and drink samples are in progress.

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