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Headspace in-tube microextraction coupled with micellar electrokinetic chromatography of neutral aromatic compounds

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ABSTRACT

Headspace (HS) extraction can be carried out easily and aptly via single drop microextraction coupled with capillary electrophoresis (CE). However, one drawback is the difficulty of keeping the single drop stably at the capillary tip. To solve this problem, we have recently demonstrated HS in-tube microextraction (ITME) of acidic compounds such as chlrophenols in an acidic sample using a basic run buffer plug in the separation capillary for CE as an acceptor phase. In this report, an organic acceptor plug in a capillary was used to extract neutral organic volatile pollutants such as BTEX (benzene, toluene, ethylbenzene, and *m*-xylene). After extraction, the analytes enriched in the organic acceptor plug were analyzed with micellar electrokinetic chromatography (MEKC). The enrichment factors for BTEX in a standard solution were up to 350 under an optimal condition of 25 °C for 20 min. As an application, BTEX spiked into bottled water were analyzed with HS-ITME-MEKC, and the enrichment factors for BTEX were up to 320. The limits of detections were 1–4 ppb, which are at least 200 times lower than the US Environmental Protection Agency guidelines for drinking water, except benzene. The entire procedure of HS-ITME-MEKC was carried out automatically using a commercial CE instrument.

1. Introduction

The methods mainly used for headspace (HS) extraction, which is useful for the concentration of volatile materials in a complex matrix, include solid phase microextraction (SPME) [1–7] and liquid phase microextraction (LPME) [8–10]. While SPME is mostly performed using commercial devices with limited choices of extraction configurations, LPME does not require special instrumentation and is flexible to adopt various extraction configurations [10]. Among the LPME methods used for HS extraction, single drop microextraction (SDME) is frequently coupled with gas chromatography or liquid chromatography in an off-line manner using a single acceptor drop hanging on the tip of an injection syringe needle [11–15]. SDME offers high sample enrichment factors in a short extraction time, owing to a very large sample-to-acceptor drop volume ratio and surface-to-volume ratio of the acceptor drop [16]. In capillary electrophoresis (CE), a single acceptor drop can be formed at the separation capillary tip, which makes the injection afterwards in an in-line manner [17] and enables full automation with a commercial CE instrument [18]. After sample injection, an on-line sample preconcentration technique of CE may also be used for further sensitivity improvement [16,19–25].

The performance of SDME depends on the size of the drop. However, the repeatability and stability of the drop are difficult to control. This shortcoming can be overcome by in-tube microextraction (ITME) using the liquid plug inside a separation capillary as an acceptor phase instead of the hanging acceptor drop in SDME [26]. The acceptor phase is protected by the capillary, which ensures stable extraction in various environments. ITME has an additional advantage of analyzing all extracted analytes since the extraction and injection processes are carried out simultaneously. In HS-ITME, the extraction process is extremely simple as the extraction starts when the capillary with a short acceptor plug is placed in the HS. HS-ITME using an aqueous acceptor plug was demonstrated for the analysis of chlorophenols in red wine of a very complex matrix.

In this report, neutral aromatic carcinogens, BTEX (benzene, toluene, ethylbenzene, *m*-xylene) [27,28], were analyzed with HS-ITME using an organic acceptor phase. In contrast to the first HS-ITME of acidic chlrophenols driven by the pH difference between the aqueous donor and acceptor phases, hydrophobic BTEX were enriched by their favorable partitioning into an organic acceptor phase such as chloroform. After extraction micellar electrokinetic

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chromatography (MEKC) [29] was applied to separate the neutral analytes in the organic solvent. The entire procedure was operated automatically with a commercial CE instrument. Under optimal conditions, BTEX in an aqueous sample were enriched up to 350-fold with 20 min HS-ITME at room temperature. The limits of detections (LODs) for the BTEX in bottled water obtained with UV absorbance detection were about 3 ppb.

2. Materials and methods

2.1. Reagents

Benzene, toluene, ethylbenzene, *m*-xylene, sodium tetraborate decahydrate, HPLC-grade HCl, sodium dodecyl sulfate (SDS), and Sudan-III were purchased from Sigma-Aldrich (St. Louis, MO, USA). Boric acid was purchased from Merck (Damstadt, Germany). HPLC-grade methanol was purchased from J.T. Baker (Phillipsburg, NJ, USA). Deionized water was obtained with a LabTower EDI Water unit (Thermo Scientific, Langenselbold, Germany). 2 mM stock solutions of BTEX were prepared in methanol and stored in the dark at 4 °C before use. Standard samples for MEKC were prepared by diluting the corresponding stock solutions with the borate buffer containing SDS, and sample donor solutions for HS-ITME-MEKC by diluting the corresponding stock solutions with water. Bottled water samples for HS-ITME-MEKC were prepared by adding 10 μL of a standard sample to 990 μL of bottled water. Every solution, except for the donor solution, was filtered through a 0.45 μm syringe filter (Whatman, Clifton, NY, USA) before use.

2.2. MEKC

MEKC analyses were performed by a P/ACE MDQ CE instrument (Beckman, Fullerton, CA, USA) with a fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) of 50 μm id × 363 μm od × 60 cm (50 cm to detector). The sample tray was modified to accommodate a jacketed beaker for controlling the sample vial temperature as previously reported [26]. MEKC for BTEX was based on the published protocol [29] but modified to improve the resolution between ethylbenzene and *m*-xylene; a run buffer of 70 mM sodium borate with 30 mM SDS, whose pH was adjusted to 9.2 by titrating with saturated boric acid solution, was used. The capillary was conditioned with 0.1 M NaOH, water, and run buffer, each for five min at 50 psi before each run. For electrophoresis, a normal potential of +20 kV was applied across the capillary and the absorbance at 193 nm was monitored. The capillary temperature was set at 20 °C.

2.3. HS-ITME-MEKC

HS-ITME procedures were previously described [26]. A sample vial with a perforated cap (#144648, Beckman) was filled with a donor phase of 1.2 mL, and then covered with plastic household wrap. The temperature of the donor phase and HS was controlled by a jacketed beaker, which was connected to a thermostat (LAUDA, Lauda-Königshofen, Germany). After the rinsing step as described above, an acceptor phase was injected at 0.2 psi for a desired time into the capillary containing the run buffer. When the lowest pressure of 0.2 psi available from the commercial CE instrument was used, its accuracy was not reliable and the actual injection volume could be different from the one calculated from the injection pressure and time using the Poiseuille equation. The actual volume of an acceptor plug inside the capillary was estimated from the peak area of 25 mM Sudan III dissolved in the acceptor phase using the relation between the peak area and the plug volume obtained beforehand for more accurate higher pressure operations. The capillary inlet pierced the wrap and was placed at the HS above the donor phase in the sample vial. The capillary outlet was placed in an empty vial. After extraction, a pre-injection step was employed before separation in order not to lose analytes enriched at the entrance surface of the acceptor plug. The capillary inlet and outlet were immersed in run buffer vials and a short time elapsed for dissolving the pre-injected HS vapor plug inside the capillary. MEKC was then carried out.

3. Results and discussion

3.1. Acceptor phase

In HS-ITME, an analyte is transferred from the donor phase (d) to the HS (h) by evaporation, and then transferred from the HS to the acceptor phase (a). Since BTEX are neutral aromatic chemicals, the micellar run buffer and organic solvents commonly used in liquid phase extraction such as 1-octanol, *n*-hexane, and chloroform were tested as an acceptor phase. The enrichment factor (EF) of the analyte is defined as the ratio of its concentration in the acceptor phase (C_a) to the initial concentration in the donor phase ($C_{d,i}$) [30]. Fig. 1a shows EFs obtained from 10 min HS-ITME at 25 °C using various acceptor phases. The volume of the injected acceptor plug was 0.7 nL except for the case of the run buffer which was already inside the capillary. Chloroform EFs were

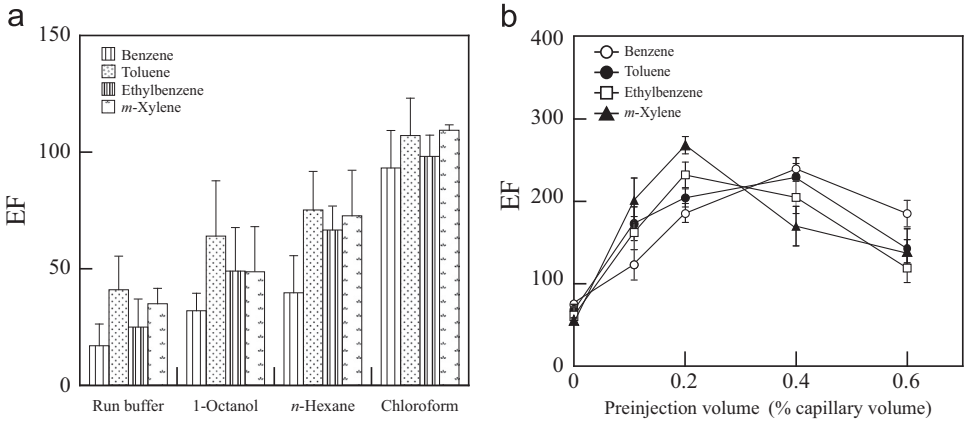

Fig. 1. (a) Comparison of acceptor phases; 0.7 nL run buffer, 1-octanol, *n*-hexane, and chloroform. (b) Pre-injection volume; 0.7 nL chloroform. Extraction; 10 min at 25 °C. Donor phase; 2 μM BTEX in deionized water. MEKC; fused silica capillary of 50 μm id × 50/60 cm, 70 mM borate run buffer with 30 mM SDS (pH 9.2), absorbance at 193 nm, and +20 kV. Error bars represent the standard deviations ($n=4$).