Journal of Chromatography A, 1281 (2013) 46–53

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Membrane assisted solvent extraction coupled with liquid chromatography tandem mass spectrometry applied to the analysis of alkylphenols in water samples

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ARTICLE INFO

Article history:
Received 27 November 2012
Received in revised form 15 January 2013
Accepted 15 January 2013
Available online 23 January 2013

Keywords:
Alkylphenols
Nonylphenol
Membrane assisted solvent extraction
LC-ESI-MS/MS
Water samples
Water Framework Directive

ABSTRACT

This work describes the development and validation of a novel, simple, sensitive and environmental friendly analytical method for the determination of alkylphenols in different types of water samples. The methodology was based on a membrane assisted solvent extraction of only 15 mL of water sample with 500 μL of hexane in combination with liquid chromatography-electrospray ionization tandem mass spectrometry in negative mode (LC-ESI-MS/MS). Acquisition was performed in the multiple reaction monitoring (MRM) mode recording two transitions for the identification of the target compounds. Quantitation is based on the use of deuterated labelled standards as surrogate standards. The figures of merit were satisfactory in all cases: absolute recoveries were close to 50% for most investigated compounds and relative recoveries varied between 81 and 108%. Repeatability and intermediate precision were <20% for all compounds. Uncertainty assessment of measurement was estimated on the basis of an in-house validation according to EURACHEM/CITAC guide. Quantitation limits of the method (MQL) were lower than 0.04 $\mu g\,L^{-1}$ in all cases, which allow the achievement of the limits established by the Directive 2008/105/EC for surface and seawater samples and by the new proposal COM (2011) 876 final. The feasibility of the proposed method was demonstrated analyzing seawater, surface water and drinking water samples from different areas of A Coruña (Northwest of Spain). The analyses evidenced the presence of nonylphenol in seawater (MQL-0.13 $\mu g\,L^{-1}$) and surface water samples (0.12–0.19 $\mu g\,L^{-1}$). The highest concentration was observed in drinking water (0.25 $\mu g\,L^{-1}$).

1. Introduction

Alkylphenols (APs) are considered estrogenic endocrine-disrupting compounds which could have negative effect in human reproduction at low concentrations, acting on the estrogens receptors [1]. These compounds are constituents of household and industrial products as herbicides, detergents and plasticizers. Furthermore, octyl- and nonylphenol are used in the production of their derivates ethoxylates (alkylphenol ethoxylates), one of the main non-ionic surfactants [2].

Due to their wide use and their hazardous properties, alkylphenols were listed as priority substances in the field of water policy by Water Framework Directive 2000/60/EC [3] and Directive 2008/105/EC [4] which establishes Environmental Quality Standards (EQS) for these compounds. The annual average (AA) for 4-nonylphenol in seawater and surface waters is 0.3 $\mu g\,L^{-1}$, whereas the maximum allowable concentration (MAC) is 2 $\mu g\,L^{-1}$. In the case of 4-*tert*-octylphenol, the AA is 0.01 $\mu g\,L^{-1}$ in seawater and 0.1 $\mu g\,L^{-1}$ in surface water. However, the MAC is not applicable since the AA values are lower than the values derived on the basis on acute toxicity. Recently, a new proposal for water legislation COM (2011) 876 final [5] has been published and maintain the same EQS for these compounds. No limits for APs in drinking water have been established yet; however, the analysis of these analytes in this kind of water is mandatory in order to protect human health.

Several techniques have been used to analyze alkylphenols. In the last years, gas chromatography-mass spectrometry (GC-MS) has been widely employed in environmental analysis of these compounds. Two ISO standard methods for the analysis of alkylphenols in water sample are based on liquid–liquid extraction (LLE) [6] and solid-phase extraction (SPE) [7] coupled with GC-MS. Other proposed extraction techniques in combination with GC-MS were liquid-phase microextraction [8], microextraction by packed sorbents (MEPS) [9] or stir bar microextraction (SBSE) [10,11].

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http://dx.doi.org/10.1016/j.chroma.2013.01.069

Nevertheless, the presence of polar groups complicates the analysis of alkylphenols by GC-MS. Thus, an additional derivatization step could be required to obtain symmetric chromatographic peaks and good precision [12]. A more convenient alternative, which avoids losses of analytes and simplifies the experimental procedure is liquid chromatography-tandem mass spectrometry (LC-MS/MS) [13]. Novel LC-MS/MS interfaces such as electrospray (ESI) and atmospheric pressure chemical ionization (APCI) were employed in analysis of alkylphenols [14]. Better results were obtained with ESI due to its high sensitivity; although ESI is commonly affected by co-eluting matrix compounds, this problem could be corrected with the use of internal standard [15].

Solid phase extraction is commonly used combined with LC-MS/MS in order to remove possible interferences and pre-concentrate the analytes [16,17]. Classical extraction techniques are required time-, solvent- and labour-consuming. Nowadays, newer, solvent-free and solvent-reduced techniques were employed, according with the principles of the Green Chemistry [18]. Analysis of alkylphenols by microextraction techniques such as single-drop microextraction (SDME) [19], dispersive liquid–liquid microextraction (DLLME) [20], hollow fibre-protected liquid phase microextraction [21] or microporous membrane liquid–liquid extraction [22] can be found in the literature.

Other alternative technique, based on the use of membranes, is membrane-assisted solvent extraction (MASE). The principle of MASE, described at first by Hauser et al. [23] in 2001, is based on the diffusion of organic compounds dissolved in an aqueous sample through a membrane bag into a small amount of organic solvent [24]. Hydrophobic porous or non-porous polymeric membranes are the most common devices used in MASE applications. Although porous membranes can be employed as a filter, non-porous membranes are not only considered as a barrier for particles, macromolecules and polar species; they can also provide selectivity and specificity in terms of permeation and transport through the membrane [25].

This technique was applied to the analysis of UV filters [25], volatile organic compounds [26], polycyclic aromatic hydrocarbons [27], polycyclic musk compounds [28], pesticides [29,30], phosphoric acid triesters [31], polychlorinated byphenyls [24,32] triazines and organochlorine compounds [33,34]. Recently, endocrine disrupting compounds were also analyzed by MASE [35], however, the determination was carried out by GC-MS. To the best of our knowledge, no previous work specifically focused on the analysis of alkylphenols in waters by MASE-LC-MS/MS can be found in the literature.

The main novelty of this work is the development and validation of a novel, simple, fast and sensitive miniaturized method for the determination of APs in water samples based on membrane-assisted solvent extraction followed by the quantification using LC-ESI-MS/MS. According with the principles of the Green Chemistry, small volume of organic solvents (500 μL) was employed. The low method quantitation limits (MQL) obtained enables the determination of alkylphenols at ultratrace levels according to the restrictive legislation (Directive 2008/105/EC) analyzing only 15 mL of sample. Furthermore, these MQLs were lower than 30% of EQS in compliance with the requirements set by Directive 2009/90/EC [36]. The small volume of sample required facilitates the sampling, transport, manipulation and storage of the samples; consequently, this method could be an important tool in monitoring programmes to control the fate and occurrence of alkylphenols in the environment.

2. Experimental

2.1. Standards and reagents

Nonylphenol technical mixture (NP) 94% purity (±1% tolerance) and 4-n-nonylphenol (4-n-NP) 99.9% purity (± 0.5% tolerance) were from Riedel-de Haën (Seelze, Germany). 4-tert-octylphenol (4-tOP) 97% purity (±0.5% tolerance) and 4-octylphenol (4-OP) 99% purity (±0.5% tolerance) were obtained from Sigma-Aldrich (Steinheim, Germany). All standard solutions (1000, 10 and 1 mg L^{-1}) containing all the target compounds were prepared in methanol (SPS grade) from Romil Ltd (Cambridge, United Kingdom) and stored at 4 °C.

As surrogate internal standard, 4-n-nonylphenol-2, 3, 5,6-d_4 (4-n-NP-d_4) 99.3% was obtained from CDN Isotopes (Pointe-Claire, Canada).

For the extraction procedure, n-Hexane for organic trace analysis (UniSolv®) was from Merck (Darmstadt, Germany) and methanol (SPS grade) from Romil Ltd (Cambridge, United Kingdom).

For the determination, methanol LC-MS PAI and ammonia (30%) for instrumental analysis were from Panreac (Barcelona, Spain). Water was purified with a Direct 5 Milli Q system (Millipore, Bedfore, MA, USA). Seawater, surface water and drinking water were used for the optimization and validation of the proposed method.

2.2. Sampling

Water samples were collected in the metropolitan area of A Coruña (Galicia, NW Spain), which comprises a population of ca. 420,000 inhabitants. Surface water samples were collected along the Mero river basin, at four different points. Seawater samples were collected in eight beaches situated close to urban and industrial zones. Drinking water samples were collected in six private houses distributed in different zones of the studied metropolitan area, the same day and at same hour approximately. In this area, river water (supplied from Cecebre dump) was treated by sand filtration, coagulation/flocculation and chlorination in a drinking water treatment plant (DWTP) for human consumption. The sampling locations are shown in Fig. 1.

All samples were collected in amber glass 1 L bottles (pre-cleaned with acetone and methanol and rinsed with each water samples) and stored at 4 °C before the analysis. No modifier was added to the samples in order not to affect the extraction process. To avoid the adsorption of alkylphenols to the glassware, water samples should be analyzed before 5 days when no modifier was added [37].

2.3. Extraction

The MASE device commercially available by Gerstel (Mülheim, Germany) consists of a 20 mL glass vial with a membrane insert made of dense polypropylene (4-cm long with a wall thickness of a 0.03 mm and an internal diameter of 6 mm). This synthetic solid polymer has a good stiffness and stays stable during the possible highest agitation speed.

The membrane bag is fixed to a metal funnel (using a Teflon ring) suspended in the opening of the glass vial. Finally, the vial is sealed with a metallic crimp cap. Membrane bags should be cleaned and preconditioned with the extraction solvent before the extraction.

In the optimized extraction procedure, 15 mL of water samples were placed in the 20 mL vial. The membrane bag was filled with 500 μL of hexane, which is used as extractant solvent. Then, the vial was vigorously shaken at room temperature using an agitation plate Vibrax-VXR by IKA (Staufen, Germany) during 60 min at