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Zeolite-loaded poly(dimethylsiloxane) hybrid films for highly efficient thin-film microextraction of organic volatiles in water

Tao Wang[a], Toshihiro Ansai[b], Seung-Woo Lee[a,*]

[a] *Graduate School of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Kitakyushu 808–0135, Japan*
[b] *Division of Community Oral Health Development, Kyushu Dental University, 2-6-1 Manazuru, Kitakyushu 803–8580, Japan*

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ABSTRACT

ZSM-5 zeolite-loaded poly(dimethylsiloxane) (PDMS) hybrid thin films were demonstrated for efficient thin-film microextraction (TFME) coupled with gas chromatography–mass spectrometry for analyzing organic volatiles in water. The extraction efficiency for a series of aliphatic alcohols and two aromatic compounds was significantly improved owing to the presence of ZSM-5 zeolites. The extraction efficiency of the hybrid films was increased in proportion to the content of ZSM-5 in the PDMS film, with 20 wt% of ZSM-5 showing the best results. The 20 wt% ZSM-5/PDMS hybrid film exhibited higher volatile organic content extraction compared with the single-component PDMS film or PDMS hybrid films containing other types of zeolite (e.g., SAPO-34). Limits of detection and limits of quantitation for individual analytes were in the range of 0.0034–0.049 ppb and of 0.010–0.15 ppb, respectively. The effects of experimental parameters such as extraction time and temperature were optimized, and the molecular dispersion of the zeolites in/on the hybrid film matrix was confirmed with scanning electron microscopy and atomic force microscopy. Furthermore, the optimized hybrid film was preliminarily tested for the analysis of organic volatiles contained in commercially available soft drinks.

1. Introduction

Among small-molecule metabolites that are emitted from the human body, organic volatiles have great potential as biomarkers for the early detection and treatment of diseases, particularly cancer [1]. For instance, the detection of volatile organic compounds (VOCs) in blood samples or the headspace of cancer cells, and consequently in exhaled breath [2,3], is an emerging approach for diagnosing lung cancer. Breath samples have been investigated to test not only cancer but also other types of diseases that can be detected by profiling VOCs in exhaled breath [4], for example, ethanol and pentane from oxidative stress, acetone from diabetes mellitus and ketonemia, and nitrogen-containing compounds such as ammonia, dimethylamine, and trimethylamine from uremia and kidney impairment [5].

To achieve effective detection of analytes that are present at trace levels by gas chromatography–mass spectrometry (GC–MS)-based analytical methods, a preconcentration step is usually introduced during sample preparation. Solid-phase microextraction (SPME) is the most widely used sample preparation technique, and has several advantages over traditional analytical methods, such as the convenient integration of extraction, preconcentration, and sample introduction [6]. The SPME technique is rapid, solvent-free, and relatively inexpensive, and has been used with increasing success in many applications, such as environmental, food, and drug analyses, since its development [7–10]. SPME is based on the interaction of analytes in the sample matrix and the extraction phase (coating) via absorption or adsorption, depending on the nature of the coating [11]. The extraction selectivity and efficiency of SPME largely depends on the physical properties of the coating (i.e., porosity, specific surface area, and size) as well as its interactions with the analytes (i.e., its chemical properties). The sensitivity can be improved by increasing the volume of the extraction phase; however, longer equilibration time (driven by the diffusion of analytes into the coating material) is required.

The best option for improving the sensitivity is to use a thin extraction phase with a high surface area-to-volume ratio [12]. Membrane SPME, known as one alternative for effective sample extraction, has been successfully combined with GC–MS [13,14] or high-performance liquid chromatography (HPLC) [15–17] for the rapid analysis of biosamples such as blood, skin emanations,

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* Corresponding author.
E-mail address: leesw@kitakyu-u.ac.jp (S.-W. Lee).

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saliva, and urine. Highly porous structures, such as microporous and mesoporous materials, can be used for this purpose, along with poly(dimethylsiloxane) (PDMS), which is the most well-known material for SPME [18,19]. Zeolites are a class of high-silica crystalline aluminosilicates with defined pore diameters smaller than 2 nm. ZSM-5, a zeolite that was initially developed by the Mobil Oil Company, is the most studied zeolite of the past decade because of its unique channel structures with pore opening sizes that are close to the sizes of many industrially important organic molecules [20]. Thus, molecules with sizes smaller than the pores of ZSM-5 can enter and be adsorbed by the zeolite with equilibrated retention. Hence, ZSM-5 is widely applied in catalytic applications [21,22], and can be used for selective adsorbtion and filtration of chemicals, for instance, for recovery of alcohols from complex mixtures [23] and for gas separation [24,25].

Recently, several types of zeolite/polymer composites have been applied for the solid-phase extraction of hazardous chemicals from aqueous solutions [26–28]. In our previous work, a composite thin film of ZSM-5 and Tenax-TA has been employed as an extraction phase for the equilibrium-based extraction and preconcentration of organic solvents from aqueous media [29]. In this study, we have demonstrated a novel thin-film microextraction (TFME) method based on a ZSM-5/PDMS hybrid film, and assessed it in the direct extraction of organic volatiles from aqueous samples.

2. Experimental

2.1. Materials

ZSM-5 (SiO_2/Al_2O_3 molar ratio = 30, Lot: 110421) and SAPO-34 ($SiO_2/P_2O_5/Al_2O_3$ = 0.2: 1: 1, Lot: HAH140811) were purchased form JGC Catalysts and Chemicals Ltd., Kawasaki, Japan. A PDMS solution kit (Sylgard 184 Silicone Elastomer Kit) was purchased from Dow Corning Ltd., Tokyo, Japan. This kit included a base solution A (Sylgard 184A) and a curing agent solution B (184B) that is mixed in a 10:1 ratio to produce the PDMS polymer. Methanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-nonanol, 1-decanol, 1-undecanol, and 1-dodecanol were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. 1-Propanol and 1-octanol were purchased from Kanto Chemical Co., Inc., Tokyo, Japan, and phenol was purchased from Nacalai Tesque, Inc., Tokyo, Japan. All of these chemicals were analytical grade and used without further purification. Deionized pure water (18.3 MΩ cm) was obtained by reverse osmosis followed by ion exchange and filtration using a Direct-QTM (EMD Millipore, Billerica, MA, USA).

2.2. Preparation of ZSM-5/PDMS hybrid films

A glass bottle (volume = ca. 50 mL) was used as the support substrate for the ZSM-5/PDMS hybrid film. PDMS was supplied as a two-part liquid component kit comprised of a base and a curing agent to be mixed in a 10:1 wt ratio. Before the PDMS was solidified, it was mixed with ZSM-5 zeolite at 0, 10, and 20 wt% to confirm the optimum content of ZSM-5 in the PDMS matrix, and 1.0 g of the mixture was placed in a glass bottle. The ZSM-5/PDMS hybrid film was left at 25 °C for 72 h and then heated at 100 °C for 1 h. The film was then washed in methanol for three days to remove the silane compounds that are discharged from PDMS. Similarly, a 20 wt% SAPO-34/PDMS film was also prepared for use in comparative experiments. SAPO-34, which has a CHA framework, is a small-pore silicoaluminophosphate molecular sieve with 3.8 × 3.8 Å openings.

2.3. Characterization of ZSM-5/PDMS hybrid films

Scanning electron microscopy (SEM) measurements were performed on pieces of PDMS and ZSM-5/PDMS hybrid films using a S-5200 SEM (Hitachi, Japan). The surface morphology of the films was studied with a JSPM-5200 atomic force microscope (AFM) (JEOL, Japan) working in noncontact mode using a MicroMash NSC12/Ti-Pt/15 silicon cantilever (curvature tip radius < 40 nm, tip length 15–20 μm).

2.4. Sampling and analysis

During the extraction, the aqueous sample was continuously agitated at 200 rpm using a multi-shaker FMS-1000 (EYELA Tokyo Rikakikai Co., Ltd., Tokyo, Japan). The extraction temperature was controlled using an electronic cooling thermostat bath TB-1 (BAS Co., Ltd., Tokyo, Japan). A 50 mL standard aqueous solution (10 μg/mL, 10 ppm) containing 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, benzyl alcohol, and phenol was extracted by a PDMS film or ZSM-5/PDMS hybrid films with 10 and 20 wt% ZSM-5 contents. The aqueous solution sampling was conducted with film-coated sample bottles for 3 h at 30 °C, which were washed with pure water and dried under nitrogen gas. Methanol (100 μL) was used to release the VOCs from the thin film for 30 min at 30 °C. Finally, the methanol sample (1.0 μL) was injected into the GC port. The proposed GC–MS analysis of organic volatiles via ZSM-5/PDMS hybrid thin-film extraction is schematically illustrated in Fig. 1.

A mixed standard solution (50 mL) consisting of twelve reference compounds as shown in Table S1 with a concentration of 10 μg/mL (10 ppm) for each component was used for the determination of optimal extraction conditions, such as extraction time and temperature, using a 20 wt% ZSM-5/PDMS hybrid film. The extraction of the sample solution was performed for 3 h at the three sample temperatures of 10 °C, 20 °C, and 30 °C. The release time and temperature, using methanol, were within the range of 0–30 min and at the three sample temperatures of 10 °C, 20 °C, and 30 °C, respectively. Inter-film reproducibility studies were performed for every sampling using three different ZSM-5/PDMS hybrid films prepared by the same method. Extraction experiments using commercially available soft drinks A (Otsuka Pharmaceutical, Japan) and B (Coca-Cola, Japan) were carried out using a 20 wt% ZSM-5/PDMS hybrid film under the optimum condition.

The developed 20 wt% ZSM-5/PDMS hybrid film was compared with a commercial poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) (65 μm) fiber. To perform the SPME, the 65 μm PDMS/DVB fiber was immersed in a 50 mL standard solution that contained 1.0 μg/L (1 ppb) of each of the twelve reference compounds, for 3 h at room temperature. Magnetic stirring with a Teflon coated stir bar was used to agitate the solution at 1000 rpm. After extraction, the fiber was removed from the vial, washed in water, and dried under nitrogen gas. Then, the fiber was transferred to the GC port for analyte desorption.

2.5. GC–MS conditions

Chromatographic analysis with mass-spectrometric detection was performed with a JMS-Q1000GC (JEOL, Japan) GC–MS system consisting of an Agilent 7890A gas chromatographer coupled to a quadrupole mass spectrometer in electron ionization (EI) mode at 70 eV. The temperatures of the ion source and the GC interface were 200 °C and 230 °C, respectively. A DB-WAX capillary column (polyethylene glycol-based high-polarity stationary phase, 30 m length, 0.25 mm inner diameter, 0.5 μm film thickness, Agilent J & W, part number 19091J-413) was used for separation. Ultrahigh-purity helium gas (purity 99.999%) was flowed at a rate