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Determination of organic priority pollutants and emerging compounds in wastewater and snow samples using multiresidue protocols on the basis of microextraction by packed sorbents coupled to large volume injection gas chromatography–mass spectrometry analysis

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ABSTRACT

This paper describes the development and validation of a new procedure for the simultaneous determination of 41 multi-class priority and emerging organic pollutants in water samples using microextraction by packed sorbent (MEPS) followed by large volume injection–gas chromatography–mass spectrometry (LVI–GC–MS). Apart from method parameter optimization the influence of humic acids as matrix components on the extraction efficiency of MEPS procedure was also evaluated. The list of target compounds includes polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalate esters (PEs), nonylphenols (NPs), bisphenol A (BPA) and selected steroid hormones. The performance of the new at-line microextraction-LVI–GC–MS protocol was compared to standard solid-phase extraction (SPE) and LVI–GC–MS analysis. LODs for 100 mL samples (SPE) ranged from 0.2 to 736 ng L^{-1} were obtained. LODs for 800 μL of sample (MEPS) were between 0.2 and 266 ng L^{-1}. In the case of MEPS methodology even a sample volume of only 800 μL allowed to detect the target compounds. These results demonstrate the high sensitivity of both procedures which permitted to obtain good recoveries (>75%) for all cases. The precision of the methods, calculated as relative standard deviation (RSD) was below 21% for all compounds and both methodologies. Finally, the developed methods were applied to the determination of target analytes in various samples, including snow and wastewater.

1. Introduction

Generally, simultaneous multi-residue analysis of organic pollutants is a helpful tool to get a fast survey of the contamination levels of samples. Priority hazardous substances are recognized on the basis of their wide spread occurrence in environment and their toxic properties. In compliance with national and international directives e.g. by Environmental Protection Agency (EPA) and European Community (EC) [1,2] regular comprehensive environmental monitoring is demanded which requires appropriate analytical methods for fast and sensitive detection of relevant compounds. Within the last decades several studies have revealed that organic trace substances suspected for ecological and health risks are increasingly detected in natural or treated water bodies. Concerning to the compounds, analytes such as polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs) and so on have been so far included in the lists of priority pollutants. However, many other compounds such as steroid hormones, pharmaceuticals or personal care products among others have now also become prominent agents of concern to environmental scientists. For screening and monitoring programs with high sample throughput, automated, cost-effective and user-friendly strategies for water analysis are needed. Usually, the determination of traces of organic compounds in water needs combinations of analyte enrichment and GC-(FID, ECD, MS) or HPLC analysis [3,4]. Solid phase extraction SPE [5], solid phase microextraction [6,7] and stir bar sorptive extraction (SBSE) [8,9] have been reported as sensitive and reliable techniques for analyte extraction. Whereas SPME is suited for an automated online combination with several instrumental methods, its capability to detect low concentrated substances in little sample volumes (1–2 mL) is limited. SPE and SBSE are known as more difficult to automate but semi-automated protocols have been described already [10,11]. Microextraction by packed sorbent (MEPS) is a recently developed technique that was introduced by Abdel-Rehim [12–14] in the field of sample preparation. MEPS can combine sample processing, extraction and injection steps fully automated as an at-line sampling/injecting device to GC or LC [15–19]. In MEPS approximately 2 mg of the sorbent is thermo packed inside a syringe (100–250 μL) as a plug or

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between the barrel and the needle as a cartridge. Sample extraction and enrichment takes place on the sorbent bed.

MEPS is not only a miniaturized format of solid-phase extraction (SPE) which is able to handle sample volumes as small as 10 μL, this technique integrates the sorbent directly into the syringe not in a separate column as in commercial SPE. Thus, a fully automated method using MEPS is a promising approach to reduce time and labor effort in sample preparation and analysis [20–30].

In the present work, MEPS coupled to large-volume injection gas chromatograph mass spectrometer (LVI–GC–MS) has been optimized to the simultaneous determination of a large variety of analytes including PAHs, PCBs, phthalate esters (PEs), nonylphenols (NPs), bisphenol A (BPA), mestranol (MeEE2) and 17α-ethynylestradiol (EE2) in water samples. Comparison of a MEPS protocol with a common SPE method optimized in terms of different phases and elution solvents was also carried out. The presence of dissolved humic substances (HS) generally influences the determination of organic compounds in water [31,32]. The extent of this matrix effect depends both on the concentration and the origin of HS. Thus, apart from optimization and evaluation of the MEPS and SPE methodologies, an aim of this study was to investigate the influence of humic acids on the extraction efficiency of the target compounds and sensitivity of their determination in real samples such as snow and wastewater.

2. Experimental

2.1. Reagents and materials

The abbreviations and analytically relevant data of the target analytes are present in Table 1. PAHs (kit 610-N) were obtained from Supelco (Bellefonte, PA, USA). CEN PCB Congener Mix 20 (10 ng μL^{-1} in iso-octane), dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, n-butyl benzyl phthalate, bis(2-ethylhexyl) phthalate and di-n-octyl phthalate (10 ng μL^{-1} each in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

The technical mixture of nonylphenols (94%), 17α-ethynylestradiol (99.4%) and mestranol (99.4%) (Pestanal®) were obtained from Riedel-de Haën (Seelze, Germany) and Igepal® (4-n-nonyphenol) and bisphenol A (>99%) from Sigma-Aldrich (Milwaukee, WI, USA).

PCBs labelled ^{13}C mix, 99% (5 ng μL^{-1} in nonane), fluorene-d$_{10}$ (98%), fluoranthene-d$_{10}$ (98%), 6-methyl chrysene (10 ng μL^{-1} in acetonitrile), benzo [a] pyrene-d$_{12}$ (10 ng μL^{-1} in cyclohexane) and bisphenol A-d$_{16}$ (98%) were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA).

Methanol, acetone, ethyl acetate and *n*-hexane (chromatographic analysis grade) were purchased from Merck (Darmstadt, Germany).

Individual stock solutions were prepared at a concentration of 1000 mg L^{-1} in methanol. Mix standard solutions at different concentrations were prepared in acetone and used to spike bi-distilled water (Modulab® Analytical purification system, Christ, Stuttgart, Germany).

The humic acid mixture was obtained from Carl Roth GmbH (Karlsruhe, Germany, technical grade). Two modified artificial wastewaters were prepared in accordance to DIN 38412 T24 [33]. German standard methods for the analysis of water, wastewater and sludge; bio-assays (Group L): determination of biodegradability by use of special methods of analysis (L 24, Beuth Verlag GmbH, Hennef) by dissolving 14.72 g of NH_4Cl, 0.825 g of $MgCl_2{\cdot}6H_2O$, 2 g of $CaCl_2{\cdot}2H_2O$ and 22.2 g of Na_2SO_4 (water A) and 53.56 g of $C_7H_5NaO_2$, 102.45 g of $C_2H_3NaO_2$, 14.07 g of $KHSO_4$ and 3.5 g of NaCl (water B) in 1 L of water in both cases.

A treated wastewater sample from a wastewater treatment plant at Leipzig (input from about 10,000 inhabitant equivalents) was taken in March 2010. Snow samples were collected near a busy street at Leipzig (Germany) and from the institute's area of the Helmholtz Centre for Environmental Research- UFZ in February 2010.

2.2. SPE procedure

SPE of samples was carried out with Visiprep SPE manifold (Supelco, Bellefonte, PA, USA). In order to select the most efficient elution solvent for the MEPS procedure and finally to compare the MEPS performance with a common SPE protocol, a series of SPE experiments with spiked water were carried out. Under optimized conditions, 200 mg of C-18 sorbent (polar plus® C-18 bonded phase from J.T. Baker, Phillipsburg, NJ, USA) in 2 mL cartridges and 30 mL hexane:ethyl acetate mixture (50:50, v/v) for elution, 100 mL of spiked water at 250 ng L^{-1} of each analyte which contained 10% methanol (MeOH) were extracted and subsequently analyzed by LVI–GC–MS. MeOH was added according to A. Prieto et al. [9] in order to reduce the adsorption of the lipophilic substances on glassware surfaces. After conditioning using 5 mL of both hexane:ethyl acetate (50:50, v/v) mixture and bi-distilled water and loading of the sample, the cartridges were washed with 5 mL Milli-Q water and dried with nitrogen during 30 min. This wash step is useful particularly for the removal of polar matrix compounds as humic matter. Elution of analytes was performed using three portions of 10 mL of hexane:ethyl acetate mixture (50:50, v/v) and the extract concentrated using a TurboVap® II evaporator (Zymark, Idstein, Germany) at 50 °C to 0.25 mL to be 75 μL finally injected.

2.3. MEPS extraction

The microextraction was carried out with a MEPS device delivered by SGE Analytical Science (Griesheim, Germany). The 100 μL gas-tight syringe is equipped with a small container incorporated into the needle. This assembly called "barrel insert and needle" (BIN) is filled with 2 mg of sorbent commonly used for reverse phase chromatography or SPE. Silica gel sorbents (mean particle size 45 μm, pore size 60 Å) modified with C-18 were examined for the enrichment of the target analytes from water samples. The MEPS syringe was used in connection with a large volume injector type KAS 4 (Gerstel, Mühlheim an der Ruhr, Germany) and the samples were processed by a Multi Purpose Sampler MPS 2 (Gerstel) and controlled by the Maestro software of Gerstel. The extraction can be performed using two configurations which differ in sample volumes. Sample vials with volumes of 2 mL and 10 mL allow the extraction of different sample amounts despite the insertion depth of the MEPS syringe into the vial is limited. Thus, 800 μL of sample can be extracted from a 2 mL standard vial (tray "VT 98 cooler"). On the other hand, the use of 10 mL vials (tray "VT 32-10") enables to extract up to 2 mL of the sample.

The extraction process was fully automated using the MPS 2 device. Prior to each sample extraction, the MEPS-BIN was conditioned using ten 100 μL portions of hexane:ethyl acetate (50:50, v/v) mixture and three 100 μL portions of both MeOH and bi-distilled water. All portions were discarded into the waste vials. The extraction was realized in 100 μL aspiring steps at a speed of 10 μL s^{-1} (according to the experimental design). The sample was also discarded into the waste automatically. After sample extraction the BIN was dried by 5 cycles of drawing and pressing air through the sorbent at a rate of 10 μL s^{-1}. Subsequently, two portions, first of them of 50 μL and the second one of 25 μL of ethyl acetate:hexane mixture (50:50, v/v) were drawn through the BIN and each portion injected at 2.5 μL s^{-1} of injection speed (according to the experimental design)directly into the large volume injector