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Use of in-tube sorptive extraction techniques for determination of benzene, toluene, ethylbenzene and xylenes in soft drinks

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Abstract

A comparison is made between static headspace analysis and headspace solid-phase dynamic extraction (HS-SPDE) for the quantitative determination of trace level BTEX solvents (benzene, toluene, ethylbenzene and *o*-, *m*-, and *p*-xylene) in soft drinks. Two non-polar extraction phases were investigated for SPDE using an automated sampler with a gas-tight syringe equipped with a special needle coated on the inside with the extraction phase. Following adsorption onto the phase, the analytes were thermally desorbed directly into a GC–MS. The techniques were optimised and evaluated by analysis of spiked soft drink samples. The use of the SPDE device gave comparable results to the static headspace method, with lower detection limits for some compounds, and also offers advantages for applications where lower temperatures are preferred.

Keywords: Sample preparation; Sorptive extraction; Headspace; Gas chromatography; Solid-phase microextraction; Solid-phase dynamic extraction

1. Introduction

The unintentional presence of organic solvents in food and beverages can originate from a number of sources, including transfer from packaging materials, degradation or reaction of preservatives, heat or processing conditions or as environmental contaminants. One group of solvents which are often determined due to concerns over their toxicity, are known as the BTEX solvents (benzene, toluene, ethylbenzene and the xylenes). One approach is direct static headspace analysis, which has been extensively used for the determination of volatile compounds in foodstuffs [1]. Increasingly, sorptive extraction techniques are also being utilised for the determination of volatiles in food matrices [2] as they can provide the high concentration factors required for quantitative determinations at trace levels. For the determination of BTEX compounds in aqueous samples, traditionally purge and trap methods [3] and more recently solid-phase microextraction (SPME) [4,5] have been used.

An alternative is needle trap devices [6], which use multiple extraction cycles to draw the sample through a packed or internally coated tube or needle [7]. Wang et al. [8] compared on-line, in-tube SPME and fibre SPME for the GC analysis of contaminants (alkanes, polycyclic aromatic hydrocarbons (PAHs) and selected pesticides) in water. The analysis of aqueous samples using in-tube SPME, for BTEX compounds, PAHs, *n*-alkanes, *N*,*N*-dibutylalkylamides, halogenated solvents, atrazine and substituted benzenes, phenols and anilines, has been reported [9–11]. An automated in-tube sorptive extraction device, known as solid-phase dynamic extraction (SPDE) is now commercially available. This uses a syringe which can repeatedly draw up the liquid or vapour sample through a needle, which is coated on the inside with a liquid extraction phase, before desorption into a GC. Bicchi et al. [2] applied this method to the headspace solid-phase dynamic extraction (HS-SPDE) of a series of food components and Jochmann et al. [12] have used the technique for polar volatile organic compounds in water.

This paper describes the development and validation of a static headspace method, based on a reported method [13], for the quantitative analysis of BTEX compounds in aqueous-based soft drinks and the optimisation and evaluation of alternative methods using the SPDE headspace sampling technique.

2. Experimental

2.1. Reagents

Methanol was Merck HPLC grade and ultra-pure water was generated from a Nanopure Diamond system (Barnstead

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International, Dubuque, IA, USA). Sodium sulphate (reagent grade) was from BDH (VWR, Poole, UK).

2.2. Standards

Benzene, [$^2H_6$]benzene (benzene-d_6), [$^2H_8$]toluene (toluene-d_8), ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene (all >98% purity) and toluene (>99.9%, Fluka) were obtained from Sigma–Aldrich (Poole, UK). Stock standards were prepared in methanol and diluted to give a range of standards for spiking.

2.3. Apparatus and instrumental conditions

Instrumental analysis was carried out on an Agilent 6890 (Cheadle, UK) gas chromatograph fitted with 5973 mass selective detector and CTC Analytics CombiPAL headspace autosampler (Presearch Hitchin, UK). Headspace vials (10 ml) were fitted with silicone/PTFE septa and metal caps (Kinesis, Milton Keynes, UK). The CTC headspace autosampler was fitted with both static and SPDE capability. A split/splitless injector was used for splitless injection at 200 °C. The carrier gas was helium at 2 ml/min. The column was a DB-WAXetr 50 m × 0.32 mm i.d., 1 μm film thickness. The separations were carried out using a GC oven temperature programme of 60 °C for 0.5 min, then programmed at 2 °C/min to 100 °C then 10 °C/min to 200 °C. These conditions enabled resolution of the three xylene isomers and separation from the matrix components. The time taken for the GC run corresponded approximately to the extraction time for SPDE analysis.

Mass spectral data was collected in electron impact ionisation EI (+) selected ion mode (SIM), acquiring m/z 78, 51 and 50 for benzene, 84 and 56 for benzene-d_6, 91, 92 and 65 for toluene, 99 and 100 for toluene-d_8, 106 and 91 for ethylbenzene, *o*-, *m*- and *p*-xylene.

The SPDE analysis used a 2.5 ml gas-tight syringe, with an internally coated needle (56 mm length, i.d. 0.5 mm, ±0.05 mm), using either a polydimethylsiloxane (PDMS) 50 μm coating (Presearch part number SPDE-01-50-56), or PDMS/10% activated charcoal coating (Presearch part number SPDE-01/AC-50-56). Between extractions the SPDE needle was conditioned at 230 °C and flushed with carrier gas for 3 min (to avoid carry-over between samples [14]).

2.4. Methodology

For both static headspace and headspace-SPDE aliquots of sodium sulphate (5 g) were weighed into 20 ml headspace vials and 10 ml soft drink sample was added. All samples were spiked with 100 μl of 0.01 μg/ml internal standard (benzene-d_6 and toluene-d_8) in methanol and either 100 μl methanol or 100 μl of a standard solution of a mixture of BTEX compounds in methanol.

2.4.1. Static headspace method

The analytes were partitioned into the headspace by heating at 70 °C and agitating for 15 min at 500 rpm. An aliquot of the headspace vapour (1 ml) was then injected directly into the GC–MS.

2.4.2. SPDE method

The samples were equilibrated for 10 min at 30 °C and agitated at 500 rpm before extraction. An aliquot (1 ml) of the headspace was pulled through the needle at 50 μl/s for either 15 cycles (PDMS/AC phase) or 20 cycles (PDMS phase). The syringe was automatically transferred to the injector port and the needle was desorbed at 200 °C with 1 ml of helium at 100 μl/s.

3. Results and discussion

Experiments were performed for each method to determine the optimum extraction conditions including effect of the addition of sodium chloride or sodium sulphate to the sample. For the static headspace method the incubation temperature and time and different sample volumes were considered. For HS-SPDE the temperature, extraction phase, draw-up volumes, number of extraction cycles and the desorption parameters of gas volume, flow and temperature were also optimised.

3.1. Optimisation of extraction

To determine the optimum temperature for each technique, extraction was performed at a range of temperatures between 30 and 100 °C. For the static headspace method, it was found that equilibration between the headspace and the liquid was achieved after 15 min at the optimum temperature of 70 °C. In contrast, the optimum extraction temperature was found to be only 30 °C for HS-SPDE with a pre-extraction incubation of 10 min (Figs. 1 and 2). The optimum number of extraction cycles (number of 2.5 ml sample flushes of the needle) for the HS-SPDE to give the maximum signal size at the optimum temperature was determined to be 20 extraction strokes for the PDMS phase (Fig. 3) and 15 extraction strokes for the PDMS/AC stationary phase (Fig. 4) phase. Following the initial increase in response with the number of extraction cycles, a plateau is reached, where further extraction does not increase the response. After a certain time a small decrease in response may be noted due to losses of volatiles from the coating.

The differences in optimum temperature when comparing direct static headspace and sorptive headspace sampling techniques have been observed in previously reported work using headspace SPME for BTEX extraction [4], and for other volatile analytes with both headspace SPME [13] and SPDE sampling [2] and the differences were ascribed to the two competing partitions involved in sorptive extraction. Partition coefficients are temperature-dependent and an increase in temperature leads to more analyte being released into the headspace. However, as the temperature is increased, the coating-headspace partition coefficients decrease and analytes will prefer to remain in the headspace rather than 'extract' onto the coating. Increasing the temperature can therefore have a negative effect on response.

For the PDMS phase, although the response dropped as the temperature was raised above 30 °C, above 90 °C, the response