Journal of Chromatography A, 1361 (2014) 16–22

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Fiber-assisted emulsification microextraction coupled with gas chromatography–mass spectrometry for the determination of aromatic amines in aqueous samples

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ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 23 July 2014
Accepted 24 July 2014
Available online 1 August 2014

Keywords:
Fiber-assisted emulsification microextraction (FAEME)
Gas chromatography–mass spectrometry
Aromatic amines
Kapok fiber
Glass fiber

ABSTRACT

A novel fiber-assisted emulsification microextraction (FAEME) method was developed for the determination of eight aromatic amines (AAs) in aqueous samples. In this method, the extraction solvent (100 μL chlorobenzene) and the dispersive material (1.0 mg kapok fiber fragments) were added successively into the aqueous sample (5.0 mL), and then the mixture was emulsified by ultrasound to form the cloudy solution. Phase separation was performed by centrifugation, and the sedimented phase was transferred to micro-inserts with a microsyringe for analysis. All variables involved in the extraction process were identified and optimized. By coupling the analysis with gas chromatography–mass spectrometry (GC–MS), excellent detection limits (0.01–0.2 $\mu g\,L^{-1}$), good precision (RSDs, 3.33–6.56%) and linear ranges (0.10–160 $\mu g\,L^{-1}$ and 1.0–160 $\mu g\,L^{-1}$) were obtained. Compared with the traditional solvent-emulsification method, the extraction recoveries of the proposed method were much higher. Satisfactory recoveries were achieved when the method was used for the analysis of AAs in spiked real water samples.

1. Introduction

Aromatic amines (AAs) are important intermediates in the synthesis of azo colorants, which are used in a variety of products, such as foodstuffs, cosmetics, medicines, plastics, leather, and textiles [1,2]. AAs can arise from the reduction of the azo groups (N=N) in azo colorants and may directly contact human skin or the oral cavity during usage [3]. Some AAs have been reported and classified as substances known to be or suspected to be human carcinogens [4–6]. In 2002, the European Parliament issued the European Directive 2002/61/EC to restrict the marketing of the use of azo dyes that might form any of the proscribed AAs [7,8].

Because AAs are highly toxic, it is recognized that they must be monitored to adequately assess the potential risk to humans and the environment. The most commonly used methods, including some current standards, such as EN 14362, BVL B 82.02, and CEN ISO/TC 17234, have been developed in the past and are based on conventional liquid–liquid extraction (LLE). Recently, efforts have become oriented toward new, miniaturized, and economical LLE, which can be grouped in the so-called liquid-phase microextraction (LPME). To overcome the limitations of LLE, such as its time-consuming nature and the consumption of a large amount of organic solvent, LPME emerged from LLE and has evolved into various extraction types [9] that can be classified as dispersive liquid–liquid microextraction (DLLME) [10–12], hollow-fiber LPME (HF-LPME) [13–15], and single-drop microextraction (SDME) [16–19].

As the fastest extraction procedure among these LPME [20,21], DLLME is based on a ternary solvent system: a few microliters of extraction solvent, an aqueous sample containing analytes and a disperser solvent with miscibility in both the extraction solvent and the aqueous sample. When the ternary solvent system is subjected to a physical disturbance such as turbulence or ultrasonication, the extraction solvent is emulsified, and a cloudy solution is produced. After centrifuging, the emulsified extraction solvent can be sedimented and separated for instrumental analysis. The emulsification effect provides a large contact surface area between the extraction solvent and the aqueous sample and therefore shortens the equilibrium extraction time. This advantage has encouraged researchers to further investigate the extraction

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http://dx.doi.org/10.1016/j.chroma.2014.07.070
0021-9673/

parameters of DLLME, including various types of extractive solvents, dispersive solvents, and emulsification conditions. To date, several formats of DLLME have been reported and can be classified as ultrasound-assisted dispersive liquid–liquid microextraction [22–30], ionic liquid-based dispersive liquid–liquid microextraction [31–33], low-density solvent-based dispersive liquid–liquid microextraction [34–37], dispersive liquid–liquid microextraction based on the solidification of a floating organic drop [38–41], and air-assisted dispersive liquid–liquid microextraction [42,43].

The selection of appropriate extraction and dispersive solvents is important to achieve high extraction efficiency. Usually, the introduction of a dispersive solvent into a binary solvent system decreases the partition coefficient of the analyte between the extraction solvent and the sample matrix [9]. In addition, because the dispersive solvent can easily dissolve in the extraction solvent and the aqueous sample, the final volume of the extract solvent after centrifugation usually differs from the original added amount. For example, Almeida and Cunha observed that the final volume of the extract solvent increased with increased dispersive solvent and thereby decreased the extraction efficiency [44,45]. Moreover, solvent contamination is inevitable due to the consumption of the dispersive solvent in the conventional DLLME methods [9,20].

Because finely divided solids (μm-scale or less) have often been used as the emulsifier [46,47], the stabilization [48] in emulsification is due to its interfacial interactions with the two immiscible liquids [49]. In this paper, we introduce for the first time the use of kapok fiber instead of a dispersive solvent as a novel dispersive material, not only to overcome the drawback of the solvent-assisted DLLME but also to enhance the effect of the ultrasound-assisted DLLME, and a fiber-assisted emulsification microextraction (FAEME) method was developed to determine the AA content in the aqueous sample. Method development was conducted, including optimization of the extraction solvent, dispersive fiber, sample pH, salt addition, and sonication and centrifugation conditions. The developed method was then applied to determine the AAs in the real water samples.

2. Experimental

2.1. Chemicals and materials

Standards of eight AAs, 2,4,5-trimethylaniline (TMA), 4-chloro-*o*-toluidine (CT), 3,3′-dimethyl-4,4′-diaminobiphenylmethane (DMDAB), 3,3′-dimethylbenzidine (DMB), 3,3′-dichlorobenzidine (DCB), 4,4′-methylene-bis-(2-chloroaniline) (MBCA), 3,3′-dimethoxybenzidine (DMOB), and 4-aminoazobenzene (AAB), were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The standards were dissolved in methanol (HPLC grade from Fluka) to obtain a stock standard solution with a concentration of 100 mg L^{-1}, which was stored at 4 °C in a brown bottle before use. A working standard solution was freshly prepared by dilution of the stock solution as required. Tetrachloroethylene (TCE), dichloroethane (DCE), carbon tetrachloride (CTC), chlorobenzene (CB), and ether of analytical grade were purchased from the Guangzhou Chemical Reagent Factory (Guangzhou, China).

The centrifuge (model TDL-50B) was obtained from Anke (Shanghai, China), and ultrasonic water bath (Crest®, 120 W, 45 kHz) was obtained from Crest Ultrasonics Corporation (New Jersey, USA). Two syringes (50 and 100 μL) were purchased from Agilent. The kapok fiber was prepared in our laboratory, and glass fiber (10 μm in diameter) was obtained from ANPEL Scientific Instrument Co., Ltd (Shanghai, China).

2.2. GC–MS analysis

Analyte separation and quantification were performed on a Finnigan Trace GC Ultra-DSQII(GC-MSD) system equipped with an AS 3000 Series autosampler and a DB-5MS fused silica capillary column (30 m × 0.25 mm × 0.25 μm film thickness).

Helium (purity 99.999%) was employed as carrier gas at a flow rate of 1.0 mL min^{-1}. The temperature of the GC injection port was set at 250 °C, and the splitless mode was selected. The oven temperature was programmed as follows: the initial temperature of 70 °C was held for 2 min and ramped to 140 °C at 10 °C min^{-1} and held for 1 min, then ramped to 170 °C at 20 °C min^{-1}, successively ramped to 230 °C at 5 °C min^{-1} and held for 6 min and, afterward, ramped to 310 °C at 20 °C min^{-1}. The total run time was 33 min.

The MS parameters were set as follows: EI ionization energy, 70 eV; ion source temperature, 250 °C; and MS transfer line, 230 °C. Selective ion monitoring (SIM) mode was chosen with a solvent delay of 5 min.

2.3. Preparation and characterization of the dispersive fiber

As shown in Fig. 1A–C, the fibers were obtained according to a cutting and cleaning process of AATCC Test Method 20-2011. A bundle of fibers was pulled through the hole of a slicing device with a trimming nut. A sharp razor blade was used to obtain very thin fiber fragments (length, 50 μm) by trimming. The fibers were collected

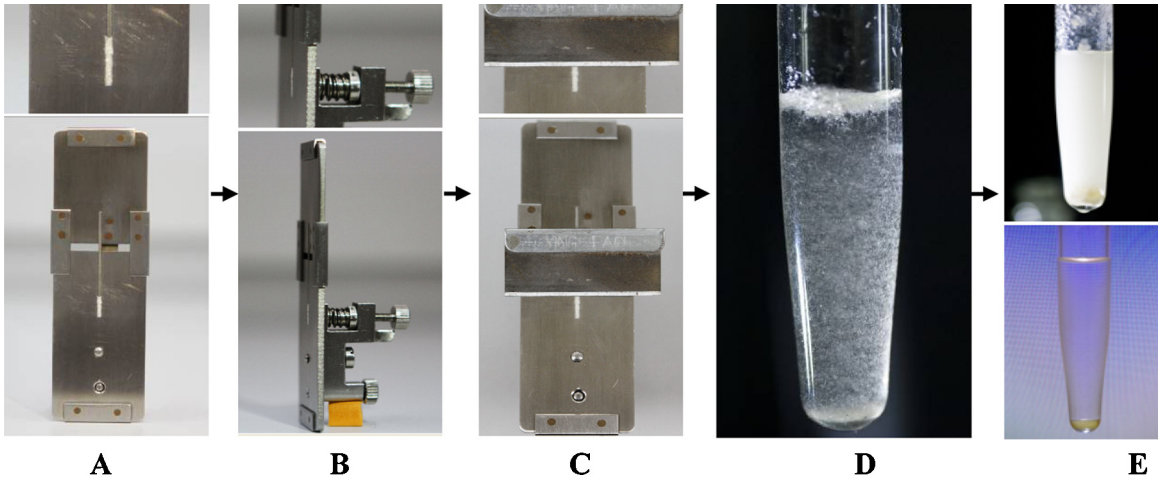

Fig. 1. Fiber preparation and sample emulsification. (A) Packing of the fiber; (B) adjusting the fiber length with a trimming nut; (C) fiber cut; (D) dispersed fiber in an aqueous sample; and (E) emulsification and sedimentation.