

Automatic and predictive fractionation of organic micropollutants in contaminated water

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Environmental context. The safeguarding of water supplies and drinking water is a major issue when considering human health risk management. In this context, an automatic and on-site fractionation system for the detection of organic contaminants has been developed. The main goal of this system is to establish an initial diagnosis by identifying a class of substances involved in a case of pollution.

Abstract. This paper proposes a new approach for the preconcentration, fractionation, prediction and detection of organic micropollutants in water. The main aim of this study was to implement an innovative fractionation method and a prediction model based on the physicochemical properties of compounds and interactions with the sorbent of solid-phase extraction cartridges. Two sorbents (Strata-SAX and Oasis-HLB) and three specific eluting solvents (mixture of methanol and sodium chloride and mixtures of acetonitrile and ultrapure water) were used to separate organic compounds into five specific fractions according to their physicochemical properties (anionic and cationic or neutral compounds with various polarity). More than 75 molecules (43 molecules individually studied and a mixture with 43 molecules, including 11 molecules individually studied) including pesticides, pharmaceuticals, endocrine disruptors and polycyclic aromatic hydrocarbons, with various properties were studied, and the results showed that the elution fraction can be predicted for more than 85 % of the compounds. This methodology could simplify the analytical chain by reducing detailed analysis on limited categories of compounds, and could be used for a rapid and on-site screening of organic compounds.

Additional keywords: diagnosis, high performance liquid chromatography, spectrophotometry, pollution.

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Introduction

The number of automated systems for water-quality analyses and other monitoring applications (in biology, environment and food) is continually increasing, thanks to breakthroughs in electronics and automation. For this purpose, analytical flow techniques have been developed in order to simplify sample preparative procedures and to limit sample handling. Among them, flow injection analysis (FIA) and sequential injection analysis (SIA) are widely used. Whereas most FIA procedures use continuous, unidirectional pumping of carrier and reagent solutions, SIA procedures are based on the use of a programmable, bidirectional, discontinuous flow that is accurately computer-controlled.^[1] Moreover, in conventional FIA systems, the sample volume is injected and mixed on-line with reagents, whereas SIA systems work with the sequential aspiration of definite volumes of sample and reagents. SIA systems are based on the use of a multiposition valve to handle sample and reagents through a syringe pump and a detector.^[2] These flow systems are used with various detection systems such

as spectrophotometry, spectrofluorimetry, electrochemistry, and chromatographic systems with different degrees of sensitivity, selectivity and accuracy.^[3–6] They have been mainly used to monitor inorganic compounds, heavy metals (sulfate, nitrite, nitrate, Cu^{II}, Fe^{II} and Fe^{III}) and in certain situations organic compounds (pesticides, pharmaceuticals, endocrine disruptors).

Sample preparation can be also carried out by automated solid-phase extraction (SPE). In general, such systems are coupled with a separation and detection system and are used in laboratories for the detection of organic compounds (pesticides, pharmaceuticals, drugs). Some of these have been developed for on-site applications (Table 1).

Commercial automatic SPE systems (e.g. Smartprep, Horizon technology, or X-271-ASPEC, Gilson) propose automatic sample preconcentration by elution of several fractions from one specific SPE cartridge. A superposition of SPE cartridges has also been tested manually, mainly to decrease matrix complexity.^[7,8]

Table 1. Example of detector and matrices used with automated solid-phase extraction (SPE)

HPLC-MS, high-performance liquid chromatography–mass spectrophotometry; HPLC-MS/MS, high-performance liquid chromatography–tandem mass spectrophotometry; GC-MS, gas chromatography–mass spectrometry; PAH, polycyclic aromatic hydrocarbon

Detector	Target	Matrix	References
SPE in laboratory			
HPLC-MS or HPLC-MS/MS	Pesticides, endocrine disruptors, pharmaceuticals	Groundwater, surface water, wastewater, drinking water	[22–30]
HPLC-MS or HPLC-MS/MS	PAH, alkylphenols	Food, shellfish, cereals, milk	[31–33]
UV spectrophotometry	Pharmaceuticals	Milk	[34]
HPLC-MS or HPLC-MS/MS	Drugs, pharmaceuticals, pesticides	Urine, human plasma	[35–37]
UV spectrophotometry	Morphine	Urine	[38]
SPE on-site			
GC-MS	Musks	Municipal sewage effluents	[39]
Spectrofluorimetry	PAH	Drinking water, surface water	[40]
HPLC-MS	Pesticides, phenols and phthalates	Surface water, groundwater, drinking water	[41]

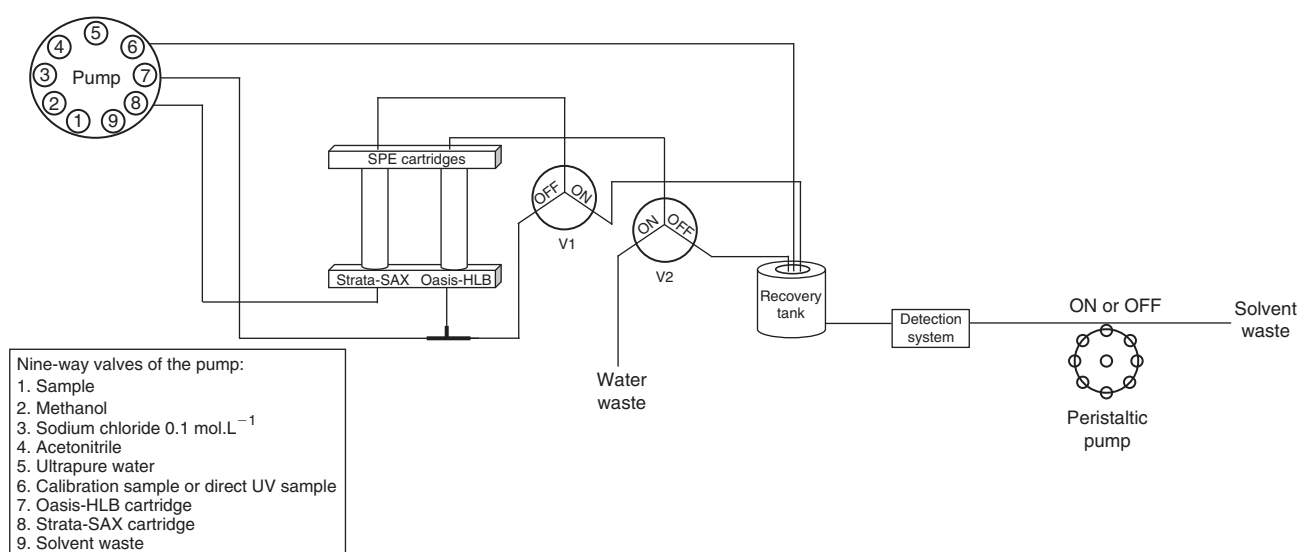


Fig. 1. Scheme of the analytical system used for the pre-concentration and determination of micropollutants in water (V1; V2: three-way valves).

Sample preparation can also be achieved based on molecule size. For example, the field-flow fractionation (FFF) system (coupled with UV-Vis diode array or fluorescence detectors) is an automatic system with a separation channel (equipped with a membrane as an accumulation wall), which produces different fractions characterised by the molecular weight of their constituents. Such a system has mainly been applied to the characterisation and fractionation of organic matter in water.^[9–13]

In our work, we present the development of an automatic and on-site fractionation system for the detection of organic contaminants (pesticides, pharmaceuticals, endocrine disruptors and polycyclic aromatic hydrocarbons (PAHs)) in water. The system is based on a MSP2E (multiple solid-phase double extraction) method developed earlier.^[14] The present paper proposes an improvement of the method through an increase in fractionation selectivity (production of five specific fractions) and an experimental prediction model of the composition of each fraction based on the (1) physicochemical properties of each substance (acid dissociation constant, pK_a , and octanol–water partition coefficient, $\log K_{ow}$), and (2) specific interactions with the adsorbent. The system can be coupled with various detection systems for field or laboratory applications.

Experimental method

Flow analyser: MSP2E system

The analyser comprises an extraction module (SPE cartridges) coupled to a UV spectrophotometer (Fig. 1).

All parts of the analyser in contact with the liquid substances are chemically resistant polymers, namely Teflon or polytetrafluoroethylene (PTFE) tubing of 1-mm internal diameter.

A module of nine-way valves (Pump) can pump different solutions from outside, or inject them into the analyser. Valve V1 enables a choice between Oasis-HLB (OFF position) and recovery tank (ON position). Valve V2 enables a choice between recovery tank (OFF position) and water waste (ON position). The solutions used in the pumping system are: sample solution in P1; methanol in P2; 0.1 mol L⁻¹ sodium chloride in P3; acetonitrile (ACN) in P4; and ultrapure water in P5.

The extraction module and the ultraviolet spectrophotometer system are connected by an RS232 serial interface to a PC for software control.

Solid-phase extraction cartridges

Strata-SAX and Oasis-HLB sorbents were purchased from Phenomenex (Torrance, CA, USA) and Waters (Milford, MA,

Table 2. Individual compounds studied
na, not available; log K_{ow} , octanol–water partition coefficient; p K_a , acid dissociation constant

Compound	CAS number	log K_{ow}	p K_a	Compound	CAS number	log K_{ow}	p K_a
Pesticides (21 compounds)							
2,4-D	94-75-7	2.7–2.8	[42]	Hexazinone	51235-04-2	1.4	[43] na
2-Nitrophenol	88-75-5	2	[44]	Isoproturon	34123-59-6	2.3	[45] 0.9
Alachlore	15972-60-8	3.5	[46]	Linuron	330-55-2	3.2	[46] 12.1
Atrazine	1912-24-9	2.6	[47]	Metazachlor	67129-08-2	2.11	[45] 1.3
Carbaryl	63-25-2	2.4	[48]	Metolachlor	51218-45-2	3.13	[47] na
Chlortoluron	15545-48-9	2.5	[49]	Paraquat	1910-42-5	−4.5	[16] na
Diazinon	333-41-5	3.3	[50]	Parathion	56-38-2	3.8	[48] na
Dichlorprop	120-36-5	3.4	[42]	Simazine	122-34-9	1.5–2.3	[51] 1.6
Dinoterb	1420-07-1	5.6	[52]	Terbutylazine	5915-41-3	3.04	[53] 2
Diquat	85-00-7	−4.6	[15]	Terbutryn	886-50-0	3.7	[54] 4.4
Diuron	330-54-1	2.8	[45]				
Pharmaceutical and personal care products (PPCP) (13 compounds)							
1,7 α -ethynylestradiol	57-63-6	3.7	[47]	Diclofenac	15307-79-6	0.7	[55] 4.2
Acetaminophene	103-90-2	0.5	[47]	Ibuprofen	15687-27-1	4	[47] 4.4
Clofibrac acid	882-09-7	2.6	[56]	Methylparaben	99-76-3	1.7	[57] 8.4
Caffeine	58-08-2	−0.07	[47]	Sulfamethoxazole	723-46-6	0.9	[47] 6
Carbamazepine	298-46-4	2.5	[47]	Trimethoprim	738-70-5	0.9	[47] 7.1
Ciprofloxacin	85721-33-1	0.3–1.3	[58]	Warfarin	81-81-2	2.7	[46] 5
Diatrizoate	737-31-5	1.8	[59]				
Others (9 compounds)							
4,4'-diaminophenylmethane	101-77-9	1.6	[60]	Bis-2-ethyl-hexylphthalate	117-81-7	7.6	[61] na
4-nonylphenol	104-40-5	4.5	[61]	Fluorene	86-73-7	4.2	[47] na
Acenaphthene	83-32-9	4.2	[62]	<i>m</i> -Toluidine	108-44-1	1.4	[63] 4.7
Bisphenol-A	80-05-7	3.3	[61]	Naphthalene	91-20-3	3.3	[47] na
Dibutylphthalate	84-74-2	5.4	[64]				

USA) respectively. Cartridges were manually manufactured from empty 1-mL SPE tubes, SPE frits (Interchim, Montluçon, France) and were filled with 200 ± 0.5 mg of sorbent for the Strata-SAX cartridge and 300 ± 0.5 mg of sorbent for the Oasis-HLB cartridge.

Reagents and chemicals

Solvents and reagents (chromatography quality) were purchased from VWR (Radnor, PA, USA) for acetonitrile and sodium chloride, and Sigma–Aldrich for methanol (St Louis, MO, USA). Ultrapure water was obtained from a Purelab classic water purification system (Siemens, Alpharetta, GA, USA).

Forty-three compounds having a wide range of physico-chemical properties (Table 2) were used in the current study. These were purchased from Sigma–Aldrich with the exception of clofibrac acid and sodium diatrizoate, which were from VWR. All were high-purity (greater than 97 %).

Experiments on individual compounds were conducted from stock solutions of pollutants (400 – 600 mg L^{−1}) prepared in methanol or in ultrapure water, and stored in the dark at 5 ± 3 °C. Working solutions were prepared daily by a series of dilutions of stock solutions with ultrapure water. Prior to extraction, water samples were spiked with targeted compounds at a concentration of 50 µg L^{−1}.

A mixture of 43 pesticides (Table S1) was provided by a certified laboratory (Environment and Health Research laboratory, LERES, Rennes, France). It was prepared in acetonitrile from a stock solution at 1 g L^{−1} of certified standards (purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany) except for mesotrione (Sigma–Aldrich)). The purity of these certified standards exceeded 96 %.

Prior to extraction, water samples were spiked with the mixture of targeted compounds at a concentration of 40 µg L^{−1}.

Ultraviolet analysis

A spectrum (between 200 and 400 nm) of each eluting fraction was obtained by UV spectrophotometry. A charge-coupled device (CCD) array spectrophotometer was used as a detector. It was directly coupled to a 20-mm path-length flow cell by optical fibres. Measurement parameters such as integration time were calculated for each calibration solution for each experiment. An optical fibre of 450-µm core diameter was used to connect the cell to a deuterium light source.

High-performance liquid chromatography–mass spectrophotometry (HPLC-MS) analysis

Analyses were performed using a Waters Alliance 2695 separation module coupled to a Waters Micromass ZQ mass spectrometer (Waters, St-Quentin-en-Yvelines, France) fitted with a Z-Spray electrospray ionisation (ESI) source. The chromatographic separation was performed at a flow rate of 0.2 mL min^{−1} on a Waters Xterra MS C18 column (150-mm length \times 2.1-mm internal diameter, 3.5-µm particle size) held at a constant temperature of 35 °C. The binary mobile phase comprised ultrapure water (solvent A) and acetonitrile (solvent B), both acidified with 0.1 % methanoic acid. The sample injection volume was 10 µL. The samples were dissolved in the mobile phase at initial conditions (82 % A) before injection. The gradient elution program was as follows: 0–10 min, 82–70 % A; 10–20 min, 70–50 % A; 20–35 min, 50–20 % A; 35–40 min, 20 % A; 40–40.1 min, 20–82 % A (return to initial conditions); 40.1–50 min, 82 % A (equilibration). The ESI parameters were as follows: capillary voltage, 2.0 kV for negative ion mode and 3.0 kV for positive ion mode; extractor voltage, 3 V; source and desolvation temperature, 100 and 350 °C respectively; cone and desolvation gas (nitrogen, Air Liquide, France) flow, 150 and 500 L h^{−1} respectively. The mass spectrometer was

operated in single ion recording (SIR) mode. The two most sensitive and specific ions were monitored for each compound using the ESI positive or negative ion mode, depending on the compounds. Dwell times ranged from 100 to 1000 ms in 16 acquisition windows (nine in the ESI positive ion mode and seven in the ESI negative ion mode) containing 1 to 14 compounds (1 to 28 ions). Inter-scan and inter-channel delays were set at 0.3 and 0.02 s respectively. Analytical characteristics of measured compounds (monitored ions and cone voltages) are reported in Table S1. *MassLynx* (4.1) software (Waters, Milford, MA, USA) was used for instrument control, data acquisition and quantification.

The limits of quantification (LOQ) were defined as the lowest concentrations of compounds for which the relative standard deviation (RSD) of replicate injections was less than 20% and the signal-to-noise ratio (S/N) greater than 10. The instrumental LOQ was 20 $\mu\text{g L}^{-1}$ for all pesticides. The quadratic calibration curves were plotted for each compound by analysing at least five calibration solutions from the LOQ (20 $\mu\text{g L}^{-1}$) to 200 $\mu\text{g L}^{-1}$.

Results

The MSP2E system was used not only to extract and pre-concentrate the analytes of interest, but also to separate them. Ultraviolet spectrophotometry or HPLC-MS was used to analyse each fraction and check the fractionation strategy.

Fractionation strategy and experimental prediction model

The MSP2E method entails loading a sample into two superposed SPE cartridges, followed by the elution of each cartridge by specific solvents. Work performed earlier allowed

determination of the SPE phases (Strata-SAX and Oasis-HLB) and the composition of the corresponding eluting solvents (mixture of methanol and sodium chloride and mixtures of acetonitrile and ultrapure water respectively) for the extraction of anionic and neutral or anionic compounds respectively.^[14]

In the latter case, the percentage of acetonitrile allowed the fractionation of neutral/cationic compounds according to their physicochemical properties, in particular their hydrophobicity ($\log K_{ow}$).^[14] Solvent S2 (30% ACN) eluted highly polar substances ($\log K_{ow}$ ranging from -0.1 to 1.7), whereas solvent S3 (70% ACN) was specifically more effective on medium-polarity substances ($\log K_{ow}$ ranging from 0.9 to 4.2). An experimental plan (data not shown) on a dozen molecules having $\log K_{ow}$ ranging from -0.1 to 5 allowed us to determine four eluting fractions, allowing their more thorough separation (Fig. 2). According to its $\log K_{ow}$, a compound can be eluted in one fraction (for example for $-0.1 < \log K_{ow} < 0.6$), can be partially eluted in two different fractions (for example for $0.9 < \log K_{ow} < 1.7$), or cannot be eluted ($\log K_{ow} > 4.2$).

Thus, given the specificity of the MSP2E system (structure of each cartridge, volume of the whole system, hydraulic flow rate), the final fractionation strategy was as follows:

1. Loading of the sample (100 mL) onto the two superposed SPE cartridges,
2. Collection of eluting fractions:
 - a) One fraction from the Strata-SAX cartridge, by eluting 1.5 mL of solvent S1 (fraction A1).
 - b) Four fractions from the Oasis-HLB, by using two different eluting solvents (S2–S3): fraction E1: 1 mL of S2, and fraction E2: 2 mL of S2; fraction E3: 2.5 mL of S3, and fraction E4: 2 mL of S3 (Fig. 3).

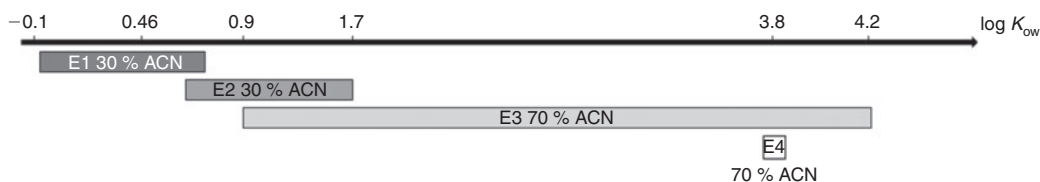


Fig. 2. Elution of Oasis-HLB cartridge depending on polarity of eluting solvents and substances. (ACN, acetonitrile.)

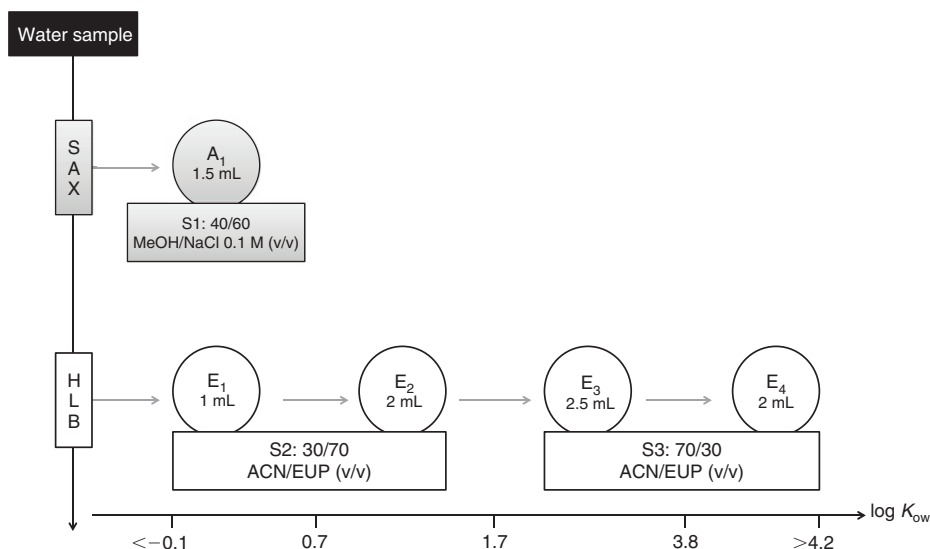


Fig. 3. Fractionation strategy. (ACN, acetonitrile; EUP, ultrapure water; $\log K_{ow}$, octanol–water partition coefficient.)

Table 3. Identification of elution fraction for 43 individual micropollutants and comparison with predicted fractionAnionic compounds are highlighted in bold. $\log K_{ow}$, octanol–water partition coefficient; pK_a , acid dissociation constant; na, not available; ne, no elution

Compound	$\log K_{ow}$		pK_a	Prediction	Recovery in ultrapure water	
Diquat	−4.6	[15]	na	E1	✘	No retention
Paraquat	−4.5	[16]	na	E1	✘	No retention
Caffeine	−0.07	[47]	0.8	E1	✓	
Acetaminophen	0.5	[47]	9.3	E1	✓	
Ciprofloxacin	0.3–1.3	[58]	5.9; 8.9	E1 + E2	✓	
Diclofenac	0.7	[55]	4.2	A1	✓	
Trimethoprim	0.9	[47]	7.1	E2	✓	
Sulfamethoxazole pH 8	0.9	[47]	6	E2 + E3	✓	
Hexazinone	1.4	[43]	na	E2 + E3	✓	
<i>m</i> -Toluidine	1.4	[63]	4.7	E2 + E3	✓	
4,4'-Diaminophenylmethane	1.6	[60]	na	E2 + E3	✓	
Methylparaben	1.7	[57]	8.4	E2 + E3	✓	
Diatrizoate (sodium)	1.8	[59]	3.4	A1	✓	
2-Nitrophenol	2	[44]	7.2	E3	✓	
Metazachlor	2.11	[45]	1.3	E3	✓	
Isoproturon	2.3	[45]	0.9	E3	✓	
Simazine	1.5–2.3	[51]	1.6	E3	✓	
Carbaryl	2.4	[48]	10.4	E3	✓	
Carbamazepine	2.5	[47]	14	E3	✓	
Chlortoluron	2.5	[49]	0.1; 14.4	E3	✓	
Atrazine	2.6	[47]	1.7	E3	✓	
Clofibric acid	2.6	[56]	3.2	A1	✓	
Warfarin	2.7	[46]	5	A1	✓	
Diuron	2.8	[45]	3.6	E3	✓	
2,4-D	2.7–2.8	[42]	2.6–3.3	A1	✓	
Terbutylazine	3.04	[53]	2	E3	✓	
Metolachlor	3.13	[47]	na	E3	✓	
Linuron	3.2	[46]	12.1	E3	✓	
Naphthalene	3.3	[47]	na	E3	✓	
Diazinon	3.3	[50]	2.6	E3	✓	
Bisphenol A	3.3	[61]	9.9–10.0	E3	✓	
Dichlorprop	3.4	[42]	2.9–3.5	A1	✓	
Alachlor	3.5	[46]	0.6	E3	✓	
Terbutryn	3.7	[54]	4.4	E3	✓	
1,7 α -ethynylestradiol	3.7	[47]	10.2	E3	✓	
Parathion-ethyl	3.8	[48]	na	E3+E4	✓	
Ibuprofen	4	[47]	4.4	A1	✓	
Fluorene	4.2	[47]	na	E3	✓	
Acenaphthene	4.2	[62]	na	ne	✓	
4-Nonylphenol	4.5	[61]	10.3	ne	✓	
Dibutylphthalate	5.4	[64]	na	ne	✘	E3
Dinoterb	5.6	[52]	3.5	ne	✓	
Bis-2-ethyl-hexylphthalate (DEHP)	7.6	[61]	na	ne	✓	

−4.6

 $\log K_{ow}$

7.6

Such methodology allows:

1. Automatic extraction and preconcentration of organic compounds,
2. Automatic sample fractionation into five specific characteristic fractions:
 - a) Fraction A1, composed of anionic substances.
 - b) Fractions E1 to E4, composed of cationic or neutral compounds with $\log K_{ow}$ in the range of: <0.1–0.7, 0.7–1.7, 1.7–3.8, >3.8.
 - c) Pre-identification of positive fractions through UV spectrophotometry.

It thus becomes possible to predict the fraction any compound will elute in. Conversely, it is possible to positively attribute a fraction to categories of compounds.

Both methodology and prediction were validated using solutions of individual compounds and a complex mixture.

Validation of fractionation prediction for individual substances

Individual solutions of 43 micropollutants (including pesticides, pharmaceuticals, preservatives, detergents and PAHs) selected according to their different physicochemical properties (pK_a and $\log K_{ow}$) (Table 2) were percolated through the system (superposed cartridges). In each case, five eluting fractions (one from Strata-SAX and four from Oasis-HLB) were collected, analysed (UV and HPLC) and compared with the prediction as described above (Table 3).

On the whole, more than 90% of the results follow the prediction. Anionic compounds (seven) were retained at above

Table 4. Physicochemical properties of the 43 pesticides in mixture
 log K_{ow} , octanol–water partition coefficient; pK_a , acid dissociation constant; na, not available

Compound	log K_{ow}	pK_a	Compound	log K_{ow}	pK_a
Sulcotrione	−1.7 [65]	3.1	Boscalid	2.96 [66]	na
Nicosulfuron	−0.35 [67]	4.8; 7.6	Tebutam	3 [68]	na
Trichlopyr	−0.45 [69]	2.7	Terbutylazine	3.04 [53]	2
Mesotrione	0.11 [70]	3.1	Mecoprop	3.1–3.6 [42]	3.1–3.7
Oxadixyl	0.7 [71]	na	Metolachlor	3.13 [47]	na
Imazamethabenz-methyl	1.54–1.82 [72]	na	MCPA	3.2 [42]	3.1
Simazine	1.5–2.3 [51]	1.6	Linuron	3.2 [46]	12.1
Fluroxypyr	1.74 [73]	2.9	Fluthiamide	3.2 [74]	na
Metazachlor	2.11 [45]	1.3	Dichlorprop	3.4 [42]	2.9–3.5
Isoxaflutol	2.19 [75]	na	Epoxiconazole	3.44 [76]	na
Isoproturon	2.3 [45]	0.9	Alachlor	3.52 [46]	0.6
Carbofuran	2.32 [54]	na	Prochloraz	3.53 [48]	3.8
Bentazone	2.34 [42]	3.3	Tetraconazole	3.56 [61]	4.95
Metosulam	2.39 [73]	5.3	Tebuconazole	3.7 [61]	3.4; 13.7
Propachlor	2.41 [77]	2.8	Ioxynil	3.94 [78]	4.5
Dimethenamid	2.47 [79]	na	Cyprodinil	4 [80]	4.4
Chlortoluron	2.5 [49]	0.1; 14.4	Oxadiazon	4.09 [81]	na
Isoxaben	2.64 [82]	1.3	Acetochlor	4.14 [83]	na
Terbutometon	2.7 [84]	4.7	Diflufenican	4.9 [85]	na
2,4-D	2.7–2.8 [42]	2.6–3.3	Azoxystrobin	5.13 [86]	0.67
Diuron	2.8 [45]	3.6	Pendimethaline	5.18 [81]	na
Bromoxynil	2.8 [76]	3.9			

90 % (and all were eluted) on the Strata-SAX cartridge and the neutral or cationic compounds (36) were 94 % retained (34/36) on the Oasis-HLB cartridge and were 88 % eluted (30/34) from this cartridge. The missing molecules concern compounds with extreme physicochemical properties (high hydrophilicity or hydrophobicity). Indeed, only diquat and paraquat are not adsorbed in the cartridges, probably owing to their hydrophobicity being too high (log K_{ow} = −4.6^[15] and −4.5^[16] respectively). In addition, only four compounds (4-nonylphenol, dinoterb, acenaphthene and bis(2-ethylhexyl) phthalate, DEHP) were not eluted under our experimental conditions (probably owing to their high hydrophobicity) and these required the use of another organic solvent for their elution. Examples of such compounds (phthalates, acenaphthene and 4-nonylphenol) have been shown to require dichloromethane-based solvent added to methanol,^[17,18] acetone^[19] or hexane.^[20]

Validation of fractionation prediction for a complex mixture

The fractionation strategy (prediction) was tested on a mixture of 43 pesticides (at 40 $\mu\text{g L}^{-1}$) (Table 4) in ultrapure water and in river water (2.7 mg L^{-1} of total organic carbon, 22.1 mg L^{-1} of nitrate). Note that 11 compounds have already been tested individually, as described previously.

After percolation through the cartridges, five eluting fractions were collected, analysed and compared with the predictions (Table 5).

The UV measurement of all fractions obtained from both ultrapure and river water was positive (UV peaks or marked shoulders, absorbance greater than 0.2), demonstrating the presence of one or several organic compounds. For example, Fig. 4 shows the UV spectra of each eluting fraction from river water without a guard cartridge.

Unlike the UV spectra of fractions A1, E1, E2 and E3, the UV spectrum of the last fraction (E4) showed no relevant UV signal.

Concerning ultrapure water, the experimental results (adsorption and elution) were accurate in relation to the prediction. The complexity of the mixture (43 pesticides) did not alter the method efficiency. Only one substance (oxadixyl) failed to completely support the assumption, because it was eluted in E2 and E3.

Behaviour was different when the mixture was spiked into river water. Unlike anionic compounds, there is good correspondence for neutral or cationic compounds (90 % of experimental results matched the prediction). Indeed, we observed a matrix effect that was probably due to the interference of anionic inorganic compounds (22.1 mg of nitrate and 350 $\mu\text{S cm}^{-1}$ of conductivity) on the Strata-SAX cartridge. No anionic compounds were initially adsorbed on the cartridge whereas 5 out of 13 compounds were retained on the Oasis-HLB (and 60 % eluted in the fraction corresponding to their polarity).

Moreover, no chemicals were eluted in eluting fraction E4, which closely matched the UV spectra of this fraction (Fig. 4).

To counter the interaction of inorganic anions, we added a guard cartridge of Strata-SAX to retain them.

The mass of the sorbent was calculated considering the anionic capacity of the Strata-SAX sorbent (0.9 meq g^{-1} of sorbent) and the relation between the matrix conductivity and the anion concentrations (Eqn 1^[21]):

$$\sum \text{Concentration of anions} = 10^{-2} \times \text{conductivity} \quad (1)$$

where concentration of anions is in milliequivalents per litre and the conductivity is in microsiemens per centimetre.

So the addition of a 500-mg Strata-SAX guard cartridge allows the method efficiency to be improved: 100 % of the anionic compounds were retained and eluted (4 of 13 anionic compounds were retained and eluted on the Strata-SAX cartridge). The other anionic compounds were retained and eluted on the Oasis-HLB cartridge, 78 % according to their polarity.

Table 5. Predictions and results concerning fractionation of a mixture of 43 pesticides in ultrapure water and in river water
Anionic compounds are highlighted in bold. $\log K_{ow}$, octanol–water partition coefficient; ne, no elution

Compound	Predicted fraction	Observed fraction			$\log K_{ow}$	
		Recovery in ultrapure water		Recovery in river water		
		Without guard cartridge	Without guard cartridge	With guard cartridge		
Sulcotrione	A1	A1	ne	E1	-1.7	
Nicosulfuron	A1	A1	ne	E1		
Trichlopyr	A1	A1	E1	E1		
Mesotrione	A1	A1	ne	E1		
Oxadixyl	E2	E2 + E3	E1 + E2	E2		
Fluroxypyr	A1	A1	ne	E1		
Imazamethabenz-methyl	E3	E3	E1 + E2	E3		
Metazachlor ^A	E3	E3	E3	E3		
Isoxaflutol	E3	E3	E3	E3		
Simazine ^A	E3	E3	E2	E2 + E3		
Isoproturon ^A	E3	E3	E2 + E3	E3		
Carbofuran	E3	E3	E2	E2 + E3		
Bentazone	A1	A1	ne	A1	5.18	
Metosulam	A1	A1	E3	A1		
Propachlor	E3	E3	E3	E3		
Dimethenamid	E3	E3	E3	E3		
Chlortoluron ^A	E3	E3	E3	E3		
Isoxaben	E3	E3	E3	E3		
Terbutometon	E3	E3	E3	E3		
2,4-D^A	A1	A1	ne	E1		
Diuron ^A	E3	E3	E3	E3		
Bromoxynil	A1	A1	E1	A1		
Boscalid	E3	E3	E3	E3		
Tebutam	E3	E3	E3	E3		
Terbutylazine ^A	E3	E3	E3	E3		
Mecoprop	A1	A1	E3	E3		
Metolachlor ^A	E3	E3	E3	E3		
MCPA	A1	A1	ne	E3		
Linuron ^A	E3	E3	E3	E3		
Fluthiamide	E3	E3	E3	E3		
Dichlorprop^A	A1	A1	ne	E3		
Epoxiconazole	E3	E3	E3	E3		
Alachlor ^A	E3	E3	E3	E3		
Prochloraz	E3	E3	E3	E3		
Tetraconazole	E3	E3	E3	E3		
Tebuconazole	E3	E3	E3	E3		
Ioxynil	A1	A1	E1	A1		
Cyprodinil	E3	E3	E3	E3		
Oxadiazon	E3	E3	E3	E3		
Acetochlor	E3	E3	E3	E3		
Diflufenican	ne	ne	ne	ne		
Azoxystrobin	ne	ne	ne	ne		
Pendimethaline	ne	ne	ne	ne		
Partial or total recovery in predicted eluting fraction (%)	100 %	63 %	79 %			

^APesticides already studied individually in the present study.

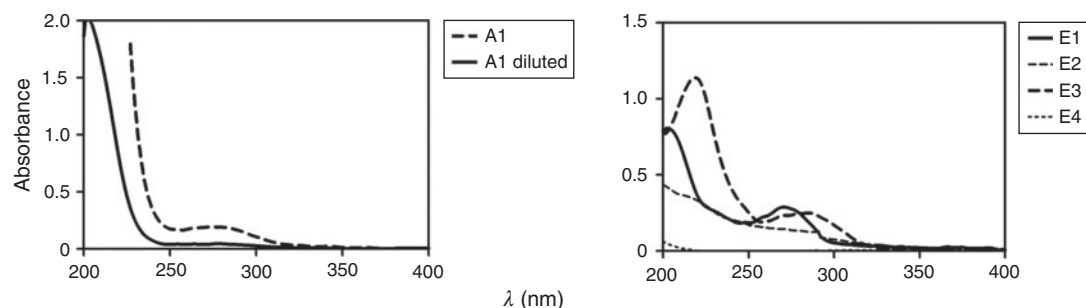


Fig. 4. UV spectra of the fractions obtained after elution of Strata-SAX (A1 and A1 diluted 5 ×) (left) and Oasis HLB (E1, E2, E3 and E4) (right) cartridges after percolation of 100 mL of river water without Strata-SAX guard cartridge.

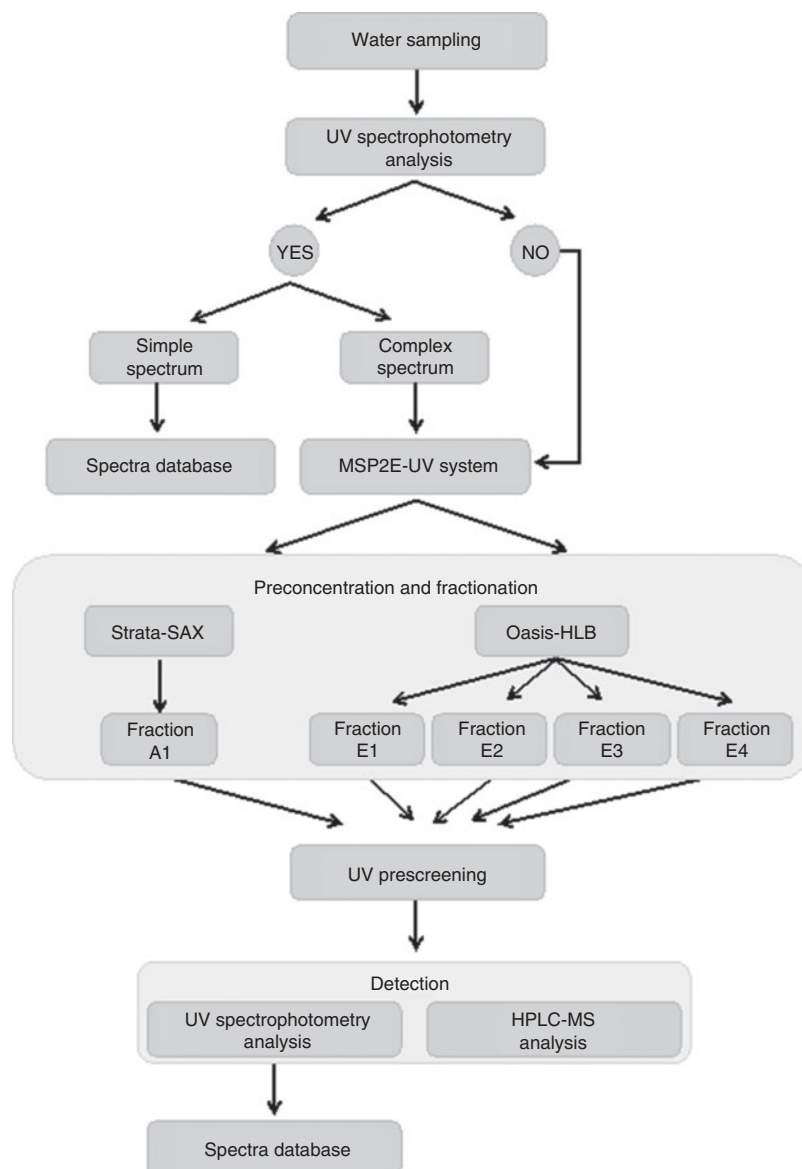


Fig. 5. Methodology of fractionation strategy (UV spectrophotometry, ultraviolet spectrophotometry; MSP2E-UV, multiple solid-phase double extraction coupled with ultraviolet spectrophotometry detection; HPLC-MS, high-performance liquid chromatography–mass spectrophotometry.)

Conclusion and perspectives

The present paper presents an innovative fractionation method based on an automatic multiple solid-phase extraction (MSP2E) to detect organic micropollutants in water. After loading the sample in the analyser, it entails obtaining five specific fractions; each of these is characteristic of a compound category: anionic and cationic or neutral compounds with various polarity.

One of the more interesting aspects of this methodology is the option of simplifying the analytical chain by focussing the more in-depth analysis on limited categories of compounds. More than 75 molecules were studied in the current work. On the whole, it was possible to predict the elution fraction of 85 % of the compounds. Work on complex matrices (in particular with inorganic anions, which can be retained on Strata-SAX cartridge) highlighted the necessity of adding a guard cartridge. In

addition, an improvement to the elution could be carried out to take into account highly apolar molecules (for example some PAHs).

The fractionation method developed in the present paper does not aim to replace conventional laboratory analytical methods. However, by coupling the MSP2E with rapid UV measurement (for characterising positive samples), it could constitute an alternative tool for rapid on-site screening for organic micropollutants, as illustrated in Fig. 5.

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