

Cleanup strategies and advantages in the determination of several therapeutic classes of pharmaceuticals in wastewater samples by SPE–LC–MS/MS

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Abstract This work describes the development and validation of an offline solid-phase extraction with simultaneous cleanup capability, followed by liquid chromatography–(electrospray ionisation)–ion trap mass spectrometry, enabling the concurrent determination of 23 pharmaceuticals of diverse chemical nature, among the most consumed in Portugal, in wastewater samples. Several cleanup strategies, exploiting the physical and chemical properties of the analytes vs. interferences, alongside with the use of internal standards, were assayed in order to minimise the influence of matrix components in the ionisation efficiency of target analytes. After testing all combinations of adsorbents (normal-phase, ion exchange and mixed composition) and elution solvents, the best results were achieved with the mixed-anion exchange Oasis MAX cartridges. They provided recovery rates generally higher than 60%. The precision of the method ranged from 2% to 18% and 4% to 19% (except for diclofenac (22%) and simvastatin (26%)) for intra- and inter-day analysis, respectively. Method detection limits varied between 1 and 20 ng L⁻¹, while method quantification limits were <85 ng L⁻¹ (both

excluding ibuprofen). This analytical method was applied to gather preliminary results on influents and effluents of two wastewater treatment plants (WWTPs) located in the urban region of Porto (Portugal). Typically, paracetamol, hydrochlorothiazide, furosemide, naproxen, ibuprofen, diclofenac and bezafibrate were detected in concentrations ranging from 1 to 20 µg L⁻¹, while gemfibrozil, simvastatin, ketoprofen, azithromycin, bisoprolol, lorazepam and paroxetine were quantified in levels below 1 µg L⁻¹. These WWTPs were given particular attention since they discharge their effluents into the Douro river, where water is extracted for the production of drinking water. Some sampling spots in this river were also analysed.

Keywords Pharmaceuticals · Wastewater · Cleanup · MAX cartridges · Liquid chromatography–tandem mass spectrometry (LC–MS/MS) · Surface water

Introduction

Emerging pollutants are defined as compounds that are not currently covered by the existing legislation in the area of water quality, whose environmental impact is not yet sufficiently studied and which are thought to be potentially harmful to environmental ecosystems and human health [1]. They encompass a wide range of products, including pharmaceuticals, personal care products, fragrances, detergents, plasticisers, flame retardants, pesticides and several other classes (NORMAN FP6 Project, http://www.norman-network.net/index.php.php?module=public/about_us/emerging&menu2=public/about_us/about_us#substances).

The environmental occurrence of pharmaceutical products is known since the 1970s, first in the USA and almost one decade later in the UK (England) [2]. Concerns about the

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