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Dynamic headspace liquid-phase microextraction of alcohols

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Abstract

A method was developed using dynamic headspace liquid-phase microextraction and gas chromatography-mass spectrometry for extraction and determination of 9 alcohols from water samples. Four different solvents, hexyl acetate, *n*-octanol, *o*-xylene and *n*-decane were studied as extractants. The analytes were extracted using 0.8 μl of *n*-octanol from the headspace of a 2 ml sample solution. The effect of sampling volume, solvent volume, sample temperature, syringe plunger withdrawal rate and ionic strength of the solution on the extraction performance were studied. A semiautomated system including a variable speed stirring motor was used to ensure a uniform movement of syringe plunger through the barrel. The method provided a fairly good precision for all compounds (5.5–9.3%), except methanol (16.4%). Detection limits were found to be between 1 and 97 μg/l within an extraction time of ∼9.5 min under GC–MS in full scan mode.

Keywords: Headspace liquid-phase microextraction; Extraction method; Food analysis; Alcohols

1. Introduction

Conventional sample preparation techniques such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have several disadvantages. LLE is time consuming and requires large volume of expensive and toxic solvents. On the other hand, although SPE uses low amounts of organic solvent, it is applicable only to non-volatile and semivolatile compounds [1].

Solid-phase microextraction (SPME) has the potential to overcome many difficulties associated with conventional extraction methods [2]. SPME is a solvent free, simple and fast extraction method. The technique has been extensively used in different fields of application such as food, environmental, clinical and forensic science. However, there are still some drawbacks in this method, including damage of fibre during sampling, limited life time of the fibre, bleeding of the SPME coating into the GC injector and sample carry-over [3,4].

Direct SPME, that is placing the fiber directly into the sample to extract organic compounds, is recommended for relatively clean samples and extraction of semivolatile and non-volatile compounds. However, for analysis of volatile analytes, especially in complex samples, direct SPME is not recommended, sampling of the analytes from the headspace above the sample matrix (HS-SPME) [5] being more adequate. However, because of the greater availability of non-polar or slightly polar fiber coatings, HS-SPME applications are mostly limited to non-polar or medium-polar analytes [6,7] and there are a few reports concerning SPME of polar compounds [8].

Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique [9–11]. This method provides analyte extraction in a few microliters of organic solvents. LPME avoids some problems of the SPME method such as fibre degradation; it is also fast, inexpensive and uses very simple equipment. Moreover, although a variety, SPME fibres is commercially available, the choice of solvents for LPME is much broader and the organic phase is renewable at negligible cost.

Similar to SPME, there are two modes of LPME sampling: direct LPME and headspace LPME (HS-LPME). The direct LPME consists of suspending a microdrop of organic solvent at the tip of a syringe, which is immersed in the aqueous sam-

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ple. HS-LPME is very similar to LPME except that microdrop of high boiling extracting solvent is exposed to the headspace of a sample. Like HS-SPME, headspace LPME is a good extraction technique to analyze volatile and semivolatile compounds in different matrices. In addition, because of availability of wide range of polar and non polar as well as water miscible solvents, HS-LPME seems to be an attractive extraction technique. However, use of microdrop LPME for headspace analysis it is relatively difficult, because most suitable organic solvents in GC have high vapour pressure, which result in them evaporating too quickly in headspace during extraction. Moreover, when using water miscible solvents, because of increase in drop size during sampling, it may drop from needle [12]. There are a few reports concerning application of a drop of solvent suspended from the tip of a syringe needle for headspace analysis [12–18]. Recently, Lee and Shen [19] have introduced dynamic HS-LPME that overcomes some limitation of static microdrop HS-LPME. In this technique the extraction is performed within the microsyringe barrel and the syringe is employed as both a separatory funnel for extraction and a syringe for direct injection into a GC column. When the syringe plunger is withdrawn, a very thin organic solvent film (OSF) is generated on the inner syringe wall. Mass transfer of the analytes occur between the gaseous sample and OSF. In each extraction cycle a fresh gaseous sample contacts with a new OSF. In comparison to droplet LPME, the described dynamic LPME provides a larger enrichment factor within a shorter analysis time and selection of solvent is more flexible [19,20].

Lee and Shen [19] used dynamic HS-LPME to analyze chlorobenzenes in a solid matrix such as soil. Because they used a manually operated extraction system the precision of the method was relatively poor (relative standard deviation, R.S.D. were between 5.7 and 17.7%).

In the present study, a semiautomatic dynamic HS-LPME system was developed in order to improve ease of operation and to achieve greater reproducibility in the sample extraction. A variable speed stirring motor was used for automation of sample extraction step. Low molecular weight alcohols were used as model compounds. The experimental parameters that affect the extraction efficiency of studied compounds from aqueous samples were evaluated and optimized. Relatively good precision and high sensitivity were obtained with the proposed method.

2. Experimental

2.1. Chemicals

Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *tert*-butanol, 1-pentanol, 2-pentanol and ethyl methyl ketone (used as internal standard) were purchased from Merck (Darmstadt, Germany). A stock standard solution of nine alcohols studied was prepared in water at concentration level of ~4000 mg/l for methanol and ethanol; and ~2000 mg/l for the rest of compounds. A mixture of these compounds was prepared weekly by diluting the standard solution with double distilled water, and more diluted working solutions were prepared daily by diluting this solution with water. The standard solutions were stored refrigerated at 4 °C.

Hexyl acetate, *n*-octanol, *o*-xylene and *n*-decane (Merck) containing a fixed concentration of ethyl methyl ketone (IS), were used as extraction solvents.

2.2. Instrumentation

A 10 μl GC microsyringe model 701N (gauge 26s and point style 2) from Hamilton (Reno, NV, USA) was used to perform LPME experiments. The sample vial was placed in a water-bath on a magnetic stirrer (CB162, Bibby, UK). A circulating water-bath (Fanazma, Iran) was used to maintain the sample at desirable temperature. The basic extraction apparatus is shown in Fig. 1. A variable speed stirring motor was attached to a circular plate (6). Rotation of the plate causes movement of syringe plunger through the barrel.

Gas chromatographic analysis was carried out using a Fisons Instrument (Rodano, Italy) model 8060 fitted with a split/splitless injector and Trio 1000 mass spectrometer (Fisons Instruments, Manchester, England) detector. Helium was used as the carrier gas with a flow rate of 0.6 ml/min. The components were separated on a 60 m × 0.25 mm i.d., 0.1 μm film thickness DB-5MS column from J&W Scientific (Folsom, CA, USA). The injector temperature was set at 220 °C and all injections were made in split mode (split ratio, 40:1). The column was initially maintained at 40 °C for 7 min; subsequently, the temperature was increased to 100 °C at a rate of 15 °C/min (1 min hold) then was increased to 240 °C (30 °C/min, 10 min hold). The mass spectra were acquired as full scans from *m*/*z* 20 to *m*/*z* 90 (2 scans/s), with a source temperature of 200 °C under a 70 eV ionization potential.

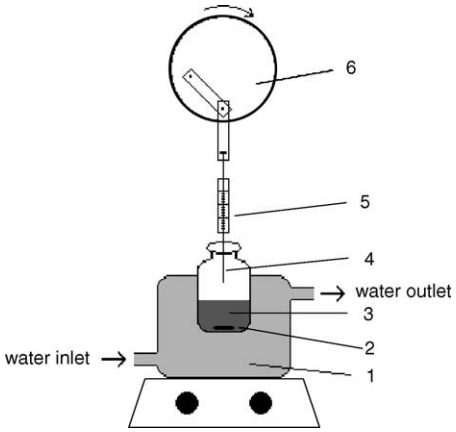

Fig. 1. Schematic diagram of the HS-LPME system. (1) water bath; (2) magnetic stirrer bar; (3) sample solution; (4) syringe needle tip; (5) microsyringe; (6) circular plate connected to a variable speed stirring motor.