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Note

Single ion monitoring of butadiene in plastics and foods by coupled mass spectrometry-automatic headspace gas chromatography

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Since the original disclosure of evidence¹ linking the inhalation of vinyl chloride monomer (VCM) with the occurrence of angiosarcoma of the liver, there has been considerable activity by Regulatory Authorities^{2,3} aimed at both surveillance and reduction of residual VCM levels in plastics and foods⁴. This work has inevitably extended to assessing possible exposure to other monomers and hence methodology for the analysis of both plastics and foods as well as allied surveillance data has been published for vinylidene chloride⁵, acrylonitrile^{6,7}, styrene^{8,9} and even ethylene¹⁰. Recent reports of the possible carcinogenic effect of 1,3-butadiene by inhalation¹¹, has once again caused concern about migration from packaging, as this compound is widely used as a co-monomer in the manufacture of food contact plastics and rubbers. One very important usage is in the production of copolymer ABS which is extensively used in the U.K. for the fabrication of tubs for soft margarine.

The analysis of 1,3-butadiene in plastics by headspace gas chromatography (GC) with flame ionization detection (FID) has previously been described by Steichen¹², with a reported limit of detection of 0.05 mg/kg. There are, however, no indications in the literature of the likely levels of residual butadiene to be expected in ABS Plastics, or of suitable methodology for monitoring migration and detection in foodstuffs.

We have previously reported coupling of an automatic headspace gas chromatograph to a mass spectrometer for determinations of styrene by single ion monitoring (SIM) mass spectrometry¹³ (MS), and this technique was subsequently utilized for an extensive survey of the occurrence of styrene in foods⁸. For styrene this approach has the obvious advantages of improved sensitivity over headspace FID¹⁴ and of speed of analysis compared to azeotropic distillation methods⁹. Also the added specificity of SIM enhances confidence in the identification of the headspace components being measured and thus this approach is frequently used for confirmation of selected samples, *e.g.* for acrylonitrile⁶, from routine surveys carried out using less specific detectors. In this article we report an extension of this headspace methodology to the sensitive analysis of butadiene in ABS and foods by SIM as well as reporting the results of some selected analyses of retail samples enabling a preliminary assessment of possible exposure to butadiene through migration.

EXPERIMENTAL

Preparation of standards and samples

Standard solutions of 1,3-butadiene (Fluka, A.G.) were prepared by bubbling the gas into a pre-weighed vial containing N,N-dimethylacetamide (DMA) (20 ml) to give a concentration of 27 mg/ml. Subsequent dilutions with DMA produced solutions covering the range of concentrations 0.2–0.0002 mg/ml which could be used directly as μ l-additions to vials to produce the desired calibration curves and standard additions.

Retail soft margarines packaged in ABS were purchased from supermarkets and included a control packed in polyolefin material. For the plastics analysis, samples (0.2 g) cut from an unprinted area of the tubs or pure polystyrene (BDH Chemicals, MW = 100,000) were weighed into F42 vials. After the addition of 4 ml of DMA the vials were capped and left overnight to dissolve the plastic.

Soft margarine samples (2 g) taken from the homogenized contents of tubs were similarly weighed into F42 vials and sealed. Due to the possibility of contamination arising from butyl rubber septa, in all cases PTFE-faced natural-rubber disc septa (Wheaton Scientific) were employed. To construct calibration graphs μ l amounts of standard solutions of butadiene in DMA were injected into sealed vials containing either dissolved polystyrene or weighed amounts of control margarine (previously shown to contain not detectable butadiene). Vials were equilibrated for 1 h at 70°C in the F42 water bath prior to analysis.

Headspace GC-MS analysis

A Perkin-Elmer F42 automated headspace gas chromatograph was coupled through an all-glass jet separator to a VG 7070H mass spectrometer as described previously¹³. Chromatography was carried out on a 2 m \times 2.2 mm I.D. stainless-steel column packed with 0.2% Carbowax 1500 on 80–100 mesh Carbowax C (Supelco) operated isothermally at 75°C with helium as the carrier gas at a flow-rate of 15 ml/min (40 p.s.i.), to give a retention time for butadiene of 2.2 min. The injector needle was set at 150°C, the injection time to 9 sec, flush time to 15 sec, analysis time to 4 min and stabilisation time to 1 min.

The mass spectrometer source was held at 200°C and operated in the electron impact (EI) mode (70 eV electron energy, 200 μ A trap current, 4 kV accelerating voltage) producing a spectrum in which the molecular ion of butadiene at m/z 54 was the base peak. Focussing was adjusted using background peaks at m/z 55 and 57, and with the source slit fully opened the collector slit was adjusted under field control and was set to pass ions at m/z 54. The output was displayed on a chart recorder, quantification being on the basis of peak height measurement.

RESULTS AND DISCUSSION

Under the conditions described above, blank analyses from vials containing 4 ml DMA and control polystyrene gave no discernible response at the retention time of butadiene when sealed, using PTFE-faced septa. However, when the normal butyl rubber septa (Perkin-Elmer) were used, a peak equivalent to 0.005 mg/kg butadiene in the plastic was obtained. Although the PTFE-faced septa required more care in

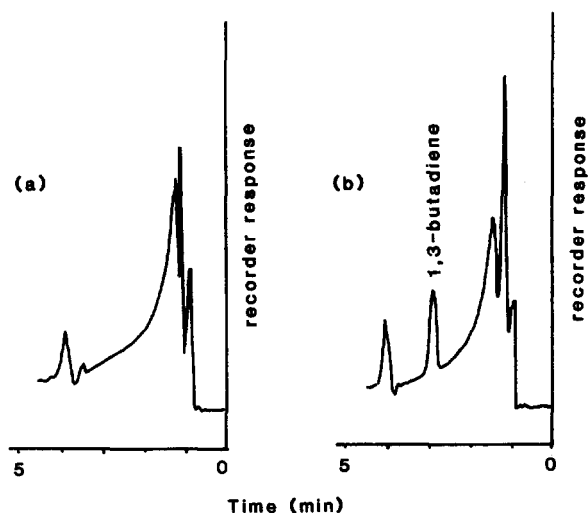


Fig. 1. Headspace chromatograms of soft margarine with SIM monitoring of $m/z = 54$. (a) Control material not previously in contact with ABS. (b) Margarine spiked with 0.001 mg/kg 1,3-butadiene. Conditions: column, 0.2% Carbowax 1500 on Carbowax C operated isothermally at 75°C; carrier gas, helium; flow-rate, 15 ml/min.

achieving a reliable seal they were used in all subsequent work. For determination of butadiene in plastics linear calibration was achieved over the range 0.02–5.00 mg/kg with a detection limit of 0.005 mg/kg.

For determinations of butadiene in soft margarine the large sample size and more favourable partition lead to a detection limit of 0.0002 mg/kg. Fig. 1 shows typical chromatograms both for control margarine and control margarine spiked with 0.001 mg/kg butadiene. Although the butadiene peak was seen to be eluted on the tail of the peak caused by disruption in the gas pressure during injection, quantification was nevertheless possible down to 0.001 mg/kg.

The methodology described in this paper encompasses all the advantages of automated headspace analysis¹⁵ together with the specificity and sensitivity of mass spectrometric detection. As described the instrumentation can be rapidly set up and

TABLE I
CONCENTRATION OF 1,3-BUTADIENE IN RETAIL SOFT MARGARINE

Brand	Concentration 1,3-butadiene (mg/kg)	
	Tub	Margarine
A	< 0.005	< 0.0002
B	0.31	< 0.0002
C	0.07	< 0.0002
D	0.11	< 0.0002
E	0.10	< 0.0002

causes minimum disruption to the normal chromatographic coupling of the mass spectrometer.

The results for the analysis of five soft margarine tubs and their contents (representative of different major brand names in the UK) are shown in Table I. Levels of butadiene in the ABS Plastics ranged from <0.005 to 0.31 mg/kg and for the soft margarines were not detectable at a detection limit of 0.0002 mg/kg. Although this survey is rather limited the levels of butadiene in the ABS tubs are significantly lower than those of acrylonitrile which have been found to range from 0 to 10 mg/kg with an averaged around 2 mg/kg⁶. The absence of butadiene in the margarine (in comparison with acrylonitrile, which measured 0.01–0.02 mg/kg) suggests that this monomer is unlikely to present a problem through migration into foods.

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