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Stir bar sorptive extraction and liquid chromatography–tandem mass spectrometry determination of polar and non-polar emerging and priority pollutants in environmental waters

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ABSTRACT

An analytical method based on stir bar sorptive extraction (SBSE) was developed and validated for the determination of environmental concern pollutants in environmental waters by liquid chromatography–tandem mass spectrometry (LC–MS/MS). Target compounds include six water and oil repellents (perfluorinated compounds), four preservatives (butylated hydroxytoluene and three parabens), two plasticizers (bisphenol A and di(2-ethylhexyl)phthalate), seven surfactants (four linear alkylbenzene sulfonates, nonylphenol and two nonylphenol ethoxylates), a flame retardant (hexabromocyclododecane), four hormones, fourteen pharmaceutical compounds, an UV-filter (2-ethylhexyl 4-methoxycinnamate) and nine pesticides. To achieve the simultaneous extraction of polar and non-polar pollutants two stir bar coatings were tested, the classic polydimethylsiloxane (PDMS) coating and the novel ethylene glycol modified silicone (EG-silicone). The best extraction recoveries were obtained using EG-silicone coating. The effects of sample pH, volume and ionic strength and extraction time on extraction recoveries were evaluated. The analytical method was validated for surface water and tap water samples. The method quantification limits ranged from 7.0 ng L⁻¹ to 177 ng L⁻¹. The inter-day precision, expressed as relative standard deviation, was lower than 20%. Accuracy, expressed as relative recovery values, was in the range from 61 to 130%. The method was applied for the determination of the 48 target compounds in surface and tap water samples.

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1. Introduction

In the last years, there has been a growing concern about the presence of organic pollutants in environmental waters not only because they can affect aquatic organisms, but also because they can be accumulated in the ecosystems and could even imply a threat to human health [1–3]. As a result, some regulations have been published fixing concentration limits for some micropollutants in environmental waters. For instance, the European Parliament published in 2008 a directive, in the field of water policy, in which a list of 33 substances for priority action was included [4]. Then, in 2013, the list was revised and increased to 45 substances including pesticides, perfluorinated compounds and flame retardants [5]. Two years later, the European Union published the first “watch list” of substances to be monitored [6]. The watch list includes, among other pollutants, hormones, pharmaceutical

compounds, pesticides, a food additive and a solar filter. Many studies have reported the occurrence and removal of some of the compounds included in the EU watch list, such as the hormones, diclofenac and macrolide antibiotics [3,7,8]. Nevertheless, there is a lack of knowledge about the occurrence of some of the other watch list compounds such as some of the pesticides, the food preservative and the UV solar filter [3]. To obtain information about the occurrence and fate of such organic pollutants in water samples, sensitive and accurate methods are needed. The analytical methods reported for the determination of organic pollutants in the aquatic media are commonly based on solid-phase extraction [9]. In the last two decades, an increase of the use of microextraction techniques has occurred because of their advantages such as the simplification, strong reduction or even removal of the use of toxic organic solvents and the reduction of required sample volumes [10]. Among the novel microextraction techniques, especial attention has been devoted to stir bar sorptive extraction (SBSE) introduced in 1999 by Baltussen et al. [11]. As a result of the great advantages of SBSE, a high number of papers and review studies, focused on this green extraction technique have been reported [10,12–14].

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SBSE has even been applied in passive samplers for determination of hydrophobic compounds in environmental waters. The main drawback of SBSE has been the reduced number of commercially available coatings that has been limited to polydimethylsiloxane (PDMS). PDMS is a non-polar phase so it is not suitable for the extraction of polar compounds especially those with log *K*_{ow} values lower than 3 [10,16,17]. Therefore, for years, the application of SBSE has been limited to pollutants such as polycyclic aromatic hydrocarbons [18–23], pesticides [21–26], polychlorobiphenyls [20–23], polybrominated diphenylethers [21,22], nonylphenol [22], personal care products [23] and chlorinated endocrine-disrupting compounds [27]. To overcome this limitation, many efforts have been carried out to prepare suitable home-made SBSE polar coatings [15,28–31]. Recently, two commercial polar coatings (ethylene glycol modified silicone (EG Silicone Twister[®]) and polyacrylate (PA) (Acrylate Twister[®]) are available from Gerstel (Mülheim an der Ruhr, Germany). The commercial polar coatings have the potential to extend the applicability of SBSE to the determination of polar organic pollutants. Nevertheless, the scarce extraction methods reported using this polar coatings are limited to single groups of environmental water pollutants such as pharmaceuticals and personal care products [32], a vulcanisation accelerator (benzothiazole) [33] and explosives [34].

The aim of this paper was to develop and validate an analytical method for the determination of polar and non-polar pollutants based on SBSE and liquid chromatography–tandem mass spectrometry (LC–MS/MS) determination. Target compounds include six water and oil repellents, four preservatives, two plasticizers, seven surfactants, a flame retardant, four hormones, fourteen pharmaceutical compounds, an UV-filter and nine pesticides (Table 1). They are of environmental concern in water samples because of being considered emerging or priority pollutants. Many of them are already included in environmental regulations [4–6].

2. Experimental

2.1. Chemicals and reagents

All reagents were analytical grade unless otherwise specified. HPLC-grade acetonitrile (ACN), methanol (MeOH) and water were supplied by Romil Ltd. (Barcelona, Spain). Hydrochloric acid, sodium chloride (NaCl), methyl *tert*-butyl ether (MTBE) and formic acid were obtained from Panreac (Barcelona, Spain). Ammonium formate and ammonium acetate were purchased from Sigma-Aldrich (Steinheim, Germany). Analytical standards were obtained from Sigma-Aldrich (Steinheim, Germany) except di(2-ethylhexyl)phthalate (DEHP), that was obtained from Riedel-de Haën (Seelze, Germany), and the commercial linear alkylbenzene sulfonate (LAS) mixture, containing LAS C10 (12.3%), LAS C11 (32.1%), LAS C12 (30.8%) and LAS C13 (23.4%), was supplied by Petroquímica Española (PETRESA). Isotopically labelled compounds were used as internal standards (I.S.). Phenacetin-ethoxy-1-¹³C (Phen-¹³C) and perfluorooctanoic acid-¹³C₈ (PFOA-¹³C₈) (99%) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Bisphenol A-d₁₄ (99.5%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). Propylparaben-¹³C₆ was purchased from Sigma-Aldrich (Steinheim, Germany). Individual stock standard solutions of each compound (1000 mg L⁻¹, except for pesticides (100 mg L⁻¹)) were prepared in MeOH and stored at 4 °C. Working solutions were prepared by dilution of the stock standard solutions in MeOH:water (50:50, v/v). PDMS Twister[®] (enrichment phase: polydimethylsiloxane (PDMS), film thickness 0.5 mm, length 10 mm) and EG Silicone Twister[®] (enrichment phase: EG-silicone, 32 μL phase volume, 10 mm length) stir bars

were purchased from Gerstel GmbH (Mülheim an der Ruhr, Germany).

2.2. LC-(ESI)-MS/MS analysis

Chromatographic analyses were performed on an Agilent 1200 series HPLC (Agilent, USA), equipped with an automatic injector, a binary pump, a thermostated column compartment and a 6410 triple quadrupole (QqQ) mass spectrometer (MS) using an electrospray ionization (ESI) interface (Agilent, USA). The analytical column was a HALO C-18 Rapid Resolution (50 × 4.6 mm i.d., 2.7 μm particle size) (Advanced Materials Technologies, USA). The (ESI)MS/MS parameters were optimised by direct injection of each analyte. Ionization was carried out applying a MS capillary voltage of 3000 V, a drying-gas flow rate of 9 L min⁻¹, a drying-gas temperature of 350 °C and a nebulizer pressure of 40 psi. Two chromatographic methods were developed. In method 1, the mobile phase consisted of MeOH and 10 mM ammonium acetate solution. The chromatographic elution was carried out by linear gradient from 28 to 70% of MeOH in 14 min, then to 80% of MeOH in 5 min, and then to 100% MeOH in 6 min (held for 2 min). Method 2 was applied for the analysis of the pharmaceutical compounds, the UV filter and the pesticides. In method 2, the mobile phase consisted of ACN containing formic acid 0.1% (v/v) and 15 mM ammonium formate solution containing formic acid 0.1% (v/v). The elution program was first isocratic at 6% of ACN (held for 5 min), and then three linear gradients were applied, first to 15% ACN in 2 min (held for 3 min), second to 40% ACN in 15 min (held for 5 min) and, third, to 80% ACN in 3 min (held for 7 min). The analyses were performed in multiple reaction monitoring (MRM) mode. Two MRM transitions were selected for each analyte, one was applied for quantification (MRM1) and another for confirmation (MRM2). MRM transitions, fragmentor voltage, collision energy and ionization mode are summarised in Table 2.

2.3. Sample collection

Surface water and tap water samples were used to test method applicability. Samples were collected in amber glass bottles pre-cleaned with acetone and MeOH. Surface water samples, collected from Guadalquivir River (Seville, South of Spain), were stabilized with ACN (final concentration 0.5%, v/v) and stored at 4 °C. Analysis was carried out within 48 h after sample collection.

2.4. Stir bar sorptive extraction

Prior to extraction, samples were filtered through a 1.2-μm glass-fiber membrane filter (Whatman, Mainstone, UK), and I.S. were added to achieve concentrations of 0.2 μg L⁻¹. Filtered sample (100 mL) was placed in a 250 mL Erlenmeyer flask and 38 g of NaCl were added. Then, a stir bar was placed into the Erlenmeyer flask, and the samples were stirred at 600 rpm for 24 h in a nine-position digital stirrer (Selecta, Barcelona, Spain). After extraction, the stir bar was taken out by using a magnetic rod, washed with deionised water, to remove remaining salt and adhered sample matrix, and dried on a lint-free tissue. Stirring speed and conditioning and cleaning were carried following manufacturer's recommendations. Chemical desorption was carried out by introducing the stir bar into a 2 mL vial containing 0.5 mL of MeOH and applying ultrasonication for 15 min. After desorption, the solvent was evaporated to dryness under a nitrogen stream. The extract was reconstituted in 100 μL of MeOH:water (50:50, v/v) and filtered through a 0.22 μm nylon filter. A 20-μL aliquot was injected into the HPLC-QqQ-MS instrument. Stir bars were preconditioned and cleaned to be reused, before and after each use, respectively, by soaking in ACN overnight. Each stir bar could be used at least 50 times without robustness loss.

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