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Novel molecularly-imprinted solid-phase microextraction fiber coupled with gas chromatography for analysis of furan

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ABSTRACT

This study combined a molecularly-imprinted polymer with headspace solid-phase microextraction (HS-SPME). Preparation of molecularly-imprinted polymer is not effective for volatile compounds. To overcome this limitation, pyrrole was chosen as a template for the preparation of the furan-imprinted polymer. The holes in the synthesized polymer were suitable for furan adsorption because the chemical structure of pyrrole is similar to that of furan. The extraction properties of the fiber to furan were examined using an HS-SPME device coupled with gas chromatography–flame ionization detection (GC-FID) and gas chromatography–mass spectrometry (GC–MS). The effects of the extraction parameters of exposure time, sampling temperature, and salt concentration on extraction efficiency were studied. Satisfactory reproducibility was obtained for extractions from spiked water samples at RSD < 7.5% ($n=5$). The calibration graphs were linear at 0.5–100 ng ml^{-1} and the detection limit for furan was 0.042 ng ml^{-1}. The fabricated fiber was successfully applied for headspace extraction of furan from tap water and canned tuna as shown by GC–MS analysis.

1. Introduction

Furan is a colorless five-member ring compound having high volatility and a boiling point of 31 °C. Furan can form in food during a Maillard reaction and has been of concern because it is classified by the International Agency for Research on Cancer as potentially carcinogenic to humans. The US Department of Health and Human Services includes furan on the human pathogen list. Furan is known to cause tumors, more than 90% of which are adenocarcinoma with the remaining being squamous cell carcinoma [1].

The analysis of furan in food samples is complicated because of its extremely high volatility. The US FDA has selected automated headspace sampling gas chromatography–mass spectrometry (GC–MS) using the standard addition method for accurate analysis of furan in food samples. This method is time and labor intensive because several sample preparation steps are required for each sample [2].

Headspace solid-phase microextraction (HS-SPME) is used to determine furan in samples [3–9]. HS-SPME is a simple, solvent-free extraction technique with high sensitivity, excellent reproducibility that is low in cost. In this technique, phase-coated fused silica fiber is exposed to the headspace above the liquid or solid sample. Analytes adsorb onto the phase, thermally desorb in the injection port of a GC, and are transferred to a capillary column. Selectivity can be altered by changing the phase type or thickness according to the characteristics of the analytes [10]. The main disadvantage of this method is poor selectivity, which is a significant drawback for analysis of complicated real samples. Moreover, commercially-available fibers suffer from low selectivity, stability and strength, and high cost [11].

Molecular imprinting is an attractive technique for synthesizing highly-selective polymeric receptors [12–18]. The inherent selectivity associated with molecularly-imprinted polymers (MIPs) has made these materials efficient for SPME; this combination has been successfully employed for extraction and preconcentration of analytes from different samples [19–23].

Given the vaporization of furan in the polymerization step, preparation of furan-imprinted polymers is not possible. Pyrrole was, thus, chosen as template molecule. The chemical structure of pyrrole is similar to that of furan, but it has a higher boiling point. The holes in the synthesized polymer are suitable for furan adsorption and the synthesized polymer has been used successfully for HS-SPME of furan in real samples. This fiber is monolithic and flexible enough to be placed in a homemade syringe and inserted into a GC or GC–MS injection port. After equilibrium is established between furan and the fiber, it is inserted into a GC injection port for thermal desorption of furan and determination.

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2. Experimental

2.1. Chemicals

Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 2,2-azobis-isobutyronitrile (AIBN), and acetonitrile were purchased from Merck (Germany). Furan and pyrrole were obtained from Sigma-Aldrich (UK). The SPME fiber, 100 μm carboxen polydimethylsiloxane (CAR/PDMS), was purchased from Supelco (USA) and conditioned prior to use according supplier instructions.

Stock solutions of furan at a concentration of 5 mg l^{-1} were prepared weekly in cold methanol. Working solutions were prepared daily using 5 μl of refrigerated stock solution and 10 ml cold water. All vials of stock and working solution were sealed with silicone-PTFE septa and aluminum seals and then stored at −18 and 4 °C, respectively, until analysis.

2.2. Instrumentation

The furan was analyzed using GC-FID (Varian CP-3800). The samples were separated on a CP-Sil 5 CB capillary column (30 m × 0.25 mm × 0.25 μm film thickness). The injector temperature was 250 °C. The GC oven was set to an initial temperature of 35 °C for 4 min. The temperature program was set to increase from 3 °C to 250 °C at 25 °C min^{-1} and held for 2 min. N_2 flow was maintained at 1 ml min^{-1}. The samples were injected in splitless mode. Desorption time from the fibers was 3 min.

GCMS determination was performed on an HP-6890 GC system coupled with a 5973 network mass selective detector equipped with an HP-5MS capillary fused silica column (30 m × 0.25 mm I. D. × 0.32 μm film thickness). The operating conditions were the same as described previously and used helium as the carrier gas. Chromatographic data was recorded using an HP Chemsation controlled by Windows NT (Microsoft) and equipped with a Wiley mass spectral library. SEM images were captured using a DSM 960 electron microscope (Carl Zeiss; Germany). An SPME device (Azar Electrode; Iran) was used to hold the synthesized fiber and inject it into the GCMS injection port.

2.3. Preparation of monolithic poly(methacrylic acid-co-ethylene glycol dimethacrylate) SPME fiber

An 8 mmol sample of the template molecule (furan and pyrrole) was dissolved in 30 ml of methanol porogenic solvent. Then, 30 mmol of functional monomer (MAA) and 120 mmol of cross-linker (EGDMA) were added to the solution. The resulting mixture was ultrasonically stirred for 5 min. Approximately 280 mg of initiator (AIBN) was then added and the mixture was degassed with a stream of N_2 gas for 10 min.

The laboratories were glass capillary tubes 4 cm in length and 0.3 mm in internal diameter (as molds) inserted into test tubes containing prepolymer solution to fabricate the monolithic fibers. The glass capillary tubes were immediately filled with solution and the test tubes were immediately sealed with a rubber cap. The mixture was cured in a water bath for 12 h at 60 °C. Non-imprinted polymers (NIPs) were also fabricated according to the above procedure in the absence of a template during polymerization.

2.4. Fiber conditioning

The fabricated MIP or NIP monolithic fibers were immersed in a mixture containing methanol, acetic acid, and double-distilled water 4:1:1 (v/v/v) several times until the furan or pyrrole template, porogen solvent, and other impurities were removed as thoroughly as possible. The fibers were then modified by heating at 220 °C in the presence of water vapor in a carbolite furnace for 15 min. All the modified fibers were conditioned at 280 °C for 20 min in a GC injection port under N_2 flow.

2.5. Sample preparation

Canned tuna samples were homogenized for 3 min using a homogenizer. Samples were immersed in an ice/water bath to prevent overheating of the sample and homogenizer. The homogenized samples were placed in a 20 ml headspace vial and 5 ml of chilled water was quickly added. The vials were completely filled and closed with silicone-PTFE septa and aluminum seals and stored at 4 °C until analysis.

2.6. Headspace extraction procedure

A 10 ml aliquot of aqueous solution spiked with furan was extracted with synthesized fiber housed in a manual SPME holder using HS-SPME mode. The fiber was conditioned prior to use by insertion into the GC injection port for 5 min.

Water (10 ml) containing the furan was placed in a 25 ml glass vial with a PTFE-silicon septum. After the addition of sodium chloride and a magnetic stirring bar, the vial was tightly sealed with an aluminum cap to prevent sample loss by evaporation. During extraction, the vials were thermostated using a heated circulating water bath with the temperature maintained at the desired value. The synthesized fiber was exposed to the headspace over the stirred liquid sample for 10–120 min depending on the experiment. After completion of the sampling step, the fiber was withdrawn into the needle and removed from the sample vial. The fiber was then immediately inserted into the GC injection port.

3. Results and discussion

3.1. Characterization and extraction performance of monolithic SPME fiber

3.1.1. Morphological structure of monolithic SPME fiber

The SEM image of the monolithic MIP fiber shows the detailed morphology of the SPME fibers. The pyrrole-imprinted monolithic SPME fiber exhibited a highly porous structure on the surface. The nonporous structure of the furan-imprinted monolithic SPME fiber and NIP were confirmed by SEM. The results revealed that the pyrrole-imprinted monolithic SPME fiber can increase extraction performance. The SEM of the monolithic MIP SPME fiber under × 50,000 magnification is shown in Fig. 1.

3.1.2. Infrared spectra of MIP coating

The synthesized molecularly-imprinted and control polymers were subjected to characterization by FT-IR spectroscopy. Both polymers had similar IR spectra, indicating similarity in their backbone structure. In the IR spectra, absorption caused by the presence of carboxyl OH stretch (ca. 3548 cm^{-1}), carbonyl group stretch (ca. 1721 cm^{-1}), C–O stretch (ca. 1138 cm^{-1}), and C-H vibrations (ca. 755, 1250, 1451 and 2954 cm^{-1}) were observed. In addition to the similarity of the backbones of the MIP and NIP, the MIP absorbance attributed to the C–O stretch (present only in cross linker EGDMA) was significantly stronger than that of the NIP. The IR spectra of the synthesized non-imprinted and molecularly-imprinted fibers are shown in Fig. 2.The presence of the imprint molecule (pyrrole) increased the incorporation of EGDMA into the preparation of polymers.

3.1.3. Thermogravimetric analysis of MIP monolithic SPME fiber

The thermal stability of monolithic SPME fiber is essential for