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MSPE/UV for field detection of micropollutants in water

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This paper proposes a new approach for the on-site detection of micropollutants in water in case of accidental or intentional contamination (characterized by high concentration). The technique is based on the use of an automatic multiple solid phase extraction step (MSPE) followed by direct or indirect UV spectrometry (MSPE/UV) for the detection of organic contaminants in water (such as regulated molecules (pesticides ...) as well as emerging pollutants (pharmaceutical products, endocrine disruptors ...)). The development of the system supposes firstly the choice of the most appropriate sorbent(s) and secondly conditions for the detection of targeted micropollutants, from several solid phase extraction cartridges and eluting solvents. Two different extraction sorbents were chosen. These sorbents and several eluting solvents allow the first separation of the compounds based on the physico-chemical properties of each substance (pK_a , $\log K_{ow}$) and on the specific interactions with the sorbent. Finally, a UV analysis (either at the maximum of absorbance using a calibration curve or from the whole spectrum using a multicomponent (deconvolution) exploitation method) of each fraction allows a determination and a quantification of each compound. The method is rapid (less than 2 h), sensitive enough for an accidental/intentional contamination (between 5 and 40 $\mu\text{g}\cdot\text{L}^{-1}$ according to the substances) and with a good precision (between 4 and 14%).

1. Introduction

Wastewater sources could be contaminated by a variety of organic compounds such as pesticides, pharmaceuticals, additives or personal care products, and other industrial chemicals. Though the concentration of most of these contaminants is low in environmental waters, ranging from $\text{pg}\cdot\text{L}^{-1}$ to $\text{ng}\cdot\text{L}^{-1}$ (micropollutants), they are widely recognized as a potential risk to aquatic ecosystems and to human health [1].

The concentration of such contaminants can be higher in case of exceptional events like accidental pollutions. Such events are not rare. For example in 2010, 236 high and medium severity incidents were investigated in Northern Ireland [2], 400 were reported in UK and Wales [3] and 89 in France [4], all associated to water pollution. High rainy events can also be a source of an increase of micropollutant concentration in environmental waters, in particular because of surface leaching or discharge of untreated water through combined sewer overflow. For example, caffeine was found at the dozen $\mu\text{g}\cdot\text{L}^{-1}$ level in several studies [5,6] as well as other organic chemicals such as nonylphenols, cholesterol, tris(2-butoxyethyl)phosphate (TBEP), etc. ... [7].

Water contamination is generally monitored in laboratories by standard chromatographic methods (after sampling and contaminant extraction and preconcentration) [8,9]. Such techniques are very

efficient for the identification and the quantification of lots of pollutants but they are time consuming and then not compatible with critical situations (such as accidental pollution). In this case, the deployment of field devices is required to identify rapidly the source of the problem, and the nature of the contaminant(s) and to take the remediation actions for the protection of the environment and the population.

Although field devices are available to measure water quality global parameters (COD, TSS ...), nutrients, and heavy metals, very few exist for micropollutant detection.

This work proposes a system based on multiple solid phase extraction (MSPE) coupled with UV spectrometry for the rapid detection of micropollutants.

Solid-phase extraction (SPE) is the most popular sample preparation method [10] used for extraction and preconcentration of substances from water. Basically, it consists in the retention of the substance (dissolved in water) into a sorbent followed by its elution with an adequate eluent. Generally, the elution is performed by using 100 to 1000 times less volume, resulting in the corresponding concentration of the substance. In the 90s, many improvements in formats, automation and phases have enhanced the development of SPE and currently, a broad range of sorbents is available for the specific retention of a wide range of chemicals in water. The most common retention mechanisms are non-polar (based on Van der Waals forces), polar (based on hydrogen bonding, dipole-dipole or π - π interactions), ion exchange (based on electrostatic interactions) and mixed mode (based on combination of non-polar and ion exchange interactions).

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Often used as pretreatment before chromatography analysis, SPE is used to extract and concentrate the maximum of substances prior to the speciation/separation by the chromatography column.

In this paper, SPE is used not only for its extraction and pre-concentration capacity but also, by coupling multiple phases (MSPE), for its ability on micropollutant separation. After MSPE, several fractions are obtained, each of them corresponding to the elution volume of a given sorbent and being characterized (detection/quantification) by UV analysis.

The method was developed by using substances with different physico-chemical properties and relevance in water contamination [11,12], persistence [8,13] and of regulatory interest [14]. These include some pharmaceuticals (trimethoprim, sulfamethoxazole, ibuprofen, diclofenac, carbamazepine, 5-fluorouracil and 1,7 α -ethynylestradiol), phytosanitary products (diazinon and atrazine) and a stimulant (caffeine).

The performances of 11 SPE commercial cartridges: Strata-X (Phenomenex), Oasis-HLB (Waters), Strata-SAX (Phenomenex), Strata-PAH (Phenomenex), Strata-X-C (Phenomenex), Oasis-MAX (Waters), Oasis-MCX (Waters), Sep-Pak (Waters), Lichrolut-EN (Merck), SupelMIP Triazine and SupelMIP NSAID (Supelco) were compared and a combination of two of them was developed for the application of MSPE in pure and real water samples.

2. Experimental

2.1. Instrumentation

UV spectra were obtained with a Xenius spectrofluorometer (Safas, Monaco) between 200 and 400 nm using an optical quartz cell with a path length of 10 mm.

SPE was performed by using an in house (HOCER) automatic concentrator (Fig. 1) controlled by a specific software for the different SPE steps (conditioning, loading, elution, washing). Solutions (conditioning solvent, sample, eluting solvent(s)) are charged in the system by valve 3. They are loaded or not to the cartridge by valve 1. Valve 2 allows the collection of the fractions or the elimination of the waste. Valves 4 and 5 select the cartridge.

2.2. Chemicals

Standards of the targeted pollutants (trimethoprim, sulfamethoxazole, ibuprofen, diclofenac, carbamazepine, 5-fluorouracil, 1,7 α -ethynylestradiol, diazinon, atrazine and caffeine) were purchased from Sigma-Aldrich. All compounds were of >98% purity. They were selected from their physico-chemical properties, in particular pK_a and $\log K_{ow}$ (which range from 0.8 to 13 and from 0.9 to 4 respectively) and also from their absorptivity in UV spectrophotometry (Table 1). pK_a and $\log K_{ow}$ determined their affinities for SPE supports and eluting solvents, and their behavior during the SPE step (Table 1).

Solvents and reagents are of chromatography quality. They were purchased from Panreac for acetonitrile, Merck for sulfuric acid, Fluka for formic acid, AnalaR Normapur for sodium chloride and Sigma-Aldrich for methanol and dichloromethane.

Ultrapure water was obtained from a PURELAB classic water purification system (Siemens).

Stock solutions of trimethoprim, sulfamethoxazole, ibuprofen, diclofenac, carbamazepine, 5-fluorouracil, 1,7 α -ethynylestradiol, diazinon, atrazine and caffeine (400–600 $\mu\text{g}\cdot\text{mL}^{-1}$) were prepared in methanol and stored in the dark at 5 ± 3 °C. Working solutions were prepared daily by dilution of the given stock solutions with ultrapure water. Prior to the extraction, water samples were spiked with targeted analyte at the concentration of 2 $\mu\text{g}\cdot\text{mL}^{-1}$.

2.3. Solid-phase extraction

11 commercialized cartridges (Table 2) were tested. These include universal (retention of a wide range of substances) and more specific (retention of particular substances or family) sorbents, according to the description of the manufacturers.

After the conditioning step (Table 3), 10 mL of the water samples was percolated through the cartridges and secondly eluted with a specific eluting solvent.

In some cases (SupelMIP Triazine and SupelMIP NSAID cartridges) a pre-acidification (pH 3 with 1 $\text{mol}\cdot\text{L}^{-1}$ sulfuric acid) of the sample is required (according to supplier's instructions).

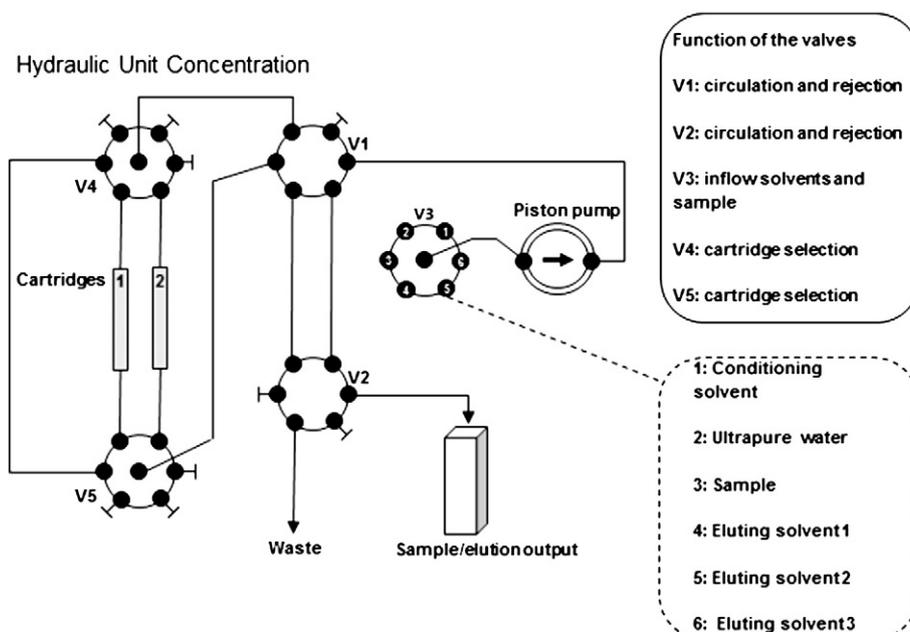


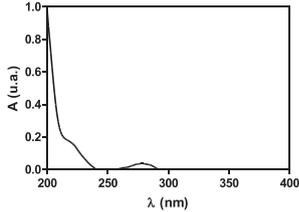
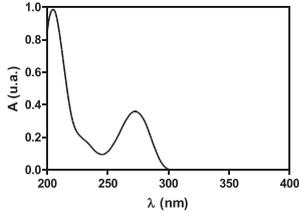
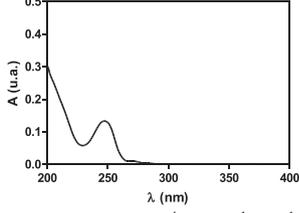
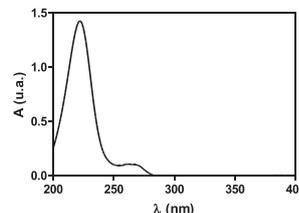
Fig. 1. Schematic diagram of the SPE arrangement for automatic sample extraction-separation determination.

Table 1
Properties of selected compounds.

| Compound | pK _a | log K _{ow} | UV absorption (pH 6.2) | SPE cartridge used in the literature |
|---|--------------------|---------------------|--|--|
| Carbamazepine CAS: 298-46-4 C ₁₅ H ₁₂ N ₂ O 236.3 g·mol ⁻¹ | 13.9 [15] | 2.5 [16] | $\epsilon_{212\text{nm}}=3.2\pm 0.1\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ $\epsilon_{285\text{nm}}=1.32\pm 0.08\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Oasis HLB [12,17-25] LiChrolut EN [9,19,26,27] Oasis MCX [8,28] RP-C18 [9] Isolut EN [9] |
| Trimethoprim CAS: 738-70-5 C ₁₄ H ₁₈ N ₄ O ₃ 290.3 g·mol ⁻¹ | 1.3 [29]; 7.1 [30] | 0.9 [16] | $\epsilon_{202\text{nm}}=4.7\pm 0.4\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ $\epsilon_{280\text{nm}}=4.6\pm 0.7\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Oasis HLB [22,24,25,31,32] LiChrolut EN [9] Strata-X [33,34] Oasis MCX [28] RP-C18 [28] Isolut EN [9] Orpheous DVB-HL [35] |
| Sulfamethoxazole CAS: 723-46-6 C ₁₀ H ₁₁ N ₃ O ₃ S 253.8 g·mol ⁻¹ | 1.8; 5.6 [36] | 0.9 [16] | $\epsilon_{260\text{nm}}=1.6\pm 0.7\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Oasis HLB [18,24,25,32] LiChrolut EN [9] Strata-X [33,34] Oasis MCX [27,28] RP-C18 [9] Isolut EN [9] Orpheous DVB-HL [35] |
| Diclofenac salt CAS: 15307-79-6 C ₄ H ₁₀ Cl ₂ NNaO ₂ 296.2 g·mol ⁻¹ | 4.2 [15] | 0.7 [16] | $\epsilon_{277\text{nm}}=1.1\pm 0.4\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Oasis HLB [12,17-22,24,25,37,38] LiChrolut EN [9,19,39] Oasis MAX [40] Strata-X [33] RP-C18 [9] Isolut EN [9] |
| Ibuprofen CAS: 15687-27-1 C ₁₃ H ₁₈ O ₂ 206.3 g·mol ⁻¹ | 4.4 [15] | 4.0 [16] | $\epsilon_{221\text{nm}}=8.4\pm 0.5\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Oasis-HLB [12,17-22,24,25,37,38] LiChrolut-EN [9,19,26,39] Oasis-MAX [40] Oasis-MCX [27] Strata-X [33,34] RP-C18 [9] Isolut-EN [9] |
| 5-Fluorouracil CAS: 51-21-8 C ₄ H ₃ FN ₂ O ₂ 130.1 g·mol ⁻¹ | 8.0; 13.0 [41] | -0.9 [42] | $\epsilon_{265\text{nm}}=7.3\pm 0.5\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Isolut-ENV + [43] |

(continued on next page)

Table 1 (continued)

| Compound | pK _a | log K _{ow} | UV absorption (pH 6.2) | SPE cartridge used in the literature |
|---|-----------------|---------------------|--|--|
| 1,7 α -Ethinylestradiol CAS: 57-63-6 C ₂₀ H ₂₄ O ₂ 296.4 g·mol ⁻¹ | 10.4 [30] | 3.7 [44] | $\epsilon_{280\text{nm}}=1.5\pm 0.2\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  | Oasis-HLB [18,19,45,46] LiChrolut-EN [19] Oasis-MCX [27] ODS C18 [47] |
| Caffeine CAS: 58-08-2 C ₈ H ₁₀ N ₄ O ₂ 194.2 g·mol ⁻¹ | 0.8 [15] | -0.1 [16] | $\epsilon_{205\text{nm}}=2.5\pm 0.2\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ $\epsilon_{271\text{nm}}=8.8\pm 0.6\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  | Oasis-HLB [19,21,23,24] LiChrolut-EN [19,26] C18 [48] |
| Diazinon CAS: 333-415 C ₁₂ H ₂₁ N ₂ O ₃ PS 304.4 g·mol ⁻¹ | 2.6 [49] | 3.3 [50] | $\epsilon_{247\text{nm}}=4.7\pm 0.2\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  | Oasis-HLB [51] C18 [48] Carbo-Prep 90 [52] |
| Atrazine CAS: 1912-24-9 C ₈ H ₁₄ ClN ₅ 215.7 g·mol ⁻¹ | 1.7; 1.95 [53] | 2.6 [16] | $\epsilon_{222\text{nm}}=3.8\pm 0.2\times 10^4\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ $\epsilon_{263\text{nm}}=3.0\pm 0.9\times 10^3\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  | Oasis-HLB [8,12,13,24,51] Bond Elut-ENV [54] C18 [48] Carbo-Prep 90 [52] Strata-X [13] LiChrolut-EN [13] Isolute SPE C18 [13] Superclean Envi-Carb [13] |

2.4. UV analyses

Analysis of each extract is performed by UV spectrometry. A spectrum (between 200 and 400 nm) of each sample was carried out before and after percolation through the cartridge. The quantification is carried out either at the maximum of absorbance using a calibration curve (for individual substances) or from the whole spectrum using a multicomponent (deconvolution) exploitation method [55] (for mixture of substances).

The calculation of the spectral contribution is carried out by using the following relation:

$$S_W = \sum_{i=1}^p a_i \text{REF}_i \pm r$$

where S_W is the sample spectrum, a_i is the contribution coefficient of the i th reference spectrum REF_i , p is the number of reference spectra used and r is the quadratic error.

Bases of reference spectra were constituted for each class of fraction as explained after.

3. Results and discussion

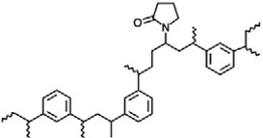
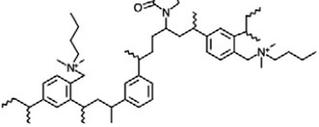
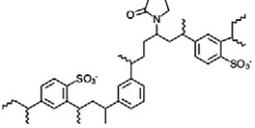
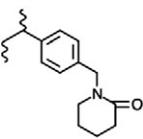
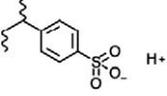
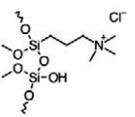
In this work, MSPE is employed not only to extract and pre-concentrate the analytes of interest but also to separate analytes in the case of mixtures. In this case, the separation is carried out by eluting different fractions before UV detection.

3.1. Assessment of SPE cartridge specificity

11 SPE commercial cartridges were considered in this study, the characteristics of which are presented in Table 2.

10 mL of spiked aqueous solutions of each selected molecule at a final concentration of $2\ \mu\text{g}\cdot\text{mL}^{-1}$ was loaded on each cartridge. At the pH of the solution (6.2 corresponding to the ultrapure water), the molecules are under their neutral form except for diclofenac (DIC), ibuprofen (IBU) and sulfamethoxazole (SMX) that are anionic. The capacity of retention of the cartridges is evaluated by the difference between the substance concentrations (measured by UV spectrometry) in the loaded solution and in the percolate. Results are shown in Table 4. Percentages of retention are represented by empty, partially full and fully dark circle (white

Table 2
Different commercialized cartridges and nature of their sorbent.

| Name of cartridge | Structure of the sorbent | Instructions of suppliers |
|---|---|--|
| Oasis-HLB 225 mg (Waters) |  | Hydrophilic lipophilic copolymer for all compounds (acidic, neutral and basic) |
| Oasis-MAX 225 mg (Waters) |  | Mixed-mode anion exchange sorbent for acidic compounds |
| Oasis-MCX 225 mg (Waters) |  | Mixed-mode cation exchange sorbent for basic compounds |
| Sep-Pak Plus PS2 300 mg (Waters) | Copolymer styrene-divinylbenzene | Usually used for hydrophobic compounds with hydrophilic function (extraction of pesticides in Japan) |
| Strata-X 200 mg (Phenomenex) |  | Polymeric based sorbent for acidic, neutral and basic compounds |
| Strata-X-C 200 mg (Phenomenex) |  | Mixed-mode polymeric sorbent, strong cation-exchange for weakly basic compounds |
| Strata-SAX 500 mg (Phenomenex) |  | Silica based sorbent, strong-anion exchange mechanism of retention for weakly acidic compounds |
| Strata-PAH 750 mg (Phenomenex) | Silica-based sorbent (proprietary) | For polycyclic aromatic hydrocarbons |
| LiChrolut-EN 200 mg (Merck) | Ethyl vinyl benzene divinyl benzene polymer | For polar organic substances |
| SupelMIP Triazine 25 mg (Supelco) | Molecular imprinted polymer | For extraction of triazine family compounds |
| SupelMIP NSAID 25 mg (Supelco) | Molecular imprinted polymer | For extraction of NSAID family compounds |

circle: <25%; one quarter dark circle: between 25 and 50%; three quarter dark circle: between 51 and 75%; black circle: >75%).

Oasis-HLB, Strata-X, LiChrolut-EN, Sep-Pak Plus PS2, Oasis-MCX and Strata-X-C present a closed behavior for all molecules, except for 5-fluorouracil (5FU); the retention percentage of which is >75% only with LiChrolut-EN. These results confirm the ability of Oasis-HLB, LiChrolut-EN, and Sep-Pak Plus PS2 to retain a wide range of compounds, which is already illustrated in a previous comparative study [13] on the extraction of pesticide (recovery of atrazine was in the range of 94–98%,

Table 3
Conditioning of the cartridges.

| Cartridges | Conditioning | pH |
|--|---|--|
| Oasis-HLB, Oasis-MAX, Oasis-MCX, Sep-Pak Plus PS2, LiChrolut-EN, Strata-X, Strata-X-C and Strata-SAX | 6 mL of acetonitrile 10 mL of ultrapure water | Neutral pH (or pH 3 in the tests where water samples were acidified) |
| SupelMIP NSAID | 2 mL of acetonitrile 2 mL of methanol 2 mL of acid formic | pH 3 |
| SupelMIP Triazine | 2 mL of methanol 2 mL of ultrapure water 2 mL of acid formic | |
| Strata-PAH | 10 mL of dichloromethane 10 mL of methanol 10 mL of ultrapure water | Neutral pH |

72–90%, and 82–86% for LiChrolut-EN, Oasis-HLB and Strata-X respectively). However, they did not follow at all the supplier information giving Sep-Pak Plus PS2 specific to pesticides and Oasis-MCX and Strata-X-C recommended for cationic compounds.

LiChrolut-EN and Oasis-MAX are the only ones being able to adsorb 5FU (>75% and partially <50% respectively), in spite of its physico-properties being rather close to other ones. The high difficulty of extraction of this molecule has already been shown by Micoli et al. without explanation [43]. But the latter also showed a good recovery with a styrene-divinylbenzene cartridge (ENVI-Chrom P) contrary to our study with Sep-Pak Plus PS2. Strata-PAH, SupelMIP Triazine and SupelMIP NSAID cartridges commercialized to be specific of PAH, triazine and anti-inflammatory respectively, are subjected to interferences because they are not specific enough for our conditions as they also retain the other molecules.

The different behaviors of the two anionic exchange sorbents (Strata-SAX and Oasis-MAX) are probably due to their structures. Indeed, in spite of the ammonium cationic charge, the copolymer base of the second sorbent confers the possibility to adsorb neutral compounds. Consequently, Oasis-MAX is less specific for anionic compounds than Strata-SAX which retains only the anionic compounds. The high specificity of Strata-SAX was confirmed by modifying the pH of the standard solution of DIC, IBU and SMX. Indeed, at pH 3 (below their pK_a), they are present under their neutral form and do not interact with the sorbent (Table 5).

This comparative study shows a lack of specificity of the SPE cartridges contrary to the specification of the suppliers. But, when coupled with chromatographic systems, such drawback appears not to be crucial for the separation and the detection of the different compounds performed in the chromatographic column under the optimal conditions (including elution gradient).

In our development, the specificity of the sorbent is central because of the simplicity constraint and the choice of the cartridge shall drive the performance of our results. Consequently, a combination of Strata-SAX (for anionic compounds) and Oasis-HLB (for neutral or cationic compounds) has been selected for application to simple mixtures. Note that LiChrolut-EN or SepPak Plus PS2 could also be used.

3.2. Selection of eluting solvents

Once adsorbed onto the cartridge, the substance should be eluted. Anionic compounds interact on the Strata-SAX sorbent due to electrostatic links. Several eluting solvents have been tested by modifying the ionic strength or by involving a strong contra-ion. After different trials, the chosen solution to use was the 4 mL mixture of methanol/0.1 mol·L⁻¹ sodium chloride (40/60 vol.%) (E1). Experiments demonstrated a dead volume of 1.0 mL, with no substances eluted.

Table 4
Capacity of retention of sorbents (pH 6.2, 10 mL at 2 µg·mL⁻¹).

| Targeted compounds | Oasis-HLB | Sep-Pak Plus PS2 | Strata-X | Lichrolut-EN | Oasis-MAX | Oasis-MCX | Strata-X-C | Strata-SAX | Strata-PAH | SupelMIP Triazine | SupelMIP NSAID |
|-----------------------|-----------------|------------------|-----------------|--------------|-----------|-----------|---------------|--------------|------------|-------------------|----------------|
| | Ac, neut., bas. | Pest | Ac, neut., bas. | Polar | Ac. | Bas. | Strong cation | Strong anion | PAH | Triazine | NSAID |
| Diclofenac | ● | ● | ◐ | ● | ● | ● | ● | ● | ● | ◐ | ● |
| Sulfamethoxazole | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| Ibuprofen | ● | ● | ● | ● | ● | ● | ● | ● | ◐ | ● | ● |
| Caffeine | ● | ● | ● | ● | ● | ● | ○ | ○ | ◐ | ○ | ● |
| Trimetoprim | ● | ● | ● | ● | ○ | ● | ● | ○ | ● | ● | ◐ |
| Carbamazepine | ● | ● | ● | ● | ● | ● | ● | ○ | ● | ● | ● |
| Atrazine | ● | ● | ● | ● | ● | ● | ● | ○ | ● | ● | ● |
| Diazinon | ● | ● | ● | ● | ● | ● | ● | ○ | ● | ● | ● |
| 1,7α-Ethynylestradiol | ● | ● | ● | ● | ● | ● | ● | ○ | ○ | ● | ● |

Ac.: acidic, neut.: neutral, bas.: basic, pest.: pesticides.

Table 5
Comparison of capacity of retention of Strata-SAX sorbents at pH 6.2 and at pH 3.

| Targeted compounds | Strata-SAX | |
|--------------------|------------|------|
| | pH 6.2 | pH 3 |
| Diclofenac | ● | ○ |
| Sulfamethoxazole | ● | ○ |
| Ibuprofen | ● | ○ |

Concerning neutral compounds, the interaction strength of each substance with the sorbent depends not only on its affinity with the sorbent (due mainly to hydrogen bond and Van der Waals) but also on the hydrophilic/hydrophobic character of the molecule (log K_{ow}). Based on these parameters, mixtures of acetonitrile ACN/water, with

different volumetric percentages have been tested. Results (not shown) showed the necessity to increase the percentage of acetonitrile when log K_{ow} increases. Then two mixtures were selected: ACN/water (30/70 vol.%) for substances with log $K_{ow} < 1$ and ACN/water (70/30 vol.%) for substances with log $K_{ow} > 1$. Tests on the different substances allow determining the minimum volume necessary to the elution of the whole fraction: 1 and 2 mL for E2 and E3 respectively. For each fraction, a dead volume of 1.0 mL and 0.5 mL respectively has been determined.

For each fraction, a UV spectrum is acquired and analyzed by deconvolution. 2 different reference bases are used according to the fraction. They all include the reference spectra of the water used and spectra of individual compounds. In addition, the base for fraction 1 (Strata-SAX) includes the spectra of anionic compounds and the

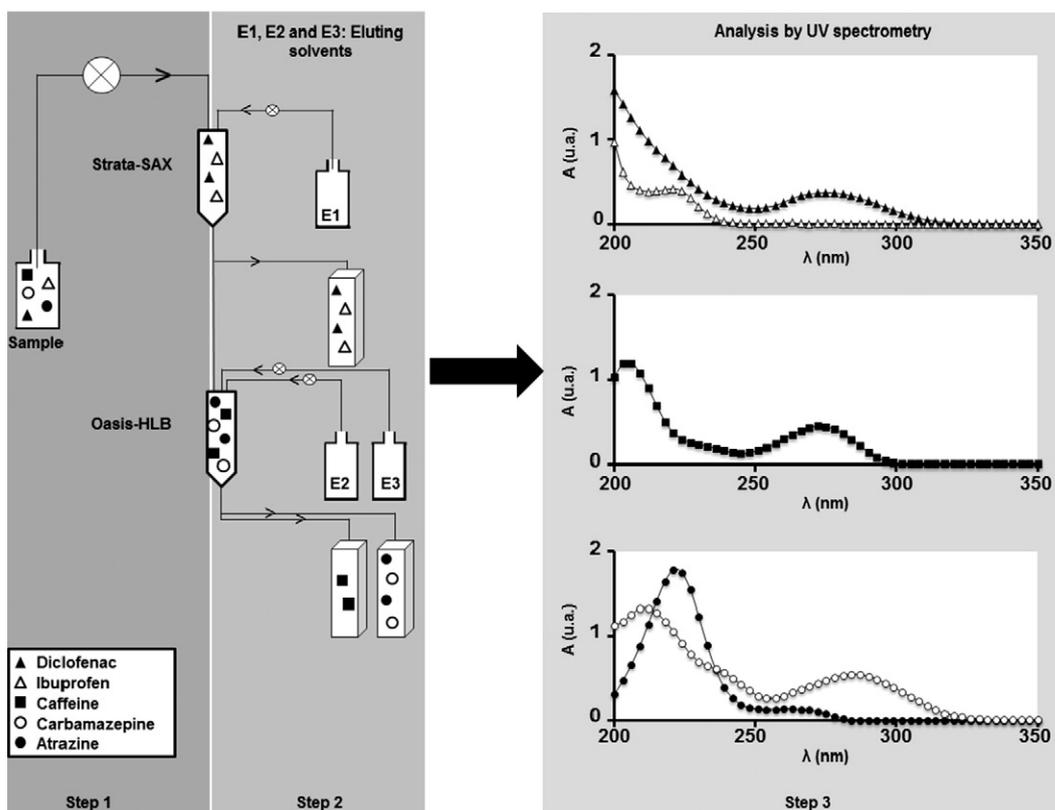


Fig. 2. Methodology used for the separation and concentration of 5 micropollutants: E1: methanol and sodium chloride (0.1 mol·L⁻¹) (vol.%=0.4 for methanol); E2: acetonitrile and ultrapure water (vol.%=0.3 for acetonitrile); E3: acetonitrile and ultrapure water (vol.%=0.7 for acetonitrile). Step 1: a preconcentration of substances by using chemical sorbents with different properties; step 2: a separation of substances based on their physico-chemical properties by using different eluting solvents; step 3: a direct or indirect (deconvolution) UV analysis of each fraction.

Table 6

Average extraction recoveries (R%) for ibuprofen and diclofenac on Strata-SAX, and caffeine, atrazine and carbamazepine on Oasis-HLB (n = 3).

| % recovery | Anionic compounds | | |
|------------|-------------------|------------|---------------|
| | Ibuprofen | Diclofenac | |
| | 104 ± 10 | 96 ± 10 | |
| | Neutral compounds | | |
| | Caffeine | Atrazine | Carbamazepine |
| 91 ± 2 | 77 ± 3 | 98 ± 16 | |

base for fractions 2 and 3 (Oasis-HLB) includes the spectra of neutral compounds.

3.3. Applications

3.3.1. Mixture in pure water

A mixture of 5 micropollutants covering a wide range of pK_a and $\log K_{ow}$, was prepared in ultrapure water and analyzed by MSPE/UV.

100 mL of ultrapure water (pH 6.2) spiked with diclofenac (anionic, pK_a 4.2, $\log K_{ow}$ 0.7), ibuprofen (anionic, pK_a 4.4, $\log K_{ow}$ 4), atrazine (neutral, pK_a 1.9 and 1.7, $\log K_{ow}$ 2.6), caffeine (neutral, pK_a 0.8, $\log K_{ow}$ -0.1) and carbamazepine (neutral, pK_a 13.9, $\log K_{ow}$ 2.5) (100 ng·mL⁻¹ each) was percolated successively through the Strata-SAX and Oasis-HLB sorbent at 10 mL/min by using an automatic HOCER SPE system. Anionic compounds (ibuprofen and diclofenac)

and the neutral ones (carbamazepine, caffeine and atrazine) were adsorbed on the Strata-SAX and Oasis-HLB cartridges respectively.

Notice that these five substances, previously studied individually with the corresponding cartridges, showed recovery yields (calculated with 10 replicates) ranging from 78 ± 4% for carbamazepine to 100 ± 14% for ibuprofen and limit of quantification ranging from 5 µg·L⁻¹ for caffeine to 40 µg·L⁻¹ for ibuprofen (data not shown); LOQ is acceptable in the context of accidental/intentional contamination.

Eluting solvents determined above were applied to elute the two cartridges. Three fractions were obtained: 1 from the Strata-SAX cartridge and 2 from the Oasis-HLB one.

4 mL of E1 has been used to elute the two anionic compounds (ibuprofen and diclofenac) retained by Strata-SAX. The fraction was analyzed by UV spectroscopy using the deconvolution analysis. The neutral compounds (caffeine, atrazine and carbamazepine) were separated in the two fractions of Oasis-HLB (1 mL of E2 and 2 mL of E3) and analyzed by UV spectroscopy (Fig. 2).

The average extraction recoveries (R%) are collected in Table 6. The 5 substances of the mixture were recovered in each expected fraction with a percentage higher than 75%. Relative standard deviations (RSD) were calculated from triplicates.

3.3.2. Contamination of river water by one chemical

A second application consisted in testing the procedure on a raw sample contaminated by one pollutant at high concentration (simulating an accidental pollution). A river water (15.3 ± 0.7 mg·L⁻¹ of TOC and 1.8 ± 0.3 mg·L⁻¹ of nitrate) has been contaminated by 50 µg·L⁻¹ of diuron, an herbicide with a partition coefficient of 2.87 [56]. Even if it is banned in several countries, it is always present in the environment and still sometimes used. 100 mL of the contaminated water was treated according to the same protocol as mentioned above: percolation onto the two cartridges and elution of three fractions (1 from Strata-SAX and 2 from Oasis-HLB). The UV spectra of each fraction are displayed in Fig. 3. Fig. 3A represents the dead volume of each fraction. They allow verifying that no chemicals have been eluted. The UV signal of the first fraction of Strata-SAX is due to nitrate, which is estimated to be 0.9 ± 0.2 mg·L⁻¹. Fig. 3B corresponds to the UV spectra of the fractions containing potentially the contaminant. The fraction corresponding to the Strata-SAX elution still contains nitrates (estimated to be 2.1 ± 2.0 mg·L⁻¹) whereas the first fraction of Oasis-HLB with 30/70 vol.% ACN/water shows no relevant UV signal. The UV spectrum of the last fraction corresponding to 70/30 vol.% ACN/water eluent shows an absorbance peak at 250 nm corresponding to the presence of the contaminant.

The analysis of each UV spectra has been made by deconvolution with the following bases of reference spectra: river water, nitrates, ibuprofen, and diclofenac for the Strata-SAX fraction and, river water, caffeine, carbamazepine, atrazine, and diuron for the Oasis-HLB ones.

Results are shown in Table 7. The average extraction recovery obtained for diuron was of 78 ± 14% (n = 4 replicates).

Further experiments with other contaminants in natural water give similar results (data not shown).

4. Conclusion

Conventional methods used to detect micropollutants in water are generally time consuming (approximately 24–48 h) and not appropriate in the case of accidental or intentional contamination (characterized by concentration in the range of µg·L⁻¹) for which a quick decision shall be made with respect to human health protection. In this context, the MSPE/UV method proposed is a first step in giving useful information on the presence of suspected substances by its rapid on-site implementation. This method could also be used for a better knowledge of micropollutant transfer in case of heavy rain events when concentrations are higher and varying rapidly. The applications in pure and raw water presented in this work show the potential of the method in

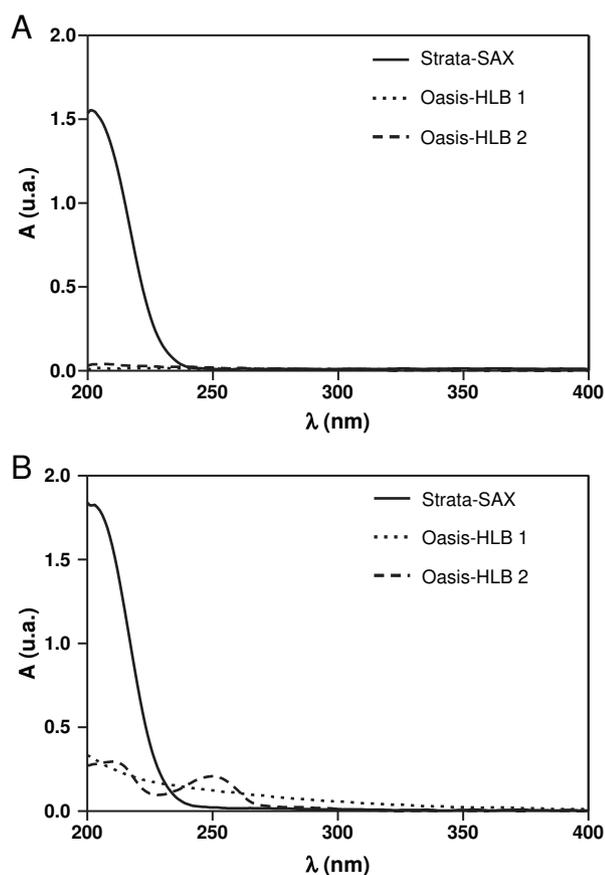


Fig. 3. UV spectra of the fractions obtained after elution of Strata-Sax and Oasis HLB cartridges: dead volume (A) and efficient volume (B). Dead volume and efficient volume for Strata-SAX were diluted by 10.

Table 7
Result of deconvolution (n=4).

| | Unknown (u.a.) | Ibuprofen ($\mu\text{g}\cdot\text{L}^{-1}$) | Diclofenac ($\mu\text{g}\cdot\text{L}^{-1}$) | NO_3 ($\text{mg}\cdot\text{L}^{-1}$) | |
|---|-------------------|--|--|--|---|
| <i>Strata-SAX elutions</i> | | | | | |
| Dead volume (1.1 mL) | 0 | 0 | 0 | 0.9 ± 0.2 | |
| Efficient volume (4 mL) | 0 | 0 | 0 | 2.1 ± 2.0 | |
| | Unknown (u.a.) | Caffeine ($\mu\text{g}\cdot\text{L}^{-1}$) | Carbamazepine ($\mu\text{g}\cdot\text{L}^{-1}$) | Atrazine ($\mu\text{g}\cdot\text{L}^{-1}$) | Diuron ($\mu\text{g}\cdot\text{L}^{-1}$) |
| <i>Oasis-HLB 1 (30/70 vol.% ACN/water) elutions</i> | | | | | |
| Dead volume (1 mL) | 0.004 ± 0.002 | 0 | 0 | 0.1 ± 0.3 | 0 |
| Efficient volume (1 mL) | 0.04 ± 0.01 | 0 | 0 | 0 | 0 |
| <i>Oasis-HLB 2 (70/30 vol.% ACN/water) elutions</i> | | | | | |
| Dead volume (0.5 mL) | 0.004 ± 0.003 | 0 | 0 | 0 | 0 |
| Efficient volume (2 mL) | 0 | 0 | 0 | 0 | 39 ± 7 |

particular for a simple detection of contamination at the level of $\mu\text{g}\cdot\text{L}^{-1}$, which is likely to occur during exceptional events that are either natural (climate change) or accidental/intentional. Further experiments shall be conducted with other types of water (for example containing humic substances giving high DOC concentrations) and other chemicals of interest. Such methodology is not intended to be used for surveillance and routine monitoring, conventional methods covered by sampling and laboratory analysis with standard methods. This new approach shall be considered as complementary and particularly designed for rapid on-site interventions. Finally, it could be included in field portable devices for improving the on-site diagnosis of water quality contamination.

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