Rapid non-target screening of organic pollutants in water by ultraperformance liquid chromatography coupled to time-of-light mass spectrometry

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We show the potential of ultra-performance liquid chromatography (UPLC) coupled to time-of-flight mass spectrometry (TOF-MS) for screening of non-target organic pollutants in water samples. The great accuracy and the resolution provided by a TOF analyzer allow the mass of any ionizable component in a sample to be accurately measured.

Efficient screening applied to environmental samples should ideally detect as many pollutants as possible in one analytical run. This makes necessary the use of powerful chromatographic deconvolution software, which can manage the huge amount of MS data acquired after sample analysis so as to detect components in the sample. It is therefore feasible to compare the experimental data versus a home-made library (empirical and/or theoretical) that can contain hundreds of compounds relevant to the environment. When a compound is not found in the library, its deconvoluted accurate-mass spectra can be used to propose its elemental composition.

We apply this strategy to several types of water samples and it has allowed detecting several pesticides (e.g., thiabendazole, imazalil, simazine and diuron) at low ppb levels. We also detected antibiotics (e.g., ofloxacin or ciprofloxacin) and drugs of abuse (e.g., benzoylecgonine, which is a cocaine metabolite). The home-made theoretical library contains more than 500 compounds, including many pesticides and transformation products, antibiotics and several drugs.

UPLC-TOF-MS is an efficient technique for the rapid screening of multi-class organic pollutants in water that requires little sample manipulation. Full-acquisition MS data obtained by TOF-MS provide valuable qualitative information, which facilitates safe identification of many different compounds in samples.

Keywords: Antibiotics; Deconvolution software; Mass spectra library; Non-target; Organic pollutant; Pesticides; Pharmaceuticals; Screening; UPLC-TOF-MS; Water

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1. Introduction

Water-pollution monitoring typically makes use of methods for target analysis, which are normally focused on priority pollutants that are legally regulated or of public concern. The scope of such methods rarely exceeds several tens of analytes, and it is quite unusual to find analytical methods applied to more than 100 organic pollutants. Target-compound

monitoring with, for example, mass spectrometry (MS)-based methods using selected reaction monitoring (SRM) mode is often insufficient to assess the quality of environmental waters as only a limited number of analytes are recorded. Other potentially harmful, non-target analytes might be therefore present in the samples and would not be detected in targeted analysis.

For analytes amenable to gas chromatography combined with MS (GC-MS), identification of non-target compounds is sometimes feasible [1,2], as forward-search methods enable library searching (e.g., the large library of the National Institute for Standards and Testing (NIST)). However, GC-MS, when used without previous derivatization, is only suitable for non-polar, volatile and semi-volatile compounds.

For semi-polar and polar compounds, liquid chromatography combined with tandem MS (LC-MS^2) is normally the technique of choice. Unluckily, in this case, the absence of mass-spectra libraries and the characteristics of collision-induced dissociation (CID) make identification of unknowns complex, time consuming, and not always successful [3–5]. Success of the procedure depends greatly on the availability of compounds databases or libraries for performing the search of an elucidated elemental composition [3–6]. Further restrictions come from the need to preselect relevant ions, which is typically based on ion abundance rather than, for example, compound toxicity.

Some authors [4] have applied genotoxicity tests in individual LC fractions to focus research on only those compounds that may cause some harm in living organisms. However, there could still be limitations with this approach as a result of the intrinsic characteristics and requirements of LC-MS, in relation to chromatography, ionization and fragmentation. Failure to identify the hazardous compound within the fraction of interest is therefore still possible [7].

To obtain an unbiased dataset, full-spectrum acquisition techniques are required. Single-quadrupole and triple-quadrupole instruments generally do not operate in full-scan mode when applied to residue analysis because of the lack of sensitivity. Quadrupole and linear ion-trap instruments normally have higher sensitivity in scan mode, but they have low selectivity because they acquire mass spectra in nominal mass, a drawback that also applies to single-quadrupole and triple-quadrupole analyzers.

By contrast, the time-of-flight (TOF)-MS analyzer provides the selectivity and the sensitivity required for efficient, wide-range screening, as it combines high, full-spectral sensitivity with high mass resolution so as to measure accurately the mass of any ionizable component in the sample. Elemental compositions can be proposed with low mass errors (typically below 5 ppm, according to manufacturers' specifications). TOF-MS can provide a notable amount of chemical information in a single experiment, so this technique is very attractive for performing non-target analysis or for searching for analytes in a post-target way, (i.e. analytes that are selected and searched after MS acquisition) [8,9].

Based on these improved characteristics, GC has been combined with high-resolution TOF-MS (GC-HR-TOF-MS) for non-target screening of GC-amenable organic (micro) pollutants in water [10].

With respect to LC, ultra-performance LC (UPLC) provides fast, high-resolution separation, which increases LC-MS sensitivity and minimizes matrix interference arising from minimal sample preparation. When coupled, UPLC and TOF-MS provide potent analysis, very rich in information on sample composition. Because of the recent development of both technologies, very few applications using UPLC-(Q)TOF-MS have been reported in the environmental field [11–13]. So far, most reported applications have been in the metabolite-profiling field [14–17] although some applications have started to appear in other fields, such as impurity profiling of pharmaceutical-drug substances [18], metabonomics [19] or food safety [20,21].

In this article, we show the applicability of UPLC-TOF-MS for both screening and identification of non-target organic (micro)pollutants in water. For this purpose, data obtained by UPLC-TOF-MS are subjected to interrogation by an application manager, which de-convolutes chromatograms and displays accurate-mass spectra from each peak. Data obtained can be compared against a wide library of relevant contaminants or used to investigate the identity of unknown compounds not included in the library, as we discuss below. A home-made library was created for around 500 compounds, mainly pesticides, but also some antibiotics and some other widely-used pharmaceuticals.

2. Screening methods

Screening methods are normally developed for rapidly determining the presence of contaminants in a sample. Different criteria can be found in the literature about the concepts of target and non-target screening [22]. From our point of view [9], three alternatives might be considered for LC-MS screening methods, depending on the objective of the analysis and, especially, the instrumentation available:

(i) pre-target screening methods, where the analytes are pre-selected before MS-data acquisition, so other positives cannot be revealed;
(ii) post-target screening methods, where all the compounds eluted from the chromatographic column are measured by MS and the m/z of target analytes are extracted afterwards from the total-ion current (TIC) chromatogram; and,