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### Single-ion monitoring of styrene in foods by coupled mass spectrometry-automatic headspace gas chromatography

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Headspace gas chromatography (GC) using an automatic electropneumatic dosing system is now widely employed for a variety of analytical applications<sup>1</sup>, and in particular for routine trace analysis of monomers in foods<sup>2</sup>. By using a flame ionisation detector (FID), adequate sensitivity (from 0.001 to 0.010 mg/kg) has been attainable for monitoring vinyl chloride in foods<sup>3,4</sup>, with more selective detection available for acrylonitrile<sup>5,6</sup> and vinylidene chloride<sup>7,8</sup>. However, for the determination of styrene there is no specific detector, and, because of the comparatively high boiling point of styrene, headspace equilibrium partition above foods is unfavourable, making the limits of detection achievable with a FID generally inadequate for most practical purposes. Hence, distillation techniques have been developed for pre-concentration in GC analysis for styrene in foods<sup>9,10</sup>; these techniques although providing sufficient sensitivity, are time consuming, involve large sample sizes and are generally inconvenient for food survey purposes.

The mass spectrometer is now routinely used in many laboratories as a highly specific chromatographic detector for quantitative measurements in either single- or multiple-ion modes, offering the additional advantage of much increased sensitivity over the FID. By using these mass spectrometric (MS) techniques, identification and quantification of monomers has been accomplished<sup>11,12</sup>, but always with manual injection of the headspace vapour above the heated foods. Although, with care, accurate results can be obtained by using this injection mode, there are many practical advantages to the use of automatic headspace analysis systems<sup>13,14</sup>, not least the increased precision obtained through better reproducibility and the convenience of unattended operation. Additionally, with manual sampling above aqueous and fatty foods, it is very difficult to avoid condensation in the syringe, with the inherent risks of sample loss, and these difficulties are circumvented by automatic techniques.

In this note we report for the first time the coupling of an automatic headspace analyser to a mass spectrometer for the routine single-ion monitoring (SIM) of monomers in foods. The limits of detection for styrene are reported for a variety of foods, and the method is shown to be capable of analysis of products that normally give interference problems with other techniques.

## EXPERIMENTAL

A Perkin-Elmer F42 automated headspace analyser was coupled through an all-glass jet separator to a VG 7070H mass spectrometer. As the mass spectrometer was interfaced to a modified Carlo Erba 4160 GC for normal applications, and in order to avoid unnecessary disruption to the system, the F42 (mounted at the correct height on a trolley) was wheeled close to the side of the Carlo Erba GC, and a stainless-steel transfer line (60 cm  $\times$  0.7 mm I.D.) was connected from the F42 GC column exit through the wall of the Carlo Erba GC oven, into the oven and thereby to the normal interface line to the mass spectrometer. The transfer line was maintained at *ca.* 200°C throughout its length, by enclosing it in a steel tube (I.D. 18 mm) wound externally with electrical heating tape.

For styrene analysis, the foods (2 g), contained in F42 vials (capacity 24 ml) sealed with rubber septa, were allowed to equilibrate at 90°C for at least 2 h. GC was performed on a 2 m  $\times$  2 mm I.D. stainless-steel column packed with 5% Carbowax 20M on Diatomite C AW (100–120 mesh). The carrier gas (helium) was operated at 25 ml/min with an injection time of 9 sec, and the oven was maintained isothermally at 120°C.

The mass spectrometer source was operated in the electron impact mode (70 eV electron energy; 200  $\mu$ A trap current) and was maintained at 200°C; the accelerating voltage was 4 kV. The magnet current was set to monitor the ion current at  $m/z$  104 (base peak and molecular ion of styrene) with source and collector slit widths adjusted to give flat-topped peaks with just sufficient resolution to separate unit masses at  $m/z = 104$ . The electron multiplier was operated at  $3.3 \cdot 10^3$  gain; in this mode, the amplifier output displayed on a 10-mV recorder had low signal noise and remained sufficiently stable to operate unattended for the course of a day.

## RESULTS AND DISCUSSION

The gas-flow disruptions during vial pressurisation and during injection of samples onto the F42, although causing changes in mass spectrometer source pressure, were not sufficient to create any difficulty, and the solvent-dump valve at the jet separator remained open throughout. The transfer line from the GC column, although longer than normally desirable, did not affect GC resolution, and peak shapes com-

TABLE I  
DETECTION LIMITS FOR STYRENE IN FOODS

<i>Foodstuff</i>	<i>Detection limit, mg/kg</i>	
	<i>Headspace F42 (FID)</i>	<i>Headspace F42 (SIM, <math>m/z = 104</math>)</i>
Double cream	0.060	0.005
Yoghurt	0.020	0.001
Cottage cheese	0.035	0.001
Soft margarine	0.350	0.015
Chocolate spread	0.200	0.001
Honey	0.015	0.001

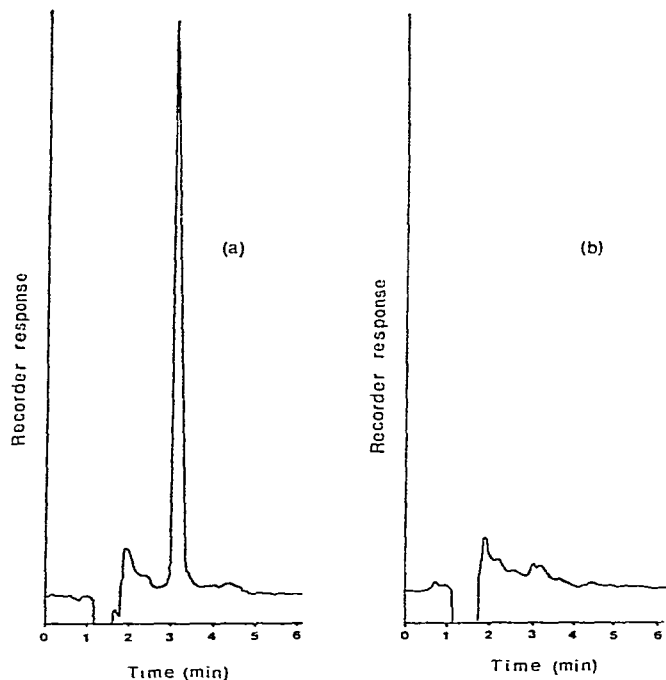


Fig. 1. Headspace chromatogram above yoghurt, with SIM. (a) Sample "spiked" with 0.02 mg/kg of styrene; (b) control material not previously in contact with polystyrene. Conditions: column, 5% of Carbowax 20M on Diatomite C AW; helium as carrier gas (25 ml/min); isothermal operation at 120°C; monitoring at  $m/z = 104$ .

pared favourably with those obtained on the F42 when the FID was used in the normal mode of operation.

In Table I, the detection limits for headspace analysis of styrene in a variety of foods by GC-FID and with SIM are compared. The limits obtained by MS were easily achievable under normal operating conditions with very low noise and a stable baseline, but, if desired, these limits could be improved by optimisation of the MS and GC conditions. In Fig. 1, a typical chromatogram is illustrated, showing a single sharp peak for styrene "spiked" into yoghurt that had not previously been in contact with polystyrene. The control foods examined showed a negligible peak in the styrene position, the only other component present in the chromatogram being a slow-running peak (retention time 15 min) produced from heating of the butyl rubber septum. A range of foods was examined by headspace MS, and such products as chocolate spread and gravy mix (in which it was not possible to determine styrene by distillation methods<sup>15</sup> due to chromatographic interference) could be easily analysed, with sensitive limits of detection.

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