

Solid-phase dynamic extraction for the enrichment of polar volatile organic compounds from water

Maik A. Jochmann, Magda P. Kmiecik, Torsten C. Schmidt*

Center for Applied Geoscience (ZAG), Eberhard Karls-Universität Tuebingen, Wilhelmstr. 56, 72074 Tuebingen, Germany

Received 14 November 2005; received in revised form 16 February 2006; accepted 21 February 2006

Available online 13 March 2006

Abstract

Headspace solid-phase dynamic extraction coupled to gas chromatography–mass spectrometry (HS-SPDE-GC/MS) was evaluated for the trace determination of polar volatile organic compounds (PVOC) from aqueous matrices. The target compounds included 3 ethers and 12 alcohols. Four SPDE needle coatings with different phase polarities and sorption properties (WAX, 1701, PDMS, PDMS/AC) were tested. The effects of extraction temperature, number of extraction cycles, and ionic strength on partitioning of the target compounds have been investigated in detail, including the determination of salting-out constants for the investigated compounds. Lowest method detection limits (MDLs) were obtained with the WAX and the PDMS/AC phase. The WAX phase showed MDLs for ethers in the range of 0.06 µg/L (MTBE) to 0.8 µg/L (1,4-dioxane) and for alcohols between 0.02 µg/L (3-methyl-1-pentanol) and 3.5 µg/L (1-propanol). The evaluated MDLs for ethers with the PDMS/AC were in the range 0.06 µg/L (MTBE) to 1.2 µg/L (1,4-dioxane) and for alcohols between 0.004 µg/L (1-hexanol) and 4.9 µg/L (ethanol). Using either of these two phases, SPDE provides comparable or better sensitivities for the investigated compounds than other enrichment techniques, high sample throughput because of full automation, and short extraction times as well as a high robustness of the extraction phase because of its protection inside the steel needle. SPDE applicability has been demonstrated for the determination of fusel oils in different alcoholic beverages. © 2006 Elsevier B.V. All rights reserved.

Keywords: Solid-phase dynamic extraction; Ethers; MTBE; Alcohols; Fusel oils; Salting-out; Setschenow constant

1. Introduction

Over the last decade, several solvent-free microextraction techniques based on a compound's partitioning between a liquid or gas phase and a fixed stationary extraction phase have been introduced in gas chromatography for many different matrices and analytes [1]. All these techniques have in common the absence of toxic organic solvents, simplicity and ease of automation. Solid-phase micro extraction (SPME) has become the most prominent and widely used solventless micro extraction technique for organic compounds in aqueous samples [2,3]. However, different variations adopted from SPME, such as stir bar sorptive extraction (SBSE) and headspace sorptive extraction (HSSE), have been developed to increase sorption capac-

ity and to overcome some drawbacks of SPME, such as fiber fragility [4,5]. Other approaches utilize flow through techniques where the stationary phase is coated or packed inside a fused-silica capillary column or stainless steel needle, including open-tubular trapping (OTT) [6], inside needle capillary adsorption trap (INCAT) [7], in-tube-SPME coupled to LC [8] and GC [9], capillary microextraction (CME) [10], and needle trap (NT) [11]. A recently commercialized technique based on the same principle is solid-phase dynamic extraction (SPDE). As seen in Fig. 1, SPDE utilizes a 2.5 mL headspace syringe with a needle that is coated on the inside similar to a fused-silica GC column with an immobilized extraction phase. SPDE needle coatings possess around four to six times larger extraction phase volumes compared with a 100-µm SPME fiber [12]. For the extraction, the needle can be immersed directly into the sample or in the headspace above it. The syringe plunger is moved up and down several times for a dynamic extraction of the sample, and the analytes are sorbed in the internal coating. After several extraction cycles (aspirating and dispensing), the analytes are thermally desorbed from the coating in the GC injector.

* Corresponding author at: University Duisburg-Essen, Chair of Instrumental Analysis, Lotharstr. 1, MF147, D-47048 Duisburg, Germany.
Tel.: +49 203 379 3311; fax: +49 203 379 2108.

E-mail address: torsten.schmidt@uni-due.de (T.C. Schmidt).

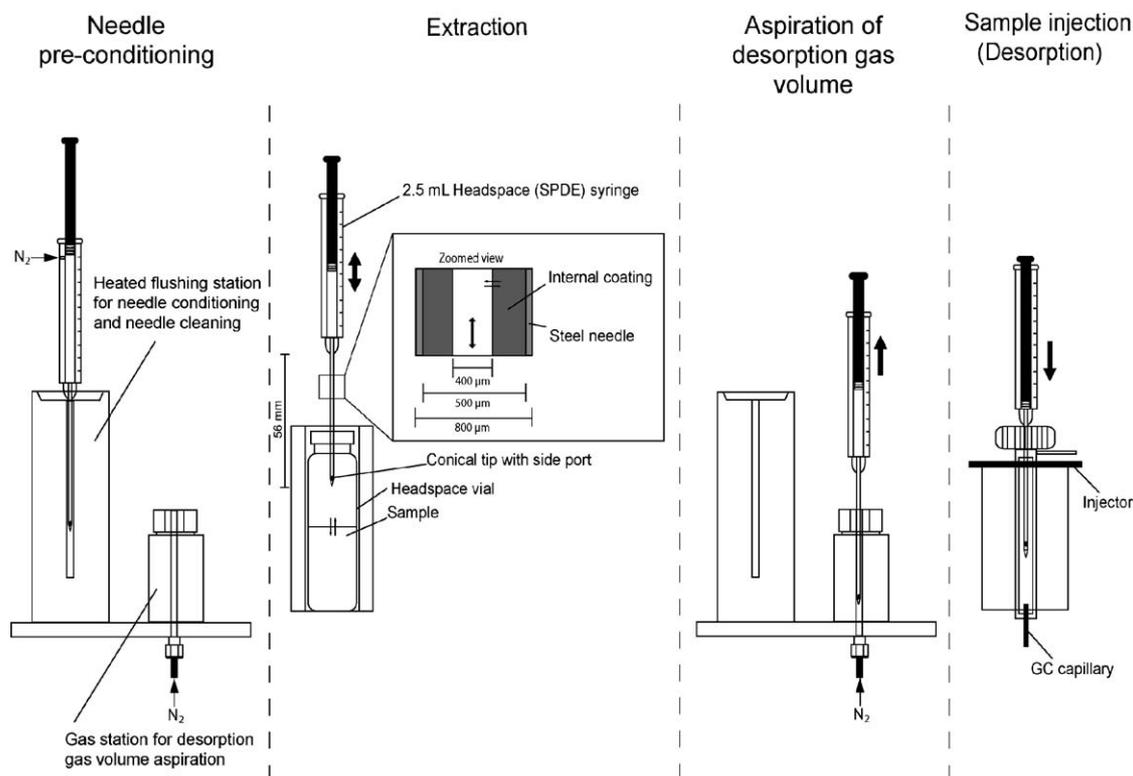


Fig. 1. Schematic overview of the various steps in a HS-SPDE procedure. The left part shows the conditioning of a needle in the flush station before first use and after each analysis. In the middle part, the dynamic extraction of the headspace is shown. The right part describes the aspiration of a desorption volume at the gas station and subsequent thermal desorption in the injector.

So far, there have been very few systematic investigations on extraction parameters and applications of SPDE, restricted to chlorinated pesticides in water [13], volatile flavours in plants and food [14], and cannabinoids, amphetamines and synthetic designer drugs in hair samples [12,15,16]. In this work, we aimed at the analysis of polar volatile organic compounds (PVOC) such as ethers and alcohols as probe compounds since these are more difficult to extract from water than nonpolar compounds. In the case of ethers, 1,4-dioxane, methyl *tert*-butyl ether (MTBE), and tetrahydrofuran (THF) were selected because of their frequent occurrence in environmental aqueous matrices (rain, surface, and groundwater) [17–19]. Some of the small chain alcohols are also used as fuel oxygenates [20] or are present in fuel at low concentrations [21], are used as partitioning tracers for the characterization of residual nonaqueous phase liquids [22,23], and are important analytes in food science, e.g., because of their presence in alcoholic beverages (“fusel oils”). The occurrence of 2-ethylhexanol in drinking water has been reported, probably from its presence in polymers as a by-product of 2-ethylhexyl phthalate synthesis [24]. Some of the investigated compounds, e.g., MTBE, tetrahydrofuran, and 2-ethylhexanol have been selected as candidates for further investigations in the OECD Screening Information Data Sets (SIDS) because of their high production rates, toxicity and physicochemical behavior [25].

The main objective of this work was to provide a sensitive, robust, and fast method for determination of PVOC in aqueous matrices using SPDE. To this end, we (i) studied in detail the

effects of the most important extraction parameters on partitioning of the target compounds (i.e., extraction temperature, ionic strength, and number of extraction cycles), (ii) compared different extraction phases for the probe compounds with regard to achievable method detection limits (MDLs), and (iii) demonstrated the application of SPDE for the determination of fusel oils in alcoholic beverages and of salting-out constants (Setschenow constants).

2. Experimental

2.1. Chemicals and reagents

Methanol (99.9%) from Merck (Darmstadt, Germany) was used to prepare stock solutions. The methanol was checked by GC–MS for its purity and the absence of the investigated low chain alcohols. As solvent for the preparation of standard solutions, Milli-Q water was used from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA). Ethanol (99%) and tetrahydrofuran (99.9%) were obtained from Merck (Darmstadt, Germany), *tert*-butanol (99.5%), 2-butanol (99.5%), 1-pentanol (99+ %), 1-propanol (99+ %), 3-methyl-1-pentanol (99%), 1-hexanol (98%), and 2-ethylhexanol (99.6%) from Aldrich (Steinheim, Germany), isopropanol (99.5%), isobutanol (99%), methyl *tert*-butyl ether were purchased from Acros Organics (Geel, Belgium) and 1-butanol (99.5%), 3-pentanol (99.5%), 1,4-dioxane (99.5%) were purchased from Fluka (Buchs, Switzerland). *Tert*-butanol- d_{10} (99%) from Acros

Download English Version:

<https://daneshyari.com/en/article/1209705>

Download Persian Version:

<https://daneshyari.com/article/1209705>

[Daneshyari.com](https://daneshyari.com)