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Trends in liquid chromatography coupled to high-resolution mass spectrometry for multi-residue analysis of organic micropollutants in aquatic environments



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ABSTRACT

The spectrum of identified organic trace compounds in the aquatic environment is most probably only “the tip of the iceberg”. Modern liquid chromatography coupled to time-of-flight and Orbitrap high-resolution mass spectrometry (HRMS) promise to extend knowledge on the environmental occurrence and fate of (un)known micropollutants. Thanks to its unique ability to measure analytes based on accurate mass, full-spectrum HRMS can simultaneously gain qualitative and quantitative information of a virtually unlimited number of analytes.

This critical review covers recent trends and advances in this field, as reported over the period 2003–14. We focus on five key topics: multi-residue aspects of HRMS-based analysis, accurate mass measurement, suspect and non-target screening, selective quantification, and the combined use of quantitative and qualitative HRMS. The acquired insights provide stepping stones to improve understanding of the specific nature of state-of-the-art HRMS, and the challenges and the prospects for future research.

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1. Introduction

Clean water is one of humans' first needs and a precious resource, so the new European Water Policy aims to “get polluted waters clean again, and ensure clean waters are kept clean” (EU Water Framework Directive 2013/39/EU). A decade of advances in environmental analytical chemistry has resulted in the discovery

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of an increasing number of anthropogenic emerging organic contaminants [1–6]. In addition, there is growing awareness that even more unknown contaminants (such as transformation products) are dispersed in the aquatic environment at very low concentrations [microgram down to sub-nanogram per liter (μg – sub-ng/L)] [7–9]. This continual chemical burden on the environment, next to the bio-recalcitrance and the intrinsic ability of contaminants to interfere with organisms, concerns the scientific community because potential (eco)toxicological effects can be a threat to the good ecological status of water bodies and to healthy drinking water.

Although, for many organic contaminants, their environmental fate is not well understood and detailed ecotoxicological knowledge is lacking, some contaminants have been shown to cause endocrine-disrupting effects [e.g., estrogens, steroids, surfactants and phthalates [10–12]], behavioral changes [e.g., psychiatric drugs in fish [13]], or other toxic effects in aquatic organisms [e.g., antidepressants in marine snail [14], and anti-inflammatory drug diclofenac in fish [15]] at environmentally-relevant concentrations. Also, the presence of antibiotics has been related to increased bacterial resistance in wastewaters and the environment [16–18]. Sustainable water-resource management therefore necessitates increasing efforts in measurement as a prerequisite to studying the occurrence and the fate of these organic micropollutants passing between wastewaters, surface waters, groundwater and drinking water.

Tandem mass spectrometry (MS/MS) coupled to (ultra)-high-performance liquid chromatography [(U)HPLC] has shown merit in meeting the demand for targeted multi-residue analysis of organic micropollutants in water, and in confirming and quantifying down to sub-ng/L [19]. However, new analytical opportunities arose with the development of modern time-of-flight (TOF) and Orbitrap high-resolution mass spectrometry (HRMS) providing appropriate sensitivity and identification over the full spectrum [20].

In the past decade, multi-residue LC-HRMS methods were developed for the analysis of organic contaminants in environmental waters, such as drinking water, groundwater, surface waters, including seawater and fresh water, and (biologically-treated) wastewaters. The majority of these methods were developed for the analysis of pharmaceuticals [21–37], pesticides [23,25,27,29–31,38–40], drugs of abuse [41–44], and their known degradation products. Interest in analyzing these classes of anthropogenic micropollutants using full-spectrum HRMS may relate to the large number of substances and degradation products (e.g., only a fraction of more than 3000 pharmaceuticals have been investigated in environmental studies so far [2]), which are continually released to the environment from anthropogenic activities [45] (e.g., (industrial) wastewaters, landfills, agriculture, aquaculture, and livestock breeding). Other classes of targeted micropollutants investigated included endocrine-disrupting substances [46], benzothiazoles and benzotriazoles [47], surfactants [48], sweeteners [49] and flame retardants [29].

This critical review covers the achievements in LC-HRMS in qualitative and quantitative full-spectrum analysis of emerging organic micropollutants in environmental waters over the period 2003–14. The backbones are two tables providing main information on 35 validated quantitative HRMS methods (Table 1) and 21 HRMS-based screening techniques (Table 2). Five key topics are postulated and used as steppingstones to give better insight into the specific nature of state-of-the-art, full-spectrum HRMS and the challenges for future research. In Section 2, we discuss general analytical aspects, which must reflect the multi-residue concept of HRMS. In Section 3, we review insights into the nature of HRMS and the related selectivity and mass accuracy. Building on the unique ability of HRMS to identify analytes from the measured accurate mass, the newest trend in HRMS is screening towards unknown contaminants. Section 4 sets out related achievements and opportunities for screening of environmentally-relevant contaminants. In Section 5, we review

quantitative aspects of HRMS and the relationship between resolving power and selectivity. Section 6 discusses the performance of (tandem) HRMS with state-of-the-art MS/MS as a benchmark.

2. General aspects of multi-residue HRMS-based analysis

An important aspect of full-spectrum HRMS is that it allows the simultaneous measurement of a variety of analytes over a broad m/z range. However, the whole analytical procedure, starting from sampling, through sample storage and sample pretreatment, to instrumental LC-HRMS analysis, must reflect the multi-residue concept. A variety of substances having very different physico-chemical characteristics must perform well throughout the whole analytical procedure.

With respect to the 35 validated HRMS methods listed in Table 1, solid-phase extraction (SPE) was used in 31 (including four methods applying online-SPE) as the sample-preconcentration and purification technique. One other author used a polydimethylsiloxane passive sampling device [27] in seawater. Although most authors aimed to develop sample-enrichment techniques, such as SPE, for a broad range of substances, some compounds are still preconcentrated selectively, and achieving acceptable recoveries for all compounds is challenging in multi-residue applications [60]. Different SPE cartridge materials have therefore been combined to achieve sufficient enrichment for a broader range of compounds [9] or, in three methods, almost no sample pretreatment and a direct large volume injection (LVI, 100–250 μL) of drinking or surface water on the LC were reported, thereby omitting selective preconcentration procedures [32,42].

For reversed-phase separation, both HPLC and UHPLC have been coupled to TOF or Orbitrap MS using, in most cases, water with methanol/acetonitrile as organic modifier and formic/acetic acid or their ammonium buffers as acidifiers {two authors used ammonium buffers as basic additives [42,52]} for electrospray ionization (ESI) in positive-ion mode (Table 1). For ESI negative-ion mode, the same solvents were applied and, in some cases, small amounts {0.01–0.05 v/v % [25,32]} of formic/acetic acid were added. Although UHPLC separation has been used in about half the studies in order to provide a high chromatographic resolution, HPLC is still widely applied and can be preferred when multiple MS modes are alternated (e.g., full-spectrum MS, MS/HRMS and all ion-fragmentation HRMS for confirmatory purposes) in order to provide sufficient data points across the chromatographic peak.

Finally, the interface, which is ESI for all the reviewed HRMS methods listed in Tables 1 and 2, must also be compatible. Particularly for screening, some authors verified whether the analytes are amenable for the ionization technique used in order to improve the screening performance [8,54]. The need for general quantitative structure-property relationship (QSPR) approaches to predict ionization behavior or ionization efficiencies for chemically different compounds is highlighted in these studies.

3. Selective and accurate mass measurement in HRMS

In HRMS, full spectra providing high mass-resolving power are acquired over the whole chromatogram. The mass-resolving power, which expresses the power to separate adjacent mass peaks, is defined in terms of the full width at half maximum (FWHM) as $\frac{m/z}{FWHM}$ with m/z the mass-to-charge ratio of the measured ion. For near-baseline separation of two adjacent masses, they should differ by at least twice the FWHM in mass [61,62]. Consequently, increasing the resolving power is a key factor in HRMS, allowing better differentiation of ions of interest from background ions and endogenous compounds (i.e., mass-measurement selectivity). As a

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