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Review

Advantages and limitations of on-line solid phase extraction coupled to liquid chromatography–mass spectrometry technologies versus biosensors for monitoring of emerging contaminants in water

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Abstract

On-line solid phase extraction (SPE) coupled to liquid chromatography–mass spectrometry (LC–MS) and biosensors are advanced technologies that have found increasing application in the analysis of environmental contaminants although their application to the determination of emerging contaminants (previously unknown or unrecognized pollutants) has been still limited. This review covers the most recent advances occurred in the areas of on-line SPE–LC–MS and biosensors, discusses and compares the main strengths and limitations of the two approaches, and examines their most relevant applications to the analysis of emerging contaminants in environmental waters. So far, the on-line configuration most frequently used has been SPE coupled to liquid chromatography–(tandem) mass spectrometry. Sorbents used for on-line SPE have included both traditional (alkyl-bonded silicas and polymers) and novel (restricted access materials (RAMs), molecularly imprinted synthetic polymers (MIPs), and immobilized receptors or antibodies (immunosorbents) materials. The biosensor technologies most frequently applied have been based on the use of antibodies and, to a lesser extent, enzymes, bacteria, receptors and DNA as recognition elements, and the use of optical and electrochemical transducing elements. Emerging contaminants investigated by means of these two techniques have included pharmaceuticals, endocrine disrupting compounds such as estrogens, alkylphenols and bisphenol A, pesticides transformation products, disinfection by-products, and bacterial toxins and mycotoxins, among others. Both techniques offer advantageous, and frequently comparable, features such as high sensitivity and selectivity, minimum sample manipulation, and automation. Biosensors are, in addition, relatively cheap and fast, which make them ideally suited for routine testing and screening of samples; however, in most cases, they can not compete yet with on-line SPE procedures in terms of accuracy, reproducibility, reliability (confirmation) of results, and capacity for multi-analyte determination.

Keywords: Biosensor; On-line solid phase extraction; Emerging contaminants; Water; Analysis

Contents

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1. Introduction. Analysis of emerging contaminants

Emerging contaminants are previously unknown or unrecognized pollutants. Most of them have been present in the environment for a long time, but their significance and presence are only now being elucidated and, therefore, they are generally not included in the legislation. There is not a clear agreement about which compounds can be considered as emerging pollutants. They can be classified under this category according to their chemical class (chemicals of totally new structure), type of use (new uses in industry or in consumer realms), type of effect (new discovered effects), source (new or previously unknown origins for existing chemicals), and exposure (pathways that had not been anticipated or had been previously discounted as not possible) [1]. Taking into account these criteria, compounds that can be considered as emerging contaminants are the so-called pharmaceuticals and personal care products (PPCPs), steroids, xenoestrogens and other endocrine disrupting compounds (EDCs), methyl *tert*-butyl ether (MTBE) and related compounds, surfactants and their metabolites (alkylphenolic compounds, linear alkylbenzenesulfonate (LAS) and sulfophenyl carboxylates (SPC)), drinking water disinfection by-products (DBPs) including *N*-nitrosodimethylamine (NDMA) and nitrosamines, gasoline additives, brominated flame retardants (polybrominated diphenyl ethers), industrial additives and agents, algal toxins, cryptosporidium, giardia (and other pathogens), organotins, perfluorooctanoic acid (PFOA) and perflluorooctanesulfonate (PFOS), pesticide degradation products, chiral contaminants, chemical warfare agents, and a variety of miscellaneous chemicals such as caffeine, cholesterol, etc.

Among the various compounds considered as emerging pollutants, alkylphenolic surfactants, steroid sex hormones, and pharmaceuticals are of particular concern, both because of the volume of these substances used and because of their activity as endocrine disruptors or as causative agents of bacterial resistance, as is the case of antibiotics [2]. Pharmaceuticals, including veterinary and human antibiotics, analgesics, anti-inflammatories, psychiatric drugs, lipid regulators, beta-blockers and X-ray contrast agents, although present at rather low levels in the environment (ranging from ng/L to μg/L), have become an important issue in the last few years due to their continuous release in the environment, mainly through excreta, disposal of unused or expired drugs or directly from pharmaceutical discharges [3,4]. Freely excreted drugs and derivatives can escape degradation in municipal sewage treatment plants (STPs) and even the conjugates can be hydrolysed back to the free parent drug [5]. Effluents of STPs are discharged to receiving surface waters, and the pharmaceuticals can subsequently be found in ground and drinking waters [6–9]. Pharmaceuticals are designed to be bioactive and to elicit a specific beneficial mode of action in humans. However, at higher doses, adverse side effects may be encountered. It can be expected that any effect, beneficial or adverse, could also occur in aquatic organisms with similar biological functions and receptors. Exposure in the aquatic ecosystem is of particular concern, since aquatic organisms are subject to continual introduction into surface waters from STPs. This fact makes these pollutants, even those that have relatively short environmental half-lives, to be assumed as "pseudopersistent". Moreover, the polar and non-volatile nature of some drugs prevents their escape from the aquatic realm [10]. A well-known example of detrimental environmental effects caused by drugs is the endocrine disrupting effect of steroid hormones in fish. Moreover, it cannot be excluded that pharmaceuticals act through additional unknown modes of toxic action on non-target organisms [11]. Steroid hormones, both natural and synthetic, can be found in the environment as a result of human or animal excretion due to growing population concentration and intensive farming. Hormones, such as estradiol, estrone and ethynylestradiol, have been found in water at ng/L levels [12–15] but, even at these low concentrations, some of them may induce estrogenic responses and cause adverse effects on aquatic and terrestrial organisms and on humans. Whereas PPCPs are defined by chemical class and type of use, EDCs are defined according to type of biological effect or mechanism of action [1,16] and thus, a wide variety of pollutants from numerous chemical classes can be collectively referred to as EDCs. Within the group of PPCPs, antibiotics are considered one of the biggest concern of all the emerging contaminants, since they can promote antibiotic resistance [17]. In fact, the increasing use of these drugs in livestock, poultry production, and fish farming during the last decades has caused a genetic selection of more harmful bacteria [18].

For most of the emerging contaminant classes there are hardly any environmental survey data, basically because they are not, or have not been, regulated in the environment. Another reason for this is the lack of analytical methods for a proper risk assessment and for monitoring of waste, surface and drinking water quality. For many years, the analysis of organic micro-contaminants has been performed by high performance liquid chromatography coupled to ultraviolet detection (HPLC–UV) and gas chromatography (GC) coupled to flame ionization detection (GC–FID), electron capture detection (GC–ECD) and mass spectrometry (GC–MS). However, after the introduction of atmospheric pressure ionization, liquid-chromatography coupled to mass spectrometry (LC–MS) has largely replaced GC methods. LC–MS presents various advantages, such as reduced