Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Chromatography A, 1072 (2005) 37–43

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Membrane-assisted solvent extraction of seven phenols combined with large volume injection–gas chromatography–mass spectrometric detection

Manuela Schellin*, Peter Popp

Department of Analytical Chemistry, UFZ-Centre for Environmental Research, Permoserstrasse 15, 04318 Leipzig, Germany

Abstract

Membrane-assisted solvent extraction (MASE) was applied for the determination of seven phenols (phenol, 2-chlorophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 4-chloro-3-methylphenol, 2,4,6-trichlorophenol and pentachlorophenol) with $\log K_{\mathrm{ow}}$ (octanol–water-partition-coefficient) between 1.46 (phenol) and 5.12 (pentachlorophenol) in water. The extraction solvents cyclohexane, ethyl acetate and chloroform were tested and ethyl acetate proved to be the best choice. The optimisation of extraction conditions showed the necessity of adding 5 g of sodium chloride to each aqueous sample to give a saturated solution (333 g/L). The pH-value of the sample was adjusted to 2 in order to convert all compounds into their neutral form. An extraction time of 60 min was found to be optimal. Under these conditions the recovery of phenol, the most polar compound, was 11%. The recoveries of the other analytes ranged between 42% (2-chlorophenol) and 98% (2,4-dichlorophenol). Calibration was performed using large volume injection (100 μL injection volume). At optimised conditions the limits of detection were between 0.01 and 0.6 μg/L and the relative standard deviation ($n = 3$) was on average about 10%. After the method optimisation with reagent water membrane-assisted solvent extraction was applied to two contaminated ground water samples from the region of Bitterfeld in Saxony-Anhalt, Germany. The results demonstrate the good applicability of membrane-assisted solvent extraction for polar analytes like phenols, without the necessity of derivatisation or a difficult and time-consuming sample preparation.

Keywords: Membrane-assisted solvent extraction; Phenols; Chlorophenols; Extraction conditions; Large volume injection; Ground water samples

1. Introduction

Phenolic compounds are present in the aquatic environment due to their industrial application. These compounds are generated in the production of plastics, dyes, drugs, pesticides, antioxidants, paper, and in the petrochemical industry. For example, pentachlorophenol is used as a wood preservative, phenol is emerged from lignin degradation in the production of paper and chlorophenols can be produced from phenols in the chlorinating of drinking water. These processes often lead to waste water and ground water contamination, hence the phenolic compounds are included in the list of priority pollutants of both the U.S. Environmental Protection Agency (EPA) and the European Union.

The determination of phenols and chlorophenols is normed by the EPA method 625, which involves liquid–liquid extraction with dichloromethane, drying and concentration of the extract and analysis with GC–MS. The achieved limits of detection (LODs) range between 1.5 μg/L (phenol) and 3.6 μg/L (pentachlorophenol) [1]. Besides the time consumption of liquid–liquid extraction, the method requires a large volume of sample and of toxic organic solvent and is difficult to automate. Solid phase extraction (SPE) is another often-applied technique for the extraction of phenols [2–4]. Additionally to carbon and silica based material there is a trend towards the usage of polymeric and modified polymeric sorbents. For example, Castillo et al. described polymeric liquid–solid extraction (LSE). Three different sorbents

---

* Corresponding author. Tel.: +49 341 2352662; fax: +49 341 2352625.
E-mail address: manuela.schellin@ufz.de (M. Schellin).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.10.066

based on polystyrene–divinylbenzene polymers were applied for a variety of phenolic compounds prior to analysis with LC-UV. LODs between 0.05 μg/L (2,4-dichlorophenol) and 0.8 μg/L (pentachlorophenol) were achieved [5]. The usage of pyrole based polymers as sorbents in solid-phase extraction in combination with RP-HPLC-UV for the analysis of phenols and chlorophenols led to LODs in the ng/L range and to relative standard deviation (R.S.D.) values lower than 7% ($n = 5$) [6]. Fontanals et al. synthesized a hydrophilic polymeric resign based on 4-vinylpyridine–divinylbenzene for solid-phase extraction of polar compounds from water. SPE was combined with LC-UV and detection limits were 0.2 μg/L for phenol [7]. Compared to liquid–liquid extraction the SPE techniques are easier to automate but still they require a certain amount of organic solvents and can have a series of many different steps like drying and conditioning of the cartridges. Another alternative to extract phenols and chlorophenols in water is Solid Phase Micro Extraction (SPME), which eliminates the need of solvents. SPME has been applied to the determination of chlorophenols in landfill leaches and in wastewater [8–10]. A more polar fibre (polyacrylate) is preferred for the analysis of polar compounds [9–11].

In GC–MS analysis of polar analytes, derivatisation can be carried out. Derivatisation may lead on the one hand to better efficiency and chromatographic behaviour, since the polarity of the compounds is reduced. On the other hand, derivatisation means an additional step in the sample preparation procedure, which can be a source of errors. The combination of SPE with derivatisation generally requires complicated procedures such as purification, extraction and concentration [12,13]. In the case of acetylation of the phenols, the pH value has to be controlled carefully in order to reach optimal extraction yields [14]. Another possibility is the conversion of the phenols into methylated phenols. However, this method requires the use of diazomethane, which is carcinogenic and explosive [15].

Membrane-based extraction methods are more and more applied as sample preparation methods [16]. Main advantages are the high degree of selectivity and cleanup from complicated matrices, the very small solvent consumption and the possibility for automation and on-line coupling to analytical instruments. Jönsson and Mathiasson [17,18] developed supported liquid membrane extraction (SLM). A porous membrane, which is soaked with an organic solvent, separates the aqueous donor phase from the aqueous acceptor phase. The pH values of the two aqueous phases are different to prevent the back-extraction of the analytes into the donor phase. For supported liquid membrane extraction of phenols in water a system with *n*-undecane was used and the membrane set-up was coupled to an LC with electrochemical detection. Detection limits in the ng/L range were achieved [19].

Membrane extraction methods are also suitable for samples with high matrix contents. Phenols in crude oil were analysed using silicone membranes as a separation barrier prior to the introduction of the sample into the chromatographic system [20,21].

The method of membrane-assisted solvent extraction (MASE) is described in this paper. The membrane system is on-line coupled to the inlet of a programmed-temperature–vaporizer of a gas chromatograph with mass-selective detection. MASE has been successfully applied for the determination of non-polar compounds, such as polychlorinated biphenyls (PCBs) and semi-polar compounds (triazines, organochlorine and organophosphorus compounds) [22–26]. The purpose of this work was to optimise this fully automated extraction technique for the determination of the very polar phenols (phenol: $\log K_{ow}$: 1.46) and chlorophenols and to extract these analytes from real water samples.

2. Experimental

2.1. Chemicals and standards

An EPA phenolic standard, consisting of the seven phenols listed in Table 1, with a concentration of 500 mg/L of each phenol was obtained from Supelco (Bellfonte, PA, USA). The calibration standard was diluted to a concentration of 10 mg/L in methanol and used to spike 15 mL water samples at the μg/L to ng/L level. The solvents methanol and ethyl acetate were obtained from Merck (Darmstadt, Germany). Reagent water for optimisation and validation consisted of deionised tap water prepared from an ion-exchange cartridge.

2.2. Samples

Two ground water samples of the Bitterfeld region, Saxony-Anhalt, Germany were analysed. After the collection the samples were kept in darkness at 10 °C. For quantification the samples had to be diluted 1:10, 1:50 and 1:100 (corresponding to the calibration range) with reagent water.

2.3. Membrane-assisted solvent extraction

The device of membrane-assisted solvent extraction is produced by Gerstel (Mühlheim, Germany) and is described in several papers [23–26]. The extraction cell consists of a conventional 20 mL headspace-vial and is filled with 15 mL

Table 1
The seven phenols with their K_{ow} values and the selected SIM ions

Compound	$\log K_{ow}$	m/z
2-Chlorophenol	2.15	128, 139
Phenol	1.46	94, 136
2,4-Dimethylphenol	2.30	107, 122
2,4-Dichlorophenol	3.06	162, 164
4-Chloro-3-methylphenol	3.10	107, 142
2,4,6-Trichlorophenol	3.69	196, 198
Pentachlorophenol	5.12	266, 268