Trends in Analytical Chemistry 82 (2016) 199–207

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices

K. Mogolodi Dimpe, Philiswa N. Nomngongo *

Department of Applied Chemistry, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg 2028, South Africa

ARTICLE INFO

Keywords:
Emerging pollutants
Sample pretreatment methods
Pharmaceuticals
Personal care products
Endocrine disrupting compounds
Environmental samples
Chromatographic techniques

ABSTRACT

Emerging contaminants such as pharmaceuticals, personal care products, and endocrine disrupting compounds are ever-present in environmental matrices and they are known to pose negative effects on living organisms. The determination of these pollutants in different environmental matrices (such as water, soil, and sediments, among others) frequently requires separation techniques that are capable of high efficiency, unique selectivity and high sensitivity. However, direct analysis of these pollutants in complex matrices is difficult. For this reason, rapid, inexpensive, efficient and environmentally friendly sample preparation techniques have been developed prior to chromatographic quantification. Therefore, the aim of this article is to review recent publications (2010–2016) on modern sample preparation techniques combined with chromatographic techniques for identification and quantification of emerging pollutants in environmental matrices. These sample preparation techniques include solid phase extraction, solid phase microextraction, liquid-liquid extraction, microwave-assisted extraction, liquid-phase microextraction techniques, stir bar sorptive extraction, and pressurized liquid extraction, among others.

Contents

Abbreviations: ASE, accelerated solvent extraction; BDE, bromodiphenyl ether; BFRs, brominated flame retardants; BSAs, benzenesulfonamides; BTRs, benzotriazoles; BTs, benzothiazoles; BZPs, benzodiazepines; CTAB, cetyltrimethylammonium bromide; DDT, dichlorodiphenyltrichloroethane; DEET, N,N-Diethyl-*meta*-toluamide; DI-SPME, direct-immersion solid phase microextraction; DLLE, dispersive liquid-liquid extraction; DSPE, dispersive solid phase extraction; DSPME, dispersive solid phase microextraction; DVB, divinylbenzene; EDCs, endocrine disrupting compounds; ESE, enhanced solvent extraction; GC-FID, gas chromatography–flame ionization detection; GC-MS, gas chromatography–mass spectrometry; GC-NCI-MS, gas chromatography negative chemical ionization mass spectrometry; HF-LPME, hollow fiber liquid-phase microextraction; HLB, hydrophobic-hydrophilic balanced; HPLC, high performance liquid chromatography; HPLC-DAD, high performance liquid chromatography-diode array detector; HSE, high-pressure solvent extraction; HS-SPME, headspace solid phase microextraction; IL-USA-DLLME, ionic liquid-based ultrasound assisted dispersive liquid-liquid microextraction; LC-MS, liquid chromatography coupled to mass spectrometer; LC-MS/MS, liquid chromatography time-of-flight mass spectrometry; LLE, Liquid-liquid extraction; LOD, limit of detection; LOQ, limit of quantification; LPME, Liquid Phase Microextraction; MNP, magnetic nanoparticles; MWCNTs, multiwalled carbon nanotubes; MAE, Microwave assisted extraction; MS-DLLME, magnetic stirring assisted dispersive liquid–liquid microextraction; NPs, nanoparticles; NSAIDs, nonsteroidal anti-inflammatory drugs; PAHs, polycyclic aromatic hydrocarbons; PBDE, polybrominated diphenyl ethers; PCBs, polychlorinated biphenyls; PDMS, polydimethylsiloxane; PFE, pressurized fluid extraction; PLE, pressurized liquid extraction; QuEChERS, quick, easy, cheap, effective, rugged and safe; RDSE, rotating disk sorptive extraction; RSD, relative standard deviation; SBSE, stir bar sorptive extraction; SUPRAS, supramolecular solvents; SPE, solid phase extraction; SPME, solid phase microextraction; TCC, triclocarban; TCS, triclosan; TG-MS, thermogravimetry-mass spectrometry; UA-LLME, ultrasound-assisted liquid-liquid microextraction; UPLC-MS/MS, ultra performance liquid chromatography coupled to mass spectrometer; UV, ultraviolet; VA-DLLME, vortex-assisted dispersive liquid–liquid microextraction; WWTP, wastewater treatment plant; XPS, x-ray photoelectron spectroscopy.

* Corresponding author. Tel.: +27 115596187; Fax: +275596425.
E-mail address: pnnomngongo@uj.ac.za or nomngongo@yahoo.com (P.N. Nomngongo).

http://dx.doi.org/10.1016/j.trac.2016.05.023
0165-9936/

1. Introduction

The presence of emerging pollutants in environmental matrices has been reported in the literature and their occurrence in the environment poses a significant risk to the ecosystem. According to EPA [1], emerging pollutants are classified as pollutants that have found their way to humans and animals due to the newly discovered source. These pollutants have no guidelines or legislative intervention that is currently available to regulate their presence in the environment [2–6]. Human activity such as personal care, healthcare, and industrial operations entails the use of chemicals that produces or generates waste [7]. The latter contains contaminants that are in water systems. The contaminants in the waste are usually resistant to degradation. Therefore, they tend to accumulate in the environment which eventually becomes a hazard to living organisms [7]. For this reason, this contaminant calls for legislative intervention because of their elevated levels in our water bodies [2]. Emerging pollutants include products that are intensively used in large quantities on daily basis such as health and beauty products [2,8]. These pollutants are mainly categorized into synthetic (man-made compounds) and natural chemicals (hormones excreted by invertebrates and vertebrates) [9].

In the last decades, extensive studies have proven the presence of emerging pollutants (parent compound) and their metabolites in groundwater, storm wastewater, drinking water, surface water, plants and wastewater [9]. However, the common playground of emerging contaminants is the industrial and domestic wastewater treatment plants (WWTPs) which receive wastewater coming from human activities and of industrial discharges [10,11]. The indication of these organic pollutants is mostly evident in municipal WWTPs [9] and other sources (agricultural and industrial activities) that spread the pollutants in various water sources such as river, dams, lakes and oceans [10]. Biosolids (sewage sludge) is one of the by-products that attract emerging pollutants and are eventually applied in an agricultural soil as a fertilizer [12]. Emerging pollutants present in fertilizers poses a possibility of getting into agricultural produce (food) which will have a negative impact on the quality of the food and may be a hazard to human health [13]. In addition, stormwater runoff is one of the possible sources of emerging pollutants such as plasticizers, flame retardants, and pesticides [9]. There are numerous types of emerging contaminants in the environment. These pollutants include pharmaceuticals (acidic and basic), personal care products (PCPs), pesticides, surfactants, endocrine disrupting compounds (EDCs), disinfection byproducts and detergents [14–16]. Among the aforementioned types of emerging pollutants, pharmaceuticals, personal care products, and endocrine disrupting compounds are of great interest. Table 1 summarizes some different types of pharmaceuticals, personal care products, and endocrine disrupting compounds that have reported in the in environmental matrices.

In this review, the most recent published work regarding the emerging pollutants will be thoroughly covered, especially the sample preparation methodologies that applied for analysis of these pollutants in environmental samples. The review also discusses the advantages and disadvantages of various sample preparation techniques as well as future perspectives related to the development of new sample preparation methods that will be specific to different kinds of emerging pollutants. Due to the fact that there is a myriad of emerging pollutants, this review focuses on emerging pollutants such as pharmaceuticals, PCPs, and EDCs present in the environment.

Table 1
Emerging pollutants found in the environment [7,17,18]

Chemical name	Sources or use
Paracetamol	Analgesic/Antipyretic
Amoxycillin	Broad spectrum antibiotic
Metoprolol succinate	β- blocker for blood pressure control
N,N-Diethyl-*meta*-toluamide (DEET)	Mosquito repellent
Triclosan	Disinfectant, antimicrobial
Benzophenone	Fixative for perfumes and soaps
Dieldrin, Aldrin, Endrin, β-endosulfan	Organochlorine pesticides
Bisphenol A	Plasticiser
Benzo[*a*]pyrene	Regulated PAHs, used in cancer research
Tributyltin, cyhexatin	Organotin compounds
vinclozolin	Fungicide
Atrazine, simazine, terbutylazine, 2,4-D, 2,4,5-T	Herbicides

2. Sample preparation techniques

Direct analysis of emerging pollutants in complex matrices is difficult because in some samples they are present low concentrations and are associated with the sample matrix [19]. For this reason, it is difficult to predict their transport and fate in the environment because of the lack of information about them [2]. In order for researchers to overcome such a predicament, sample preparation step needs to be carefully examined [2]. Sample preparation may include filtration, pH adjustment, extraction, clean-up and pre-concentration procedures to ensure that the analytes are found at a suitable concentration level [20]. Currently, sample preparation is moving towards environmental friendliness, low cost, miniaturization, automation and simplicity [21]. The following section discusses the application of different sample preparation techniques such solid phase extraction, solid phase microextraction, microwave assisted extraction, liquid-liquid extraction, liquid phase microextraction, pressurized liquid extraction and stir bar sorptive extraction method, among others, that have been used for preconcentration and extraction of different emerging pollutants in different matrices.

2.1. Solid phase extraction (SPE)

Solid phase extraction is one of the most extensively used sample preparation technique for environmental samples [11,21,22]. This technique was first developed in the 1980s and ever since then, it has proven to be the most powerful tool for the isolation and purification of target analysis [23]. The advantages of SPE include simplicity, flexibility, high selectivity, automation, rapidity, higher enrichment factors, and the absence of emulsion and use of different sorbents [24]. The latter include reversed-phase hydrophobic-hydrophilic balanced (HLB) polymeric sorbents, alkyl-modified silica