

Development of Ultrasonic Assisted Extraction Method of Emerging Contaminants in Freshwater Sediments

Diana Nara Ribeiro de Sousa¹, Guilherme Martins Grosseli¹, Mariele Barboni Campanha¹, Renato Lajarim Carneiro¹, Antonio Aparecido Mozeto¹, Pedro Sérgio Fadini¹

¹Universidade Federal de São Carlos – UFSCar, Rod. Washington Luís km 235, São Carlos/SP, Brazil.

Phone: +55-(16)-3351-8212

E-mail: psfadini@gmail.com

Introduction: The determination of emerging contaminants in water, soils, sediments, sludge and suspended matter has become a requisite stage for the partition evaluation of these contaminants. For sediment samples, extraction methods include Soxhlet, pressurized liquid extraction (PLE), microwave assisted extraction (MAE) and ultrasound assisted extraction (UAE). Among these, UAE has been shown very promising due to its lower cost, easy processing and availability [1]. In this work, different procedures of extraction by ultrasound were tested to extract 11 emerging contaminants.

Methods: Methanol, water, acetone, ethyl acetate and different mixtures of these were used as extraction solvents. Firstly, 2.00g of dry sediment, was spiked to 100 ng.g⁻¹ with a solution containing all target compounds and respective deuterated and submitted to successive steps of extraction in three different experiments. In the first one, samples were ultrasonicated with 5 mL of methanol, 5 mL methanol:water (1:1) and 2 mL of acetone successively. In each step, samples were homogenized in vortex, ultrasonicated for 30 min and centrifuged at 5000 rpm for 5 min. The supernatants of each sample were combined, homogenized and diluted to 250 mL with Milli-Q water. The other two experiments involved differentiation with respect to steps with 2 mL of ethyl acetate and 3 mL of methanol:water (1:2, pH 2), respectively. The clean-up procedure was carried out using Oasis HLB (200 mg, 6 cc) cartridges, conditioned with 2x5 mL of methanol and 2x5 mL of Milli-Q water. After extraction, cartridges were rinsed with 2x4 mL Milli-Q water and dried for 30 min. Elution was performed with 2x3 mL of methanol and 3 mL of methanol:acetone (1:1). The extract was evaporated under nitrogen stream and reconstituted with 1 mL of methanol:water (25:75). Analyses were performed in a TQD Waters system. In the next stage, it was evaluated different ultrasound exposition times, the influence of pH and recoveries values at three different levels of spiking (10, 50 and 100 ng.g⁻¹).

Results: The experiments E1 and E2 presented recoveries values above 60% for all compounds except for atenolol and propranolol.

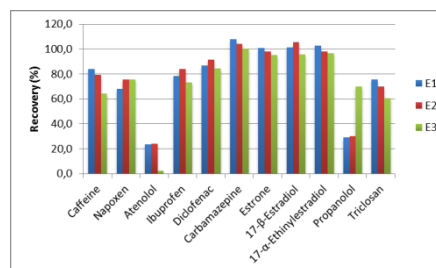


Fig. 1: Observed recoveries values for the three different methodologies investigated.

In an attempt to increase the atenolol and propranolol recoveries, it was investigated the effect of pH variation. Recoveries of propranolol and atenolol at pH 2 were 70% and 2.6%, respectively (E3) and at pH 8 both compounds presented recoveries around 40% without compromising the quality of results. The exposition time to the ultrasound was optimized in 10 minutes and experiments at different levels of spiking were performed with this time and pH 8.

Table 1: Observed recovery values at different levels (ng.g⁻¹) of spiking (n=3).

Compound	10	50	100
Caffeine	84.7	83.7	80.4
Naproxen	59.5	66.5	51.9
Atenolol	39.9	39.6	40.2
Ibuprofen	72.5	77.2	57.9
Diclofenac	81.7	88.2	79.2
Carbamazepine	95.0	93.6	93.6
Propranolol	38.0	39.4	44.1
Triclosan	95.4	73.3	92.1
Estrone	67.0	95.8	84.6
17-β-Estradiol	70.9	89.1	87.6
17-α-Ethinylestradiol	59.5	99.3	87.6

Discussion: According to results, the developed methodology allows the simultaneous determination of 11 emerging contaminants in freshwater sediments showing 9 recoveries values in accordance with the Council Directive 96/23/EC and standard deviation lower than 10% in all the replicates, pointing the potential applicability of the proposed method.

Acknowledgements: FAPESP (2010/01731-0), CNPq (142495/2011-5), PETROBRAS.

References: [1] Tadeo et al. (2012) *Cent. Eur. J. Chem.* **10(3)** : 480-520 .