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Review

Recent advancements and future trends in environmental analysis: Sample preparation, liquid chromatography and mass spectrometry

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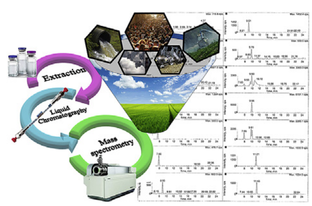
HIGHLIGHTS

- Recent techniques for the extraction of emerging contaminants have been described.
- Advancements in LC-MS analysis of emerging contaminants have been illustrated.
- Advantages and shortcomings of each technique have been discussed.
- Latest LC-MS applications in the environmental research area have been presented.
- Future trends in environmental analysis have been identified.

GRAPHICAL ABSTRACT



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ABSTRACT

Among the thousands of chemicals having potential to enter the environment, the NORMAN network has identified at least 700 substances categorized into 20 classes in the European surface waters. Pesticides, pharmaceuticals, disinfection by-products, wood preservation and industrial chemicals are the prominent classes. Since the impact of these substances on aquatic life and human health might be dramatic, action is urgently required at multiple levels; one of them is just related to the development of more and more sensible and selective analytical methods.

Abbreviations: APPI, atmospheric pressure photoionization; BEH, bridged ethylsiloxane/silica; BFRs, brominated flame retardants; CE, collision energy; CNTs, carbon nanotubes; DART, Direct Analysis in Real Time; DDA, data-dependent acquisition; DESI, Desorption Electrospray Ionization; DLLME, dispersive liquid-liquid microextraction; d-SPE, dispersive solid-phase extraction; EPA, Environmental Protection Agency; EPI, enhanced product ion; FAEs, fatty alcohol ethoxylates; FQs, fluoroquinolones; FMMs, functionalized magnetic materials; G, graphene; GCB, graphitized carbon black; HF, hollow fibre; HF-LPME, hollow fibre liquid phase microextraction; HILIC, hydrophilic interaction liquid chromatography; HPLC, high performance liquid chromatography; HRMS, high resolution MS; HSS, High Strength Silica; HTLC, high temperature liquid chromatography; IDA, Information-Dependent Acquisition; IL, ionic liquid; IMMS, Ion mobility MS; LDTD, laser diode thermal desorption; LLE, liquid–liquid extraction; LPME, liquid phase microextraction; LRMS, low resolution MS; ME, Matrix effect; MS, mass spectrometry; MAX, mixed-mode/anion-exchange; MCX, mixed-mode/cationic-exchange; MEPS, microextraction by packed sorbent; MIP, molecular imprinted polymer; MISPE, Molecularly imprinted SPE; MMIP, magnetic MIP; MOFs, metal-organic frameworks; MON, microporous organic network; MRM, multiple reaction monitoring; MWCNTs, multi-walled-CNTs; nanoLC, nano liquid chromatography; MSPE, magnetic solid-phase extraction; OMPs, organic micro-pollutants; PAHs, polycyclic aromatic hydrocarbons; PDA, polydopamine; QqQ, triple quadrupole; QqQ_{LIT}, Quadrupole-linear ion trap; RTIL, room temperature IL; SBSE, stir bar sorptive extraction; SPE, solid phase extraction; SPME, solid phase microextraction; SWCNT, single-walled CNT; SWE, subcritical water extraction; TCIL-DLLME, temperature-controlled ionic liquid; TNTs, TiO_2 nanotubes; 2D-LC, two-dimensional LC; TFC, turbulent flow chromatography; TOF, time-of-flight; US-IL-DLLME, ultrasound-assisted ionic liquid DLLME; U(H)PLC, ultra(-high) performance liquid chromatography; WAX, weak anion–exchange; ZIF-8, zeolite imidazolate framework 8.

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This review highlights the latest advancements and trends in liquid chromatography–mass spectrometry based environmental analysis. Specific sections are dedicated to novelties in sample preparation, chromatographic separation and mass spectrometry detection of emerging pollutants. The review also offers insights on last generation chromatographic and extraction materials, technological progresses and innovative methodological approaches for target and non-target analysis. As numerous papers have been published in this field, this overview covers the most representative and original works published in the 2011–2016 period.

Contents

1. Introduction

A rigorous evaluation of environmental contamination requires constant innovation in technologies, chromatographic materials and analytical approaches to gain early identification and accurate quantification of every substance able to compromise flora, fauna and public health integrity.

The first list of priority pollutants, created by the US Environmental Protection Agency (EPA), contained almost only organic compounds that were detectable with gas chromatography-mass spectrometry (GC-MS). Nevertheless, since the late 80s, liquid chromatography–mass spectrometry (LC-MS) has rapidly grown in popularity as technique for environmental control. Compared to GC-MS, it offers a series of advantages compatible with the polar nature of most contaminants: elimination of the derivatization step of non-volatile and heat-labile compounds, increase of the number of analysable chemicals and reduction of the total analysis time.

Nowadays, environmental analysis is one of the most important application areas of LC–MS, mainly related to the study of occurrence and fate of organic micro-pollutants (OMPs). Almost all OMPs are polar contaminants that enter the environment during their production, consumption and disposal at ppm level or lower. Besides classical contaminants, mainly pesticides, OMPs also include the so-called "emerging contaminants". These last are substances of natural (toxins, hormones, etc.) and synthetic origin (pharmaceuticals, nanomaterials, perfluorinated compounds, UV filters, plasticizers, flame retardants, illicit drugs, etc.) that neither were considered as a risk nor were included in national monitoring plans so far. An attempt to give an updated list of these substances has given by the NORMAN network on its website [1]. Fig. 1 provides a coarse idea of the wide application range of LC-MS and how it is the technique of choice for analysis of most OMPs.

At present, an overwhelming number of chemicals are in use worldwide. Their inevitable entry into the environment affects all compartments and, by extension, the related ecosystems. Transformation products and metabolites contribute to increase the number of OMPs to be monitored since their eco-toxicity can be comparable or more dangerous than that of the original compounds [2,3]. Hitherto, chemical structures, occurrence and effects of such by-products are only partially known. For these reasons, one of the latest trends is to expand analytical strategies to monitor a number of chemicals as large as possible and investigate their fate in wastewater treatment plants and in the environment. Nevertheless, the wide variety of compounds and their different physicochemical properties (pKa, $\log P_{ow}$, etc.) complicate the development of a "universal" method for the large-scale determination/screening of OMPs and their degradation products. It is just to reach such goal that the scientific community has spent time and energy in developing advanced instrumentation, novel chromatographic materials and more effective analytical approaches.

Due to the public interest for the environmental issues, the research in such a field is extremely active and a large number of papers have continuously been published every year. In the same way, the literature is rich of reviews that have been aimed at covering the several facets of environmental investigations: development of novel extraction strategies [4–8], fast chromatographic methods [9–11], use of mass spectrometry (MS) for target and non-target analysis [12–15], strategies for identification of transformation products [2,16]. The aim of this review is to present the current state-of the-art and future trends in approaching environmental analysis by means of the modern LC-MS techniques and the most recent techniques for sample preparation. Hundreds of publications were considered 225 of them were selected at this end. Topics of discussion have been focused on last generation chromatographic and extraction materials, technological progresses and innovative methodological approaches, by pinpointing pros and cons. Since it is almost impossible to be comprehensive in coverage of all analytes, instruments, extraction techniques and applications, we have concentrated our attention on works published between 2011 and 2016.