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Bar adsorptive microextraction (BAμE) with polymeric sorbent for the determination of emerging contaminants in water samples by UHPLC-MS/MS

Authors: Maiara P. de Souza [1], Tiele M Rizzetti [1], Mariela de S. Viera [1], Osmar D. Prestes [1], Renato Zanella [1]
Institution: [1] LARP-UFSM - Universidade Federal de Santa Maria (LARP, Depto. de Química, Campus da UFSM, 97105-900 Santa Maria-RS, Brazil)

Abstract:

In this work, a simple and low cost method was validated for the analysis of 13 emerging contaminants, including pharmaceuticals, hormones, plasticizers and flame retardant, in water using bar adsorptive microextraction (BAμE) followed by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS). Three different coating phases (Oasis® HLB, C18 and GCB) were evaluated for BAμE. The preparation, stability tests and development of BAμE devices are discussed. In order to select the best combination of experimental conditions for extraction and back extraction, central composite design (CCD) with four variables was applied. The polymeric sorbent Oasis® HLB presented the best performance. Validation results were satisfactory, since the method presented recoveries between 74 and 118% with relative standard deviations (RSD) < 19% for the spike levels of 0.04 to 8.0 μg L-1. The analytical performance presented method detection and quantification limits of 0.012 to 0.6 and 0.04 to 2.0 μg L-1, respectively. The proposed method combines a simple and effective sample preparation for the determination of emerging contaminants in water using BAμE followed by UHPLC-MS/MS analysis. The method applicability was evaluated using real samples of surface, drinking and tap water and 6 positive samples were found indicating the presence of bisphenol A (0.073 to 0.665 μg L-1) and paracetamol (0.104 to 4.2 μg L-1).

Keywords: emerging contaminants, water, microextraction

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QUANTITATIVE ANALYSIS OF NEONICOTINOID INSECTICIDE RESIDUES IN SURFACE WATER BY HPLC-MS / MS

Authors: Priscila Oliveira Amaral [1], Maíse Pastore Gimenez [1], Daniel Temponi Lebre [2], Joyce Rodrigues Marques [2], Oscar Vega Bustillos [1]
Institution: [1] IPEN/CNEM - SP - Instituto de Pesquisas Energéticas e Nucleares (Av Lineu Prestes, 2242), [2] CEMSA - Centro de Espectrometria de Massas Aplicada (Av Lineu Prestes, 2242)

Abstract:

The sudden disappearance of bees in colonies of several countries have attracted the attention of scientists, the public and the world press [1]. This phenomenon was called Colony Collapse Disorder (CCD) and is characterized by a rapid loss of adult bee population. In these colonies, the queen is still alive and accompanied by few adult bees although there are still pups and food in the hive [2]. There are several hypotheses about the causes of this phenomenon; one of them relates a bees exposure for a class of pesticides named neonicotinoids. These are a class of insecticides which began to be produced in 1985 and are based on the nicotine molecule [3]. These insecticides are used to control sucking and chewing insects because of its low toxicity to mammals, fishes and birds, and high toxicity to arthropods, especially insects and crustaceans [4]. The neonicotinoids used in this study are Clothianidin, Imidacloprid and Thiamethoxam. There is no legislation in Brazil to determine the residual limit in water to any of these pesticides, however, the EPA (United States Environmental Protection Agency) has a legislation with limits for each compound. The residual limit for chronic exposures in surface water is 2.1 µg L-1 for Clothianidin [5], 15.8 µg L-1 for Imidacloprid [6] and 0.6 µg L-1 for Thiamethoxam [7]. This study intends to develop and validate a methodology for neonicotinoids in surface water by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS / MS). The samples for this study are surface water collected from a lake in the Bauru country in São Paulo state. The choice of this lake is because its proximity to sugar cane, orange, coffee and watermelon crops. These samples were filtered through a vacuum filtration system and passed through a sample preparation process using the solid phase extraction (SPE). Strata X cartridge was conditioned with methanol - dichloromethane (1:1) and ultrapure water. The water sample was eluted from the cartridge with an alkaline pH range between 9.90 to 10.10, and the analytes of interest were eluted with methanol - dichloromethane (1: 1). The analysis of HPLC-MS / MS used a High Performance Liquid Chromatograph 1100 series by Agilent with an API 2000 mass spectrometer from Sciex. The analysis performed on Multiple Reaction Monitoring (MRM) mode selecting a quantization and confirmation ion for each compound. The quantitation limits are between 1 - 2.5 µg L-1, and the linearity are between 0.991 – 0.997 in this method.

Keywords: Neonicotinoids, Mass Spectrometry, HPLC - MS/MS, SPE, Bees

Financial support agency: CAPES

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