



Multiresidue analysis of 24 Water Framework Directive priority substances by on-line solid phase extraction-liquid chromatography tandem mass spectrometry in environmental waters



Adrià Rubirola^a, M^a Rosa Boleda^{a,*}, M^a Teresa Galceran^b

^a Aigües de Barcelona, Empresa Metropolitana de Gestió del Cicle Integral de l'Aigua, S.A., General Batet 1-7, 08028 Barcelona, Spain

^b University of Barcelona, Dpt. Anal. Chem., Diagonal, 645, 08028 Barcelona, Spain

ARTICLE INFO

Article history:

Received 20 December 2016
Received in revised form 10 February 2017
Accepted 28 February 2017
Available online 6 March 2017

Keywords:

European Water Framework Directive
Priority substances
LC-MS/MS
On-line SPE
Water analysis
Multiresidue

ABSTRACT

This paper reports the development of a fully multiresidue and automated on-line solid phase extraction (SPE) – liquid chromatography tandem mass spectrometry (LC-MS/MS) method for the determination of 24 priority substances (PS) belonging to different classes (pesticides, hormones or pharmaceuticals) included in the Directive 2013/39/UE and the recent *Watch List* (Decision 2015/495) in water samples (drinking water, surface water, and effluent wastewaters). LC-MS/MS conditions and on-line SPE parameters such as sorbent type, sample and wash volumes were optimized. The developed method is highly sensitive (limits of detection between 0.1 and 1.4 ng L⁻¹) and precise (relative standard deviations lower than 8%). As part of the method validation studies, linearity, accuracy and matrix effects were assessed. The main advantage of this method over traditional off-line procedures is the minimization of tedious sample preparation increasing productivity and sample throughput.

The optimized method was applied to the analysis of water samples and the results revealed the presence of 16 PS in river water and effluent water of wastewater treatment plants.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

In the last years, strict regulations have been established to control concentration levels of contaminants in the environment. In the field of water policy, at the beginning of the XXI century the European Union (EU) adopted the Water Framework Directive (WFD) 2000/60/EC [1] whose objectives are to improve, protect and prevent further deterioration of water quality. This directive is devoted to the monitoring of priority substances (PS) in surface waters of EU and it recommends the development of new procedures for the identification of 33 priority substances/group of substances. The list of compounds included metals, pesticides, polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds among other organic substances. PS have been defined as substances that present a risk to the aquatic environment. In 2008, Directive 2008/105/EC [2] established environmental quality standards (EQS) in the field of the WFD and the maximum allowable concentrations of these PS in different types of waters. In 2013, these two directives were amended. In the Directive 2013/39/UE [3], a

total of 12 new priority substances, with their environmental quality standards, annual averages (AA-EQS) and maximum allowable concentrations (MAC-EQS) were added. In addition, a watch list of substances was established in order to improve the information for the identification of future priority substances. The Directive 2013/39/UE recommended the inclusion of three substances in this watch list, namely two pharmaceuticals (diclofenac and the synthetic hormone 17- α -ethinyl estradiol (EE₂)) and a natural hormone (17- β -estradiol (E₂)). In 2015, a Watch list (Decision 2015/495) [4] was published where besides the substances recommended by the Directive 2013/39/UE, it adds 10 substances/groups of organic substances including three macrolide antibiotics (erythromycin, clarithromycin and azithromycin), a natural hormone (estrone (E₁)), some pesticides (methiocarb, oxadiazon, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid and triallate), a UV filter (2-ethylhexyl-4-methoxycinnamate, EHMC) and an antioxidant (2,6-di-tertbutyl-4-methylphenol) commonly used as food additive.

In general, the proposed EQS are extremely low for different reasons such as toxicity, uses and environmental fate and so, analytical methods that reach very low quantification limits are needed. This scenario encourages the development of selective and reliable analytical methods, which enable the multiclass determination of

* Corresponding author.

E-mail address: mboledav@aiguesdebarcelona.cat (M.R. Boleda).

Table 1
Physicochemical properties of the studied compounds.

Group	Compound	CAS Number	Mw	pK _a	Log Kow	
Pesticides	Thiamethoxam	153719-23-4	291.7	2.3	-0.1	
	Imidacloprid	138261-41-3	255.7	0.5	0.6	
	Clothianidin	210880-92-5	249.7	2.4	0.7	
	Acetamiprid	135410-20-7	222.7	0.9	0.8	
	Thiacloprid	111988-49-9	252.7	-0.6	1.3	
	Simazine	122-34-9	201.7	1.7	1.9	
	Atrazine	1912-24-9	215.7	1.7	2.8	
	Isoproturon	34123-59-6	206.3	14.3	2.5	
	Diuron	330-54-1	233.1	13.8	2.7	
	Cibutrine	28159-98-0	253.4	4.1	4.0	
	Methiocarb	2032-65-7	225.3	12.2	3.1	
	Chlorfenvinphos	470-90-6	359.6	4.7	3.8	
	Triallate	2303-17-5	304.7	-1	4.6	
	Chlorpyrifos	2921-88-2	350.6	4.6	4.3	
	Phenolic compounds	Pentachlorophenol	87-86-5	266.4	4.5	5.1
		4-tert-octylphenol	140-66-9	206.4	10.0	4.1
Nonylphenol		84852-15-3	220.4	10.7	4.5	
Steroidal estrogens	Estone (E ₁)	53-16-7	270.4	9.9	3.4	
	17-β-Estradiol (E ₂)	50-28-2	272.4	10.0	4.0	
	17-α-Ethinyl estradiol (EE ₂)	57-63-6	296.4	10.2	4.2	
Pharmaceutical	Diclofenac	15307-79-6	296.1	4.4	4.0	
	Antibiotics	Erythromycin	114-07-8	733.9	8.6	3.1
		Clarithromycin	81103-11-9	748.0	8.5	3.2
UV filter	2-Ethylhexyl 4-methoxycinnamate (EHMC)	5466-77-3	290.4	-	5.8	

the PS at the levels required in the WFD in environmental water samples.

In some studies about the establishment of multiresidue methods for the analysis of organic compounds in water some WFD PS have been included [5–10]. However, most of these methods employ rather tedious and time-consuming sample preparation procedures based on off-line solid-phase extraction (SPE) [5,8,9]. Nowadays, the growing increase on the number of samples and the number of compounds to be analyzed in routine laboratories that perform monitoring studies increasingly requires the use of high-throughput and fully automated multiresidue methods. In this context, on-line SPE coupled to LC-MS/MS which is capable of detecting multiple classes of emerging contaminants (i.e., pharmaceuticals, pesticides, hormones, phenols) seems to be the technique of choice for environmental monitoring programs. In fact, in the last years the use of on-line SPE coupled to LC-MS/MS technique has increased and several methods have been published, although most of them are focused on the analysis of specific classes of emerging contaminants in water samples including only some WFD PS such as pesticides [11–16], pharmaceuticals [17,18], antibiotics [19–22] or hormones [23–29]. Only a few multiresidue methods using on-line SPE coupled to LC-MS/MS have been recently reported to analyze some emerging contaminants of different families, such as pharmaceuticals, pesticides and flame retardants in water [10,30,31], although these methods are not oriented to the analysis of all WFD PS and do not include the new PS included in Decision 2015/495.

So, in this work, a reliable, fully automated multiresidue method based on on-line SPE coupled to LC-MS/MS has been developed for the determination of 24 WFD PS (Table 1), in waters (drinking water (DW), surface water (SW) and effluent wastewater (EWW)). The method has been validated and applied to analyze several water samples.

2. Materials and methods

2.1. Chemicals and materials

WFD PS standards (Table 1) of high purity grade (>92%) were supplied by Sigma-Aldrich (Steinheim, Germany). Diclofenac was purchased as sodium salt. Isotopically labeled compounds,

simazine-d5, diuron-d6, isoproturon-d6, chlorpyrifos-d10, chlorphenvinphos (ethyl)-d10, methiocarb-d3 (N-methyl d3), thiamethoxam-d4 (oxadiazine d4) and clothianidin-d3 (N-methyl d3) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Atrazine-d5, imidacloprid-d4, 4-tert-octylphenol-13C6, 4-nonylphenol-13C6 and pentachlorophenol-13C6 were purchased from Sigma-Aldrich, diclofenac-d4 from CDN Isotopes (Quebec, Canada), acetamiprid-d3 (N-methyl d3) and cibutrine-d9 (tert-butyl d9) were acquired from Analytical Standard Solutions A2S (Saint Jean d'Ilac, France), estrone-2,4,16,16-d4 from Cambridge Isotope Laboratories, INC. (Andover, USA) and erythromycin-d6 from Toronto Research Chemicals (Toronto, ON, Canada).

Individual stock standard solutions of the analytes and isotopically labeled internal standards were prepared at 1000 mg L⁻¹ by dissolving 10 mg of each compound in 10 mL of methanol (MeOH). All solutions were stored at -20 °C. Two standard mixtures of the compounds, depending on their ionization (positive and negative) mode, were prepared by appropriate dilution of individual stock solutions in MeOH. These standard mixtures were used as spiking solutions to prepare the aqueous calibration standards and to spike water samples for recovery calculations. Aqueous standard solutions did not contain more than 0.5% MeOH. LC working standard solutions (50 µg L⁻¹) were prepared in MeOH/H₂O (40:60, v/v). Also, two mixtures of isotopically labeled standards were prepared in MeOH and further diluted in MeOH/H₂O (40:60, v/v).

HPLC-grade MeOH, acetonitrile (ACN), water, formic acid 98% and ammonium hydroxide (NH₄OH) were supplied by Merck (Darmstadt, Germany).

2.2. On-line trace enrichment

Extraction of the samples and its chromatographic separation was performed on an automated on-line SPE-LC device Symbiosis Pico from Spark Holland (Emmen, The Netherlands). In this work, direct injection (LC mode) was used to optimize LC separation (mixture of the standards in MeOH/H₂O (40:60, v/v)) and on-line SPE (XLC mode) was used to optimize the procedure and to analyze water samples.

On-line SPE procedure consisted on four steps: (i) conditioning of the cartridge (6 mL of MeOH and 4 mL of HPLC grade water at a

Download English Version:

<https://daneshyari.com/en/article/5135508>

Download Persian Version:

<https://daneshyari.com/article/5135508>

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