



Comparison of molecularly imprinted, mixed-mode and hydrophilic balance sorbents performance in the solid-phase extraction of amphetamine drugs from wastewater samples for liquid chromatography–tandem mass spectrometry determination

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ABSTRACT

Recent studies have shown that amphetamines and other drugs of abuse residues occur in wastewater. Consequently, several methods have been developed for their determination by solid-phase extraction (SPE) and liquid chromatography–tandem mass spectrometry (LC–MS/MS). However, a major drawback of these methods is the lack of selectivity during SPE that results in reduced sensitivity, due to matrix effects, and in some cases in low precision and poor accuracy. In order to tackle this problem, three different SPE alternatives have been evaluated in this work for the determination of five amphetamines: common hydrophilic balance (Oasis HLB), mixed-mode (Oasis MCX) and molecularly imprinted polymers (MIPs) sorbents. Among them, Oasis HLB showed the worst performance, as three amphetamines (MDA, MDMA and MDEA) could not be determined because of interfering signals in the LC–MS/MS chromatogram, and amphetamine recoveries could not be corrected by the use of the deuterated analogue internal standard. Oasis MCX permitted the determination of all target analytes, but with still strong signal suppression: ca. 70% signal drop with wastewater samples, which could in this case be corrected by the internal standards providing acceptable trueness (overall recoveries: 101–137%), precision (RSD: 2.0–12%) and limits of detection (LOD: 1.5–4.4 ng/L). Alternatively, MIPs rendered cleaner extracts with less matrix effects (ca. 30% signal drop), and thus lower LODs (0.5–2.7 ng/L) and even better trueness (91–114% overall recovery) and precision (1.5–4.4%RSD). The final application of the method with MIP cartridges showed the presence of MDA and MDMA in the seven analysed wastewaters at the 4–20 ng/L level.

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1. Introduction

Zuccato et al. reported cocaine and its main metabolite for the first time as novel emerging pollutants in sewage and surface water in 2005 [1]. One year later, the same authors extended the analytical methodology to the determination of other illegal drugs of abuse and their metabolites, including amphetamines, cannabinoids, opiates, etc. [2]. The application of the method showed these substances occurring in wastewater at concentrations ranging from the low ng/L (e.g. amphetamines) up to the µg/L level (cocaine metabolite). In addition to their environmental concern, the determination of drugs of abuse in wastewater represents a new tool

for the estimation of drug consumption patterns, which should be more precise and direct than the actual methodologies based on population surveys, crime statistics, etc. [1,3,4].

Since those first reports, several researchers have dedicated their efforts to the development of analytical methodologies for the measurement of drugs of abuse and to the estimation of their environmental concentrations and fate. Thus, several publications have shown the ubiquity of these new pollutants, as illicit drugs occurrence in wastewater and surface waters in several European countries – Italy [3,5], Switzerland [3], UK [3,6,7], Belgium [8,9], Germany [10], Ireland [11] and Spain [12–14] – and in USA [15] has already been reported. Even some of these drugs and their metabolites have been found to resist drinking water treatment, reaching tap water at the 1–100 ng/L level [13,14]. Moreover, some recent works have also reported illicit drugs associated to airborne particulate matter [16–19].

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As recently reviewed by Castiglioni et al. [20], liquid chromatography–tandem mass spectrometry (LC–MS/MS) is the technique of choice for the determination of drugs of abuse in the environment because of its good sensitivity without need for analytes' derivatisation. However, LC–MS/MS methods have to face the well-known problem of matrix effects when analysing complex samples. Particularly, strong signal suppression effects (40–90%) have been reported during the analysis of drugs of abuse in wastewater [10,21]. Though deuterated internal standards are available for most of these drugs/metabolites, they cannot always completely compensate this problem [22], and even so, they do not avoid the inherent loss of sensitivity. Thus, more selective sample preparation methodologies that result in a lower amount of co-extracted matrix constituents are highly desirable.

Almost all published methods for the determination of illicit drugs in water environmental samples employ solid-phase extraction (SPE) as the pre-concentration technique. The sorbents employed for SPE are either hydrophilic reversed-phase Oasis HLB [10,23,24] or the mixed-mode modification of them, Oasis MCX [2,22] (or Strata-XC [11]). The second ones have been used to improve the retention of most drugs of abuse, because of their basic properties, but their dual cationic-exchange/reversed-phase character can also be exploited for improving the selectivity of the SPE process, as suggested, for instance, by the manufacturer [25], or as already proven for the determination of basic pharmaceuticals in biological samples [26,27]. A further alternative is the use of molecularly imprinted polymers (MIPs), which have very specific shape- and H-bonding-recognition characteristics. Actually, β -blocker- [28] and NSAID-class-selective [29] MIPs have recently been tested for the selective SPE of these two pharmaceutical classes from wastewater in combination with LC–MS/MS, showing an impressive reduction in matrix effects, as compared to other common SPE sorbents.

Thus, taking into account that amphetamine class-selective MIPs are commercially available, this work aims to evaluate the performance of this sorbent as compared to Oasis HLB and Oasis MCX for the extraction and concentration of amphetamine drugs from wastewater samples in combination with LC–MS/MS determination. SPE recoveries, matrix effects, overall method recoveries, repeatability and limits of detection are evaluated.

2. Experimental

2.1. Chemicals and stock solutions

HPLC grade methanol, acetonitrile, acetic acid and ammonia were supplied by Merck (Darmstadt, Germany), formic acid by Sigma–Aldrich (Steinheim, Germany) and ammonium acetate was from Riedel de Haën (Seelze, Germany). Ultrapure water was obtained from a Milli-Q Gradient A-10 system (Millipore, Bedford, MA, USA).

Amphetamine (AMP), methamphetamine (MAMP), 3,4-methylenedioxyamphetamine (MDA), N-methyl-3,4-methylenedioxyamphetamine (MDMA) and N-ethyl-3,4-methylenedioxyamphetamine (MDEA) individual standard solutions (1 mg/mL in methanol, each) were purchased from Cerilliant (Round Rock, TX, USA). The deuterated internal standards (ISs) individual solutions (0.1 mg/mL in methanol, each) were also from Cerilliant. The structures and some relevant physico-chemical data of these substances are compiled in Table 1.

Stock mixtures of all analytes (10 μ g/mL) or ISs (also 10 μ g/mL) were prepared in methanol and stored at -20°C until use. Calibration standards with increasing concentrations of analytes and 100 ng/mL of ISs were prepared in methanol/water (1/1) containing 2% NH_3 .

2.2. Samples

Municipal wastewater grab samples were taken from four different urban wastewater treatment plants (WWTPs) in NW Spain during June 2009. All WWTPs consist of a primary and an aerobic secondary treatment. WWTPs A, B and D receive wastewaters from $\sim 100\,000$ inhabitants and WWTP-C from $\sim 20\,000$ inhabitants. A single raw (influent) and treated (effluent) wastewater sample was collected from each WWTP, except from WWTP-D where only the treated wastewater was collected. All samples were collected in amber glass bottles and they were stored in the dark at 4°C until analysis. According to our experience, amphetamines are stable at this temperature in wastewater for at least a week [30].

Particulate matter was filtered just before extraction through a combination of glass fibre prefilters and $0.45\ \mu\text{m}$ nitrocellulose filters (both from Millipore). Filtration was checked not to lead to losses due to adsorption of analytes on the filter or wastewater suspended matter (data not shown). Filtered samples were adjusted to the desired pH, spiked with labelled standards (10 ng) and, in the case of recovery studies, also with the analytes.

2.3. Solid-phase extraction

2.3.1. Oasis HLB protocol

Oasis HLB 60 mg cartridges (Waters, Mildford, MA, USA) were conditioned with 2 mL of MeOH and 2 mL of pH 8 Milli-Q water. Then, 50 mL of the sample (adjusted to pH ~ 8) were percolated through the cartridges at ca. 5 mL/min. Subsequently, the cartridges were washed with 2 mL of pH 8 Milli-Q water and vacuum dried for 10 min. Finally, amphetamines were eluted with 3 mL of MeOH.

2.3.2. Oasis MCX protocol

Oasis MCX 60 mg cartridges (Waters) were conditioned with 3 mL of MeOH and 3 mL of pH 4 Milli-Q water. Then, 50 mL of the sample (adjusted to pH ~ 4) were percolated at ca. 5 mL/min, and the cartridges were sequentially washed with 1 mL of pH 4 Milli-Q water and 1 mL of MeOH. Finally, amphetamines were eluted with 3 mL of MeOH containing 5% NH_3 .

2.3.3. MIP protocol

SupelMIP-Amphetamine 25 mg cartridges (Supelco, Bellefonte, PA, USA) were conditioned with 1 mL of MeOH and 1 mL of pH 8 Milli-Q water. Then, 50 mL of the sample (adjusted to pH ~ 8) were percolated by gravity through the MIP cartridges. Interferences were successively washed off by $2 \times 1\ \text{mL}$ pH 8 Milli-Q water, 1 mL acetonitrile/water (60/40) and 1 mL of acetonitrile containing 1% acetic acid, as recommended by the supplier. Elution was finally performed with $2 \times 1\ \text{mL}$ MeOH containing 1% formic acid.

The eluates resulting from all the above-mentioned SPE protocols were blown down with a gentle stream of nitrogen, reconstituted in 100 μL of MeOH/water (1/1) containing 2% NH_3 and transferred to a vial equipped with a 200 μL insert for LC–MS/MS determination.

2.4. Liquid chromatography–mass spectrometry

The liquid chromatographic system consisted of two ProStar 210 high-pressure mixing pumps (Varian, Walnut Creek, CA, USA), a Metachem Technologies vacuum membrane degasser (Bath, UK), and an autosampler and thermostated column compartment ProStar 410 module (Varian). The LC was interfaced to a triple quadrupole 1200L mass spectrometer equipped with an electrospray interface (Varian). Nitrogen, used as nebulising and drying gas, was provided by a nitrogen generator (Domnick Hunter, Durham, UK). Argon (99.999%) was used as collision gas. Instrument

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