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Note

Determination of styrene in foods by reversed-phase high-performance liquid chromatography

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Styrene monomer residues may be present in polystyrene and may migrate slowly from packaging materials during storage and in contact with food or other materials.

Several methods for the determination of styrene monomer in foods have been published. Styrene in milk products has been determined by gas chromatography after solvent extraction^{1,2}, distillation³ or reduced-pressure steam distillation⁴. Withey⁵ and Withey and Collins⁶ described a headspace gas chromatographic method with a low detection limit, ranging from 0.0007 to 0.013 mg/kg, for various dairy products. For margarine, however, the limit of detection was 1 mg/kg. Certain food flavourings were reported to interfere in the headspace method.

Karbowski and Braun⁷ used gas chromatography–mass spectrometry (selected ion monitoring) for the determination of styrene in biological materials. The detection limit was 0.05 mg/kg for liver and kidney samples and 0.2 mg/kg for fat samples. The gas chromatographic determination of styrene as its dibromide⁸ has made it possible to detect 0.01 ng of the dibromide, using an electron-capture detector. The method has so far been applied only to air samples. Petrova *et al.*⁹ isolated styrene from food products by azeotropic distillation with methanol, followed by quantitative determination by UV spectrophotometry.

In this paper we describe a simple and rapid procedure for the determination of styrene in foods, which involves azeotropic distillation with methanol, followed by reversed-phase high-performance liquid chromatography. α -Methylstyrene is used as internal standard.

EXPERIMENTAL

Apparatus

A Spectra-Physics Model 3500 high-performance liquid chromatograph equipped with a Schoeffel Model SF 770 UV–visible continuously variable detector was connected to a Houston Omniscrite recorder. A 250 × 3 mm I.D. stainless-steel column pre-packed with Spherisorb ODS (mean particle size 5 μ m) was supplied by Spectra-Physics.

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Reagents

Pro analysi grade methanol, styrene for electron microscopy and α -methylstyrene for synthesis were purchased from Merck (Darmstadt, G.F.R.). Styrene was distilled before use. Pro analysi grade calcium chloride was obtained from Mallinckrodt (St. Louis, MO, U.S.A.).

Internal standard solution

A solution of α -methylstyrene in methanol was prepared at a concentration of 0.15 $\mu\text{g/ml}$.

Field of application

The method was tested and found to be applicable to dairy products, fruit products, meat products and mayonnaise salads.

Preparation of sample

The samples were homogenized by different techniques depending on the nature of the food.

Distillation

A 50-g amount of homogenized sample was thoroughly mixed with 50 ml of distilled water and 25 ml of methanol in a 250-ml round-bottomed flask. To samples of milk products a further 1 ml of calcium chloride solution (20%, w/v) was added to prevent foaming. After addition of a few boiling chips the round-bottomed flask was fitted to a distillation apparatus with a straight condenser and a receiver adapter. About 22–23 ml was distilled into a 25-ml volumetric flask. After the addition of 2.0 ml of internal standard solution the solution was made up to volume with methanol.

Reversed phase high-performance liquid chromatography

The mobile phase (65% methanol in water) was maintained at a constant flow-rate of 0.8 ml/min. The column eluate was monitored by UV detection at 254 nm. The detector was operated at 0.02 a.u.f.s. and the recorder was set to give a full-scale deflection at 5 mV. A 10- μl volume of the methanolic distillate was injected into the chromatograph. Standard solutions in methanol with the same concentration of α -methylstyrene as the sample distillates and with known concentrations of styrene were injected between samples.

Quantitation

The quantitation was based on a comparison of the chromatograms obtained from the sample and from a standard solution with a corresponding concentration of styrene and the same concentration of internal standard.

$$\text{Amount of styrene in sample (mg/kg)} = \frac{Y_s a X_{st}}{Y_{st} w}$$

where Y_s = mean styrene/ α -methylstyrene peak-height ratio from two injections of sample solution; a = amount of internal standard added to the distillate (μg);

X_{st} = styrene/ α -methylstyrene mass ratio in the standard solution; Y_{st} = mean styrene/ α -methylstyrene peak-height ratio from two injections of the standard solution; and w = amount of sample (g).

RESULTS AND DISCUSSION

The detector (at 254 nm) showed a linear response over a concentration range of 0.02–0.5 mg/kg (0.4–10 ng absolute). The detection limit was 0.01 mg/kg and could probably be improved by using a fixed-wavelength detector.

Fig. 1 shows a typical chromatogram obtained from a sample of fruit syrup

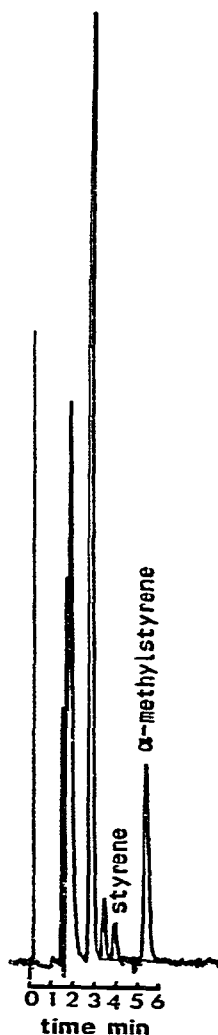


Fig. 1. Chromatogram of a fruit syrup sample containing 0.09 mg/kg of styrene. Column, Spherisorb ODS ($5\ \mu\text{m}$); mobile phase, 65% methanol in water.

containing 0.09 mg/kg of styrene. The retention times were 4 and 5.5 min for styrene and α -methylstyrene, respectively.

The recoveries of known additions of styrene to food samples are listed in Table I. The recoveries tend to decrease with increasing additions of styrene. Consequently, in order to achieve good accuracy for samples with high styrene levels a smaller sample should be weighed out. Samples with a high content of fat showed lower recoveries, probably owing to the hydrophobic nature of styrene itself and the difficulty in achieving a complete mixture of fat in methanol-water.

TABLE I
RECOVERY OF ADDED STYRENE FROM FOOD SAMPLES

Sample	Number of experiments	Concentration (mg/kg)	Recovery \pm S.D. (%)
Milk (3% fat)	13	0.18	94.0 \pm 3.6
	3	0.36	91.8 \pm 0.7
	3	0.45	87.7 \pm 1.8
Yoghurt	2	0.18	97.3 \pm 9.0
Blue cheese	1	0.18	82.6
Red fruit syrup	2	0.18	98.0 \pm 3.4
	6	0.36	75.4 \pm 4.1
	2	0.91	65.2 \pm 1.9
Strawberry jam	3	0.18	82.5 \pm 6.3
	3	0.36	79.8 \pm 5.3
	3	0.54	65.2 \pm 1.9
Minced meat	1	0.18	86.5
Brawn	1	0.18	95.6
Mayonnaise	3	0.18	78.6 \pm 6.3
	2	0.36	66.7 \pm 2.7
	3	0.54	68.3 \pm 3.7
Cooking oil	1	0.36	55.5

Together with a Dutch laboratory¹⁰ a small inter-calibration on the determination of styrene in yoghurt was carried out. Samples were spiked at each laboratory and exchanged. The styrene concentrations were in the range 0.022–0.220 mg/kg. A total of 17 analyses were performed and the mean recovery and standard deviation achieved by our method were 97.3 \pm 10.2%.

The method described permits the simple and rapid quantitative determination of styrene in foods, with the most satisfactory recoveries in the range 0.02–0.2 mg/kg. Interfering compounds from the sample matrices were observed only in distillates from some root vegetables. This makes the proposed procedure suitable as a routine method, and it has been used for the examination of polystyrene-packed food items on the Swedish market¹¹.

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