Hossein Vatani
Ali Sarafraz Yazdi

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

Received July 25, 2013
Revised August 24, 2013
Accepted October 17, 2013

Research Article

Ionic-liquid-mediated poly(dimethylsiloxane)-grafted carbon nanotube fiber prepared by the sol–gel technique for the head space solid-phase microextraction of methyl *tert*-butyl ether using GC

A headspace solid-phase microextraction method was developed for the preconcentration and extraction of methyl *tert*-butyl ether. An ionic-liquid-mediated multiwalled carbon nanotube–poly(dimethylsiloxane) hybrid coating, which was prepared by covalent functionalization of multiwalled carbon nanotubes with hydroxyl-terminated poly(dimethylsiloxane) using the sol–gel technique, was used as solid-phase microextraction adsorbent. This innovative fiber exhibited a highly porous surface structure, high thermal stability (at least 320°C) and long lifespan (over 210 uses). Potential factors affecting the extraction efficiency were optimized. Under the optimum conditions, the method LOD (S/N = 3) was 0.007 ng/mL and the LOQ (S/N = 10) was 0.03 ng/mL. The calibration curve was linear in the range of 0.03–200 ng/mL. The RSDs for one fiber (repeatability, $n = 5$) at three different concentrations (0.05, 1, and 150 ng/mL) were 5.1, 4.2, and 4.6% and for the fibers obtained from different batches (reproducibility, $n = 3$) were 6.5, 5.9, and 6.3%, respectively. The developed method was successfully applied to the determination of methyl *tert*-butyl ether in different real water samples on three consecutive days. The relative recoveries for the spiked samples with 0.05, 1, and 150 ng/mL were between 94–104%.

Keywords: Carbon nanotubes / Ionic liquids / Methyl *tert*-butyl ether / Sol–gel technique / Solid-phase microextraction
DOI 10.1002/jssc.201300796

Additional supporting information may be found in the online version of this article at the publisher's web-site

1 Introduction

Methyl *tert*-butyl ether (MTBE) is a volatile, flammable, and colorless organic compound that has a strong distinctive odor. MTBE is a gasoline additive that is used as an oxygenate agent to raise the octane number. MTBE was first added to gasoline in the 1980s as an octane enhancer to replace tetraethyl lead [1]. Unlike most gasoline constituents, MTBE is highly soluble in water. At room temperature its solubility is about 50 g/L, which is 20 times greater than that of benzene, toluene, ethylbenzene, and xylenes, the most soluble gasoline constituents [2]. Thus, MTBE is more likely to dissolve in water than other gasoline constituents. MTBE is a volatile and suspected carcinogenic organic compound. There are many reports about the toxicity of MTBE [3, 4]. Various techniques such as electrochemical removal with coated electrode [5], removal with Nafion [6], purge and trap [7, 8], direct aqueous injection [9, 10], single drop liquid-phase microextraction [11, 12], and solid-phase microextraction (SPME) [13–17] have been used for the separation and preconcentration of MTBE in environmental sample solutions. The high solubility of MTBE in water has resulted in widespread contamination of ground waters and surface waters. Thus, there is an urgent need to find technically and economically feasible method to refine water from MTBE.

The sampling and sample preparation step is one of the most important steps in the entire analytical method. In comparison with other sample preparation methods, the SPME approach is relatively simple, fast, cheap, and solvent free [18]. Because of these advantages, SPME applications have dramatically increased within two decades of its introduction [19–21]. Conventional fiber SPME, however, has some

Correspondence: Professor Sarafraz Yazdi, Azadi Sq., University Pardis, Mashhad, Khorasan 91775, Iran
E-mail: asyazdi@um.ac.ir
Fax: +98-511-8796416.

Abbreviations: CNT, carbon nanotube; **FID**, flame ionization detection; **IL**, ionic liquid; **MTBE**, methyl *tert*-butyl ether; **MWCNT**, multiwalled CNT; **PDMS**, poly(dimethylsiloxane); **PMHS**, poly(methylhydrosiloxane); **SPME**, solid-phase microextraction

Colour online: See the article online to view the Figs. 3–5 in colour.

