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Multi-residue method for determination of 58 pesticides, pharmaceuticals and personal care products in water using solvent demulsification dispersive liquid–liquid microextraction combined with liquid chromatography-tandem mass spectrometry

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ABSTRACT

A rapid and efficient sample pretreatment using solvent-based de-emulsification dispersive liquid–liquid microextraction (SD-DLLME) coupled with liquid chromatography-tandem mass spectrometry (LC–MS/MS) was studied for the extraction of 58 pharmaceuticals and personal care products (PPCPs) and pesticides from water samples. Type and volume of extraction and disperser solvents, pH, salt addition, amount of salt and type of demulsification solvent were evaluated. Limits of quantification (LOQ) in the range from 0.0125 to 1.25 μg L^{-1} were reached, and linearity was in the range from the LOQ of each compound to 25 μg L^{-1}. Recoveries ranged from 60% to 120% for 84% of the compounds, with relative standard deviations lower than 29%. The proposed method demonstrated, for the first time, that sample preparation by SD-DLLME with determination by LC–MS/MS can be successfully used for the simultaneous extraction of 32 pesticides and 26 PPCPs from water samples. The entire procedure, including the extraction of 58 organic compounds from the aqueous sample solution and the breaking up of the emulsion after extraction with water, rather than with an organic solvent, was environmentally friendly. In addition, this technique was less expensive and faster than traditional techniques. Finally, the analytical method under study was successfully applied to the analysis of all 58 pesticides and PPCPs in surface water samples.

1. Introduction

A large number of synthetic organic compounds, such as pharmaceuticals and personal care products (PPCPs), as well as pesticides, has been found in the aquatic environment [1].

The important role that pesticides play in food protection has led to their massive global use in agriculture and consequent detection in the environment. Pesticides in water sources have been a topic of considerable interest due to the detection of an increasing number of pesticides in the environment, a fact that requires the establishment of strict regulations to minimize their impact [2].

PPCPs have become emerging contaminants because of the threat they pose to drinking water, their effects on human life and wildlife, besides their incomplete removal in wastewater treatment processes [3]. In addition, approximately 3000 different substances seem to be used as pharmaceutical ingredients, such as pharmaceuticals used by humans and those that aim at veterinary use for livestock, poultry and fish farming [4].

To quantitatively evaluate the fate of these chemicals and ensure the quality of drinking water, effective analytical methods are highly desirable. Because the concentrations of pesticides and PPCPs in water are usually very low (ng L^{-1} or lower), it is necessary to incorporate a concentration step into the analytical procedure prior to gas chromatographic or liquid chromatographic determinations. Solid phase extraction (SPE) is the most commonly used extraction method to extract multiresidue compounds from water samples [5]; however, new extraction techniques, aiming at reducing the overall analytical time and solvent consumption, have been recently proposed.

Multiresidue analytical methods are preferred to single group analysis because the former provide broader knowledge about the occurrence, removal, partition and fate of pollutants in the

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environment [6]. However, the biggest challenge comes from the fact that groups of contaminants have a broad spectrum of chemical and physical properties, thus requiring a solvent which is capable of extracting this group of diverse compounds.

Since the development of Dispersive Liquid–Liquid Microextraction (DLLME) by Rezaee et al. [7] in 2006, the technique has been very popular among analytical chemists. Since then, DLLME has undergone many changes, mainly related to the requirements of the extraction and disperser solvent. Most changes attempted to use solvents which were lighter than water [8], solvents with low toxicity and more convenient practical procedures [9], such as the DLLME based on the solidification of a floating organic drop (DLLME-SFO) and the solvent-terminated dispersive liquid–liquid microextraction (ST-DLLME) [10].

ST-DLLME, also known as solvent-based de-emulsification DLLME (SD-DLLME), was first introduced by Chen et al. [10]. This change in DLLME was studied to employ low-density extraction solvents to DLLME and remove the centrifugation step. Because the oil/water (O/W) emulsion that was formed after the injection of the dispersion and extraction solvent into the sample was thermodynamically unstable, solvents-usually used as disperser solvents-were introduced as chemical demulsifiers to break up the dispersed system, considering their characteristics of low surface tension and high surface activity. After this injection, the emulsion cleared quickly into two phases. Therefore, separation of the organic phase from the aqueous bulk was achieved without the use of centrifugation.

After its development, the SD-DLLME technique has been employed to the extraction of organic compounds, such as polycyclic aromatic hydrocarbons [11,12], organophosphorus [13], and organochlorine pesticides [14], carbamates [10], s-triazine herbicides [15], chlorophenols [16], phthalate esters [17,18], chlorophenoxy acid herbicides [19] and inorganic species, such as palladium [20] and cadmium [21], from water samples.

Due to the use of solvents which are lighter than water, SD-DLLME overcomes some drawbacks of DLLME, mainly related to the number of extraction solvents that are available to be used in the method and to the ability to extract target analytes. In addition, when this technique is used, halogenated hydrocarbon solvents are avoided. Another interesting advantage is the elimination of centrifugation, which is considered to be the most time-consuming step of the method [8].

Because other solvents than the ones generally used in DLLME extractions could be employed, this technique seems to be an interesting option for the extraction of multiresidue compounds from water samples, a fact that has been poorly explored when this technique is used. With the aim of studying and expanding the applicability of DLLME, a simple and fast method based on SD-DLLME was developed by evaluating its performance when low-density extraction solvents were applied, combined with liquid chromatography-tandem mass spectrometry (LC–MS/MS) for the determination of 32 pesticides and 26 PPCPs in water samples.

To the best of our knowledge, there is no report on the use of SD-DLLME for the multi-residue analysis of pesticides and PPCPs.

2. Experimental

2.1. Reagents

Salicylic acid, amitriptyline, avobenzone, sodium diclofenac, eusolex 6300, furosemide, mebendazole and sulfamethoxazole were bought from United States Pharmacopeia (USP, USA). Albendazole, carbamazepine, clarithromycin, diltiazem hydrochloride, flurazepam hydrochloride, chlorpropamide, gemfibrozil, glibenclamide, haloperidol, methylparaben, nimesulide, miconazole nitrate, propranolol and propylparaben were provided by Fiocruz (Fundação Oswaldo Cruz, Brazil). Bisphenol A, 2,4-D, atrazine, atrazine-d5, azoxystrobin, bentazone, carbofuran, carboxin, cyproconazole, clomazone, dichloran, diuron, difenoconazole, fenoxaprop-*p*-ethyl, fipronil, ibuprofen-d3, irgarol, malathion, metalaxyl-m, metsulfuron-methyl, pyraclostrobin, pyrazosulfuron-ethyl, pirimiphos-methyl, propanil, propiconazole, quinclorac, simazine, tau-fluvalinate, tebuconazole and trifloxystrobin were bought from Sigma Aldrich (Brazil). Ibuprofen, triclocarban, triclosan, bispyribac-sodium, cyhalofop-butyl, chlorantraniliprole, epoxiconazole and penoxsulam were supplied by Dr. Ehrenstofer GmbH (Germany).

Acetonitrile, methanol, toluene and acetone (HPLC grade) were bought from J.T. Baker (USA). Hexyl acetate and octanol were supplied by Sigma Aldrich (Brazil). Magnesium sulfate (anhydrous, $MgSO_4$) was purchased from J.T.Baker (Mexico) whereas sodium chloride was bought from Merck (Germany). Calcium chloride, sodium hydroxide and ammonium sulfate were provided by Synth (Brazil). Glacial acetic acid and hydrochloridric acid were obtained from Merck (Germany). The water was purified by an Ultrapure Water System (USA).

2.2. Apparatus and software

LC–MS/MS was performed by a Waters Alliance 2695 Separations Module (Waters, Milford, MA, USA) fitted with an autosampler, a membrane degasser and a quaternary pump. Mass spectrometry was performed by a Micromass Quattro Micro API (Waters, Milford, MA, USA) with an electrospray (ESI) interface. The drying gas, as well as the nebulizing gas, was nitrogen, generated by pressurized air in an Genius NM32LA nitrogen generator (Peak Scientific). The nebulizing gas flow was 50 L h^{-1} whereas the desolvation gas flow was 550 L h^{-1}.

To operate in the MS/MS mode, the collision gas was argon 99.99% (White Martins, Brazil) with a pressure of 3.5×10^{-3} mbar in the collision cell. The optimized values were as follows: capillary voltage, 4.0 kV; extractor voltage, 2 V; source temperature, 100 °C; desolvation temperature, 400 °C; and multiplier, 650 V.

For each compound, optimum collision energies, which aimed at getting two characteristic multiple reaction monitoring (MRM) transitions with the best signal intensity, were selected. After the optimization of the collision cell energy of the triple quadrupole, two different precursor ion-product ion transitions, for quantification and for confirmation, were selected for each analyte. Table 1 shows the optimized MRM transitions for the pesticides with their respective retention times (t_R). Analytical instrument control, data acquisition and treatment were performed by the software MassLynx (Micromass, Manchester, UK), version 4.1.

The chromatographic separation was performed by a Kinetex C8 (3.0 mm × 50 mm i.d., 2.6 μm film thickness) column (Phenomenex, USA). The mobile phase components were (A) ultrapure water with 0.1% acetic acid and (B) methanol, with elution in the gradient mode. The initial composition was 20% B; it increased linearly to 90% in 20 min, held until 23 min and, then, returned to the initial composition (20% B) in 0.5 min and held for 6.5 min, totaling a 30- min analysis. The flow rates were as follows: 0–20 min, 0.2–0.4 mL min^{-1}; 20–23 min, 0.4 mL min^{-1}; 23–23.5 min, 0.4-0.2 mL min^{-1}; 23.5–30 min, 0.2 mL min^{-1}. The injection volume was 10 μL.

2.3. Analytes selection

Aiming at verifying the feasibility of the use of SD-DLLME for the extraction of multiclass analytes from water samples, a large number of analytes with different physicochemical properties, in terms of polarity and water solubility, was chosen (Table 1) [22,23]. Pesticides are widely used in agriculture. Pesticides and

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