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Determination of volatile organic compounds in water using headspace knotted hollow fiber microextraction

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ABSTRACT

An efficient and effective headspace microextraction technique named static headspace knotted hollow fiber microextraction (HS-K-HFME) has been developed for the determination of volatile organic compounds (VOCs) in water samples. The knot-shaped hollow fiber is filled with 25 μL of the extraction solvent. The excess solvent forms a large droplet (13 μL) and is held in the center of the knot. Even after 20 min of extraction time at high temperature (95 °C) without cooling, there was still enough volume of extraction solvent for gas chromatography–mass spectrometry (GC–MS) analysis, which extends the choice of solvents for headspace LPME. Moreover, the knot-shaped fiber has a larger extraction contact interface, which increases the rate of mass transfer between the headspace and extraction solvent film attached to the fiber, thus improving the extraction efficiency. The effects of extraction solvent, temperature, stirring rate, salt concentration and extraction time on extraction performance were optimized. The calibration curves exhibited coefficients of determination (R^2) ranging from 0.9957 to 0.9999 and the limit of detection (LOD) ranged from 0.2 to 10 μg L^{-1}. Relative standard deviations (RSDs) ranged from 4.5% to 11.6% for intraday measurements (n = 5). Interday (n = 15) values were between 2.2% and 12.9%. The relative recoveries (RRs) ranged from 90.3% to 106.0% for river water and 95.9% to 103.6% for wastewater.

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1. Introduction

Volatile organic compounds (VOCs) are defined as having a boiling point that ranges between 50 °C and 260 °C [1]. VOCs are widely emitted from sources such as paints, varnishes, solvents and preservatives, and become major environmental pollutants because of their high volatility and toxicity [2,3]. Due to their physical properties, VOCs can easily cross lipid membranes and distribute to well-perfused organs; exposure to VOCs may thus result in both acute and chronic health effects. Diethyl ether (DE) and ethyl acetate (EA) are two common VOCs, which are used worldwide in flavoring and perfumery and in smokeless power manufacture. They are mildly irritating to eyes, nose and throat. Exposure to high levels may cause dizziness or to pass out. Especially for DE, severe over exposure may result in death [4]. Certain VOCs are more toxic and persistent in water, soil, and organisms, such as dichloromethane (DCM), toluene, *o*-xylene, *m*-xylene, and *p*-xylene. They are considered one of the major causes of environmental pollution because of widespread occurrences of leakage from underground gasoline storage tanks and spills. Long term exposure of them has been associated with liver and kidney damage, intestinal tract disturbances and central nervous system depression [4–6]. Therefore, the United States Environmental Protection Agency (EPA) has regulated 0.005 and 10 mg L^{-1} as the maximum permissible contaminant level for dichloromethane and total xylene respectively in drinking water [7]. As a result of this low limit, it is necessary to develop highly sensitive and efficient analytical methods to detect VOCs in the aquatic environment.

Analyte extraction and pretreatment is the most challenging and time-consuming step in most chromatographic procedures. In the last few years, research trends in separation science have oriented toward minimizing the sample pretreatment steps. Solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) have been developed based on this concept. SPME was first introduced by Pawliszyn and coworkers [8] and involves the partition of analytes between sample matrices and a polymer-coated stationary phase on a silica fiber. It enables the extraction and simultaneous preconcentration of analytes from aqueous samples. There are three major types of SPME: direct-immersion [9], headspace (HS) [10–12] and membrane-protected SPME [13].

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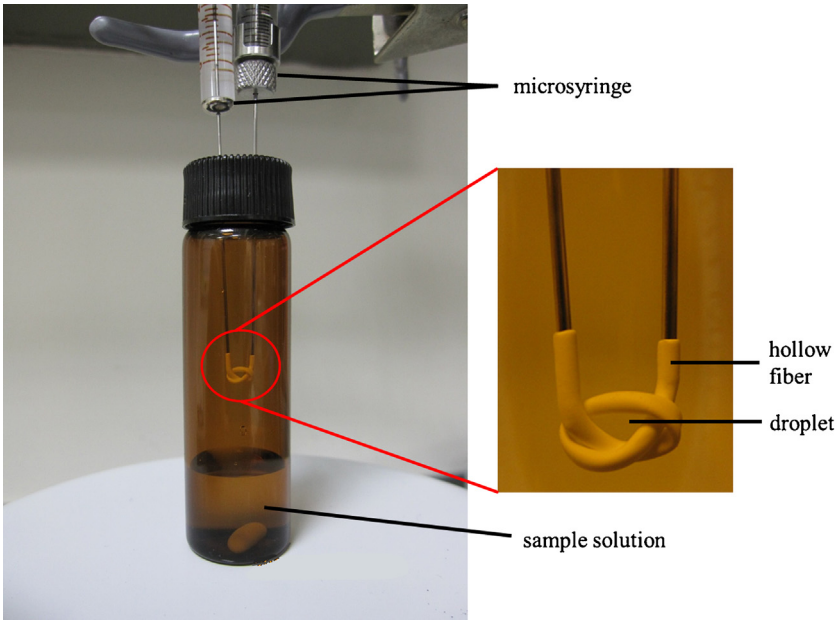

Fig. 1. The extraction equipment of HS-K-HFME.

Among them, HS-SPME analysis is the most common technique for the determination of VOCs as it significantly reduces the interference from dirty matrices, which is generally associated with direct-immersion SPME [14–16]. Lately, LPME has emerged as an attractive alternative to conventional liquid–liquid extraction (LLE). Jeannot and Cantwell proposed single-drop microextraction (SDME) in which an 8-μL droplet of organic solvent was suspended at the end of a Teflon rod and immersed in an aqueous solution to extract analyte specimens [17]. An improvement involved the use of a microsyringe to hold the solvent drop [18]. To increase the rate of mass transfer, Lee et al. developed a dynamic liquid phase microextraction technique using a short hollow fiber inserted onto a microsyringe [19,20]. The hydrophobic and porous fiber was filled with organic solvent, which stabilizes the solvent successfully in comparison with holding a droplet at the tip of the microsyringe [21–23]. The immersion mode yields high enrichment factors, high sensitivity and ruggedness. However, headspace LPME using a hollow fiber presents more challenges than other types of LPME because the extraction solvents compatible with gas chromatography (GC) usually evaporate quickly in the headspace.

For headspace LPME, SDME and fiber-protected LPME have been developed. Theis et al. [24] introduced headspace SDME using 1-octanol as the extraction solvent for analyzing VOCs, which has a relatively low vapor pressure. Shen and Lee [25] used dynamic headspace LPME to improve the stability of headspace SDME. A thin organic solvent film was formed on the inner syringe wall. The dynamic operation increased and refreshed the interface between the gas phase and the extraction solvent, thus increasing the extraction efficiency significantly. Jiang et al. [26] developed a dynamic hollow fiber-supported headspace liquid-phase microextraction (DHF-HS-LPME) technique. A hollow fiber filled with the solvent was inserted onto a microsyringe needle which was kept vertically in the headspace of the sample solution. The solvent within the fiber could be moved using a programmable syringe pump. This method enabled the use of higher solvent volumes, increased the extraction contact interface and stabilized the organic solvent within the fiber.

In such analyses, headspace gas is usually injected into a GC directly. A major concern is that the organic solvents commonly used in GC have high vapor pressures, which result in quick evaporation in the headspace and limits the possible selection of extraction solvents. In 2007, Huang and Huang [21] applied a solvent cooling system to the microsyringe which decreased the temperature of the solvent when it was drawn into the syringe. This decreased temperature minimized the loss of extraction solvent but also caused slow equilibration and led to longer extraction times. Chen et al. [27] developed a dynamic hook-type liquid-phase microextraction (DHT-LPME). The extraction solvent was easily and completely withdrawn into the microsyringe, while the hook shape removed interference from air bubbles which commonly persist when the hollow fiber is placed vertically. Subsequently the same group introduced dynamic headspace time-extended helix LPME (DHS-TEH-LPME) to overcome the slow equilibrium caused by cooling system. An aluminum heating block was used to heat the sample vial while the extraction solvent was condensed using a cooling system. The extraction temperature up to 80 °C was used for 60 min. Chen et al. [28] developed a PTFE vial cap with a cylindrical cavity to hold a 40-μL droplet of volatile extraction solvents, such as acetone, in the headspace. The cooling system, based on a thermoelectric cooler (TEC), was used to lower the temperature of the vial cap below zero. This method enabled a limit of detection (LOD) for chlorobenzenes between 4 and 8 $\mu g\,L^{-1}$. It is worth noting that, in order to extend the selection of solvents and reduce solvent loss during headspace, LPME extraction processes, a cooling system is usually required. However, this also results in slow equilibrium and longer extraction times to obtain satisfactory extraction efficiency.

To address these issues, we proposed a simple and efficient headspace LPME technique named headspace knotted hollow fiber microextraction (HS-K-HFME) for the determination of VOCs in water samples. A 2.5 cm long hollow fiber was bent into a figure eight knot shape (Fig. 1) and filled with 25 μL of extraction solvent. AA 2.5 cm fiber can hold 12 μL of solvent approximately. The excess solvent which was not held inside the fiber formed a large droplet (approximately 13 μL). The droplet was held steadily at the center of the knot. As a result of the figure eight shape, there is no interference from air bubbles in the fiber. The extraction solvent is withdrawn into the microsyringe easily and the long fiber has a large contact surface that increases the extraction interface between the headspace and the organic solvent. This large volume is sufficient to compensate for evaporative losses during sampling. Moreover, during the extraction of VOCs, the specimen solution can also be heated.

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