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Optimization of the class-selective extraction of triazines from aqueous samples using a molecularly imprinted polymer by a comprehensive approach of the retention mechanism ☆

F. Chapuis[a], V. Pichon[a,*], F. Lanza[b], S. Sellergren[b], M.-C. Hennion[a]

[a]*Department of Environmental and Analytical Chemistry, Ecole Supérieure de Physique et de Chimie Industrielles, 10 rue Vauquelin, 75231 Paris Cedex 05, France*

[b]*INFU, University of Dortmund, Otto Hahn Strasse 6, 44221 Dortmund, Germany*

Abstract

Direct, selective solid-phase extraction of triazines from aqueous samples is presented using a molecularly imprinted polymer (MIP) made with terbutylazine as template molecule. After optimization of the steps of the procedure, 14 triazines including degradation products were studied and satisfactory extraction recoveries were obtained except for thiotriazines. By comparing results obtained with the terbutylazine MIP and a similar non-imprinted polymer, it was determined that retention was achieved via specific interactions except for hydroxyterbutylazine. Selectivity of the extraction procedure was also verified by applying the MIP for the extraction of phenylureas that were not retained on it. The effects of the charge distribution and of molecular volume of the triazines (obtained by molecular modeling) on the selectivity of interactions between the analytes and the MIP were studied. However, when the optimized procedure was applied to real samples, low extraction recoveries were obtained due to strong matrix effects: ion-exchange occurs between the carboxylate groups of the MIP and the ionic species of the sample, that prevents subsequent specific interactions. By introducing an acid wash step, the procedure was successfully applied for the class-selective extraction of triazines from industrial effluent and surface water samples. Finally, increased extraction recoveries were achieved for the polar degradation products of triazines by using a mixed-phase composed of a polymeric sorbent and the MIP.

Keywords: Molecular imprinting; Solid-phase extraction; Water analysis; Environmental analysis; Pesticides; Triazines; Phenylureas

1. Introduction

Solid-phase extraction (SPE) is the technique of choice for the simultaneous extraction and concentration of many organic compounds present at trace levels in aqueous samples. Despite their attractive features, the classical SPE sorbents retain analytes by non-selective hydrophobic interactions that lead to partial co-extraction of interfering substances. More selective sorbents have been developed which are based on molecular recognition mechanisms. They include immunosorbents (ISs) that utilize selective antigen–antibody interactions. Many applications

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*Corresponding author. Tel.: +33-1-4079-4772; fax: +33-1-4079-4776.

E-mail address: valerie.pichon@espci.fr (V. Pichon).

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demonstrated their high selectivity in aqueous matrices [1] and highlighted the possibility of simultaneous extraction of a group of pollutants having a similar structure. Triazines and their degradation products were successfully extracted from water by off-line [2–4] and on-line [5–7] procedures. Nevertheless, the development of antibodies takes a long time and is costly.

Theses drawbacks have led to the development of synthetic antibody mimics, the so-called molecularly imprinted polymers (MIPs). These sorbents possess specific cavities designed for a template molecule. The most common approach consists of a non-covalent imprinting: MIPs are synthesized in solution by the complexation of a target molecule (template) with functional monomers through non-covalent bonds, followed by a polymerization step in the presence of a cross-linker. The template molecules are then removed, producing a polymer with molecular recognition sites, which are able to selectively rebind the template and analytes of similar structure. The monomer is chosen to develop strong non-covalent interactions (such as hydrogen bonds) with the template. The polymerization solvent is generally an aprotic and non-polar (or weakly polar) solvent. The choice of both parameters has been studied by several authors [8–11]. MIPs present a number of advantages compared to antibodies including easy and rapid preparation and high thermal and chemical stability [12]. Many applications dealt with chromatographic separations. Sellergren described the first use of a MIP as selective sorbent for the SPE of pentamidine present at a low concentration in urine [13]. Subsequently, the use of MIPs for selective extraction and clean-up from various samples has been described in the literature, e.g. sameridine, phenytoin and caffeine from plasma [14–16], theophylline from human serum [17] or clenbuterol from calf urine [18]. In the environmental field, nitrophenol was extracted from river water [19]. In the clinical field, nicotine was analyzed in chewing-gum [20]. Triazines were selectively extracted from different matrices such as beef liver [21], water [22,23], urine and apple extract [24]. In most cases, the MIP is packed in a cartridge or a column and used off-line. The on-line coupling of MIPs with liquid chromatography was also described using a C_{18} silica column [24] and a restricted access material (RAM) [23].

It has been demonstrated that MIPs offer the highest selectivity when the samples are dissolved in the solvent used for the MIPs preparation. Consequently, MIPs are used as clean-up sorbents [25–27]. Very few authors have carried out direct extraction of compounds from aqueous matrices [19,22]. During percolation of the water sample, trace compounds are not retained by the polar selective interactions that occur in the porogen solvent, rather by non-selective hydrophobic interactions with the polymeric matrix of the sorbent. However, Ferrer et al. [22] described the possibility to transform the non-specific interactions into specific hydrophilic interactions (hydrogen bonds) by applying a small volume of the porogen solvent after sample percolation. Though the selectivity of the MIP was demonstrated with real samples, poor recoveries were obtained compared to those obtained with pure water samples.

The aim of this work is to optimize the SPE procedure for the class extraction of triazines and their polar degradation products with the direct percolation of aqueous samples through the MIP. Special attention is given to the retention mechanism that occurs in the second step of the process when an appropriate organic solvent is applied. Both objectives of this critical step are to link the analytes of interest to the MIP by specific interactions with the cavities and to remove interferences from the MIP (i.e. other co-extracted compounds retained during the first step via non-specific hydrophobic interactions). Phenylureas will be used as models to assess the selectivity of this extraction process. Using molecular modeling, the effects of the structure of compounds on their retention on MIPs will be highlighted. Finally, special attention will be given to matrix effects from real samples, because previous studies have shown a strong decrease in recoveries compared to spiked pure water samples.

2. Experimental

2.1. Chemicals

Pesticides (triazines and phenylureas) were obtained from C.I.L. (Saint-Foy-la-Grande, France). Stock standard solutions of 100 mg/l were prepared by weighing the solutes and dissolving them in methanol or in a water–methanol (50:50) mixture for

some degradation products of triazines. The stock solutions were stored at 4 °C. A standard solution of 5 mg/l was obtained by dilution in methanol from the stock solution. HPLC-grade acetonitrile and methanol were purchased from Mallinckrodt Baker (Deventer, The Netherlands) and dichloromethane was from Pestipur SDS (Peypin, France). High-purity water was obtained from a Milli-Q purification system (Millipore, Saint-Quentin en Yvelines, France). The structures of the studied compounds are shown in Fig. 1.

2.2. Apparatus and analytical conditions

Two HPLC systems were used. The first consisted of a Waters 717 autosampler (Waters, Saint Quentin en Yvelynes, France), a Varian 9010 solvent delivery unit (Varian, Les Ulis, France) and an LDC Spectro-Monitor III monochromator (LDC, Paris, France). The second, used for analysing real water samples, is an Agilent LC 1100 series system including an autosampler, a solvent delivery system and a diode-array detector (Agilent Technologies, Massy, France). The triazines were monitored at 220 nm and the phenylureas at 244 nm. The reversed-phase column was an Equisil ODS 5 μm, 250×4.6 mm I.D. (C.I.L.) that was connected to a precolumn (Hypersil 5 μm, 20×2.1 mm I.D., Colochrom, Gagny, France). The mobile phase was a mixture of acetonitrile and phosphate buffer (5×10^{-3} *M*, pH 7). The flow-rate was set at 1 ml/min.

2.3. Synthesis of molecularly imprinted polymers

MIPs were synthesized by Sellergren's group (University of Dortmund, Dortmund, Germany). Details of the synthesis were described previously [22]. Terbutylazine was used as the template molecule, methacrylic acid as monomer and dichloromethane as polymerization solvent. A non-imprinted polymer was obtained by performing the overall procedure in the absence of the template.

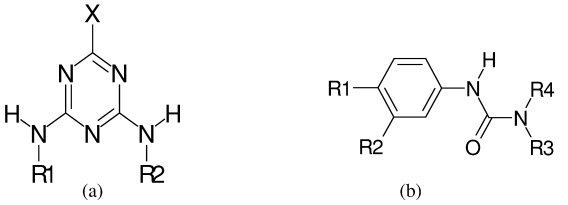

Fig. 1. General structures of triazines and phenylureas. (a) Triazines. X: Cl, OMe, SMe, OH. R1, R2: H, alkyl groups, CN. (b) Phenylureas. R1–R4: Cl, OMe, H, alkyl groups.

2.4. SPE procedure on MIP

2.4.1. Extraction of triazines from pure water

Cartridges of 3 ml were packed with 200 mg of the terbutylazine MIP or with 200 mg of the non-imprinted polymer. Before each use, the sorbent was conditioned with 15 ml of dichloromethane, 10 ml of methanol and 10 ml of pure water. The aqueous sample was percolated through the cartridge. After a drying step, dichloromethane was percolated through the sorbent in order to develop selective hydrophilic interactions. The target analytes were eluted from the cartridge with 3 ml of methanol. This fraction was then concentrated to dryness by a nitrogen stream and dissolved in 2 ml of a water–methanol (4:1) mixture. Fifty μl were analyzed by reversed-phase HPLC.

2.4.2. Extraction of triazines from real samples

Triazines from surface waters and an industrial effluent were extracted by the MIP using the same procedure. Fifty ml of surface water or diluted industrial effluent from the textile industry (dilution with pure water: 1:15 000, v/v) were filtered (Whatman filter GF/C, 47 mm, 1.2 μm, Maidstone, UK) and spiked with 1 μg/l of each compound. The sample was first percolated through the cartridge packed with 200 mg of the terbutylazine MIP. Then, 1 ml of 0.1 *M* hydrochloric acid solution was applied followed by 1 ml of pure water. After a drying step, 5 ml of dichloromethane were percolated through the cartridge. Elution was carried out by 3 ml of methanol, which were concentrated to dryness by a nitrogen stream and dissolved in 200 μl of a water–methanol (4:1) mixture, 50 μl of which were analyzed by reversed-phase HPLC.

2.4.3. Extraction of polar metabolites

Volumes of 50 and 100 ml of pure water, spiked with 0.5 μg of each metabolite, were percolated through the cartridge packed with 200 mg of the terbutylazine MIP. Extraction was carried out following the above procedure (see Section 2.4.2). The eluted fractions were concentrated to dryness by a

nitrogen stream and dissolved in 250 μl of a water–methanol (4:1) mixture, 50 μl of which were analyzed by reversed-phase HPLC.

A mixed-mode sorbent was also made by combining two layers, 100 mg of a styrene–divinylbenzene polymer (PS–DVB, 1080 m^2/g, Mallinckrodt Baker) and 200 mg of terbutylazine MIP. Extraction was carried out following the MIP procedure described for the extraction of triazines from real samples, except the washing step using 1.5 ml of HCl.

2.5. SPE procedure on classical sorbent

The industrial effluent was also extracted using a cartridge prepacked with a styrene–divinylbenzene polymer sorbent (Retain, 100 mg, 600 m^2/g, Thermo Hypersil, Les Ulis, France). Firstly, the sorbent was conditioned with 2 ml of methanol and 2 ml of pure water. After percolation of the sample, the sorbent was washed with 1 ml of pure water. The elution step was carried out using 4 ml of a methanol–water (1:1) solution. The eluted fraction was concentrated to dryness by a nitrogen stream and dissolved in 200 μl of a water–methanol (4:1) mixture, 50 μl of which were analyzed by reversed-phase HPLC.

2.6. Molecular modeling

Molecular modeling to determine the electronic charge distribution in triazines has been described elsewhere [28]. Using the HyperChemPro 6.0 software package (Hypercube, Gainesville, FL, USA), molecular mechanics permitted the finding of low energy conformations; they were then refined using semi-empirical mechanics. Finally, the conformation that possessed the lowest energy was refined with ab-initio mechanics. In addition, molecular volumes were evaluated by means of molecular modeling.

3. Results and discussion

3.1. Optimization of the extraction process in pure water

Direct, selective SPE of aqueous samples by a MIP requires three steps: (i) retention of analytes via non-specific hydrophobic interactions during percolation of the water sample, (ii) development of selective interactions between the MIP and the target analytes by percolating an appropriate solvent, a weakly polar and aprotic solvent such as dichloromethane, to generate hydrophilic interactions, (iii) desorption of the analytes from the MIP. The retention mechanism during the first step is similar to that which occurs with a classical hydrophobic sorbent. It is mainly based on the polarity of the analytes. The target analytes and many other organic compounds having similar polarity in aqueous samples can be co-extracted. The second step should allow, simultaneously, the interactions of the triazines with the specific cavities and the removal of the co-extracted contaminants. Since water and dichloromethane are not miscible, a drying step has to be introduced between those two steps. The third step consists of the elution of the triazines from the MIP, which can be easily performed by a protic and polar organic solvent such as methanol. Its role is to strongly interact, via hydrogen bonds, with the polymer to disrupt the hydrogen bonds developed by the compounds.

In order to assess whether the MIP specifically retains triazines, extraction recoveries of triazines by MIP and a non-imprinted polymer were compared. In a first experiment, samples of 50 ml of purified water were spiked with 0.5 μg of each analyte and percolated through each sorbent. After a drying step, 2 ml of dichloromethane were percolated. Elution was performed with 3 ml of methanol. The recoveries obtained for eight triazines and two metabolites with the terbutylazine MIP and the non-imprinted polymer are reported in Fig. 2. Recoveries on the MIP are above 70% for all the analytes. Recoveries are lower, about 40%, on the non-imprinted polymer except for the hydroxyterbutylazine metabolite (OHT) that is totally retained, proving the presence of specific recognition sites in the MIP. This procedure (2 ml of dichloromethane) did not remove non-specific interactions with the polymeric matrix because compounds were partially retained on the non-imprinted polymer. In order to improve selectivity, the volume of dichloromethane used for the washing step was increased to 5 ml. As shown in Fig. 3, non-specific interactions were significantly reduced because extraction recoveries on the non-imprinted polymer were lower than 5% for nine

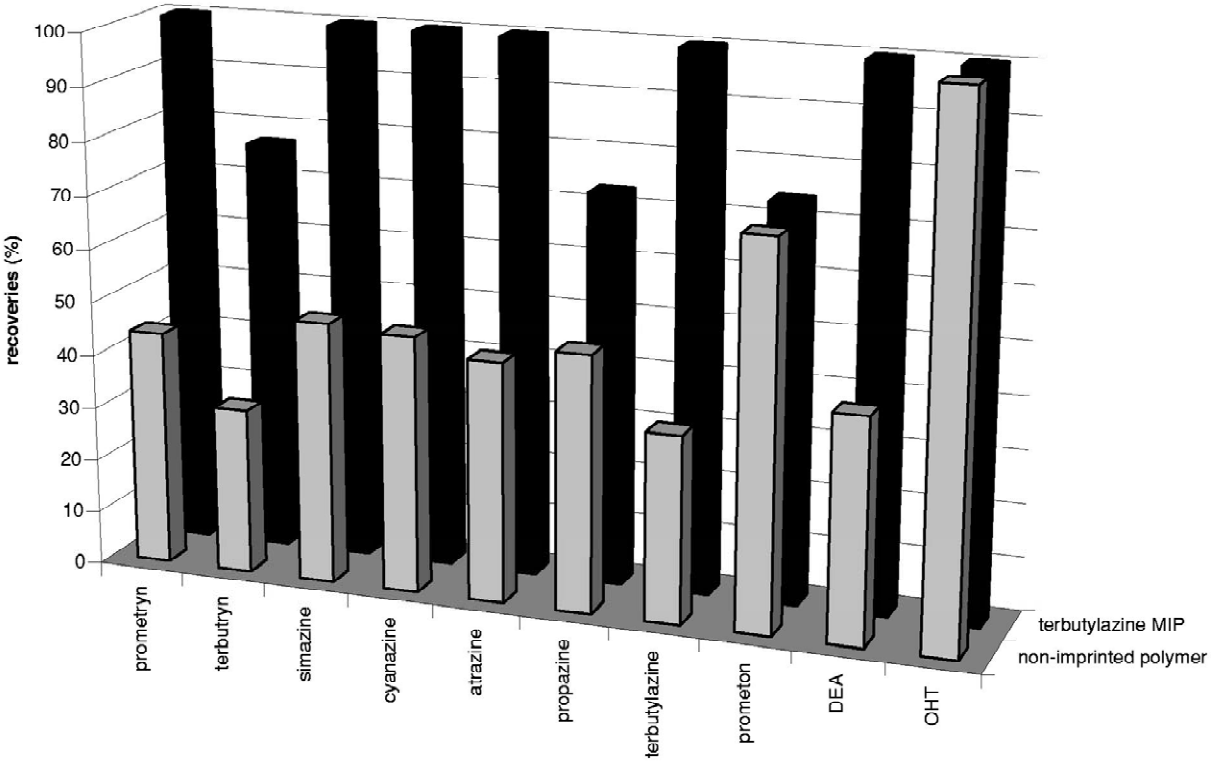

Fig. 2. Extraction recoveries (%) obtained on the terbutylazine MIP and on the non-imprinted polymer for triazines and metabolites after the percolation of 50 ml of water spiked with 500 ng of each compound and using a washing step using 2 ml of dichloromethane.

triazines and in the range of 5–10% for prometon and three dealkylated metabolites. Only the OHT metabolite was still retained with a recovery close to 100%. Five ml of dichloromethane did not affect the selective interactions because nine of the 14 analytes were retained with recoveries above 70% on the MIP. The more polar analyte, deisopropylatrazine (DIA), was retained with a recovery of 63% while three triazines which possess a thiomethoxy group in the 2-position on the heterocycle were retained selectively but with a much lower recovery around 15%.

Methanol (1%) was added to the 5 ml dichloromethane to decrease the non-specific interactions for OHT. Yet, it remained totally retained on the non-imprinted polymer, whereas recoveries for the other analytes on the MIP decreased dramatically due to the high eluting strength of the methanol (the highest recoveries were 30%). In conclusion, washing with 5 ml of dichloromethane is a satisfactory compromise to selectively retain the target analytes with low non-specific interactions during the SPE procedure.

The specificity of retention on the MIP was also tested by studying the retention of eight phenylurea herbicides with polarities and sizes similar to those of triazines. Samples made of 50 ml of purified water spiked with 0.5 μg of each phenylurea were percolated through the terbutylazine MIP and treated according to the optimized procedure. The polarity order is as follows: methoxuron, monuron, monolinuron, diuron, difenoxuron, linuron, chloroxuron, neburon with log K_{ow} values (octanol–water partition coefficient) ranging from 1.6 to 4.3. As expected, no retention was observed on the non-imprinted polymer showing the high selectivity of the procedure. Phenylureas were not retained on the MIP indicating that the cavities were very specific for the template and compounds with similar structures. A slight retention of metoxuron on the MIP was observed (27% recovery) and can be explained by the small

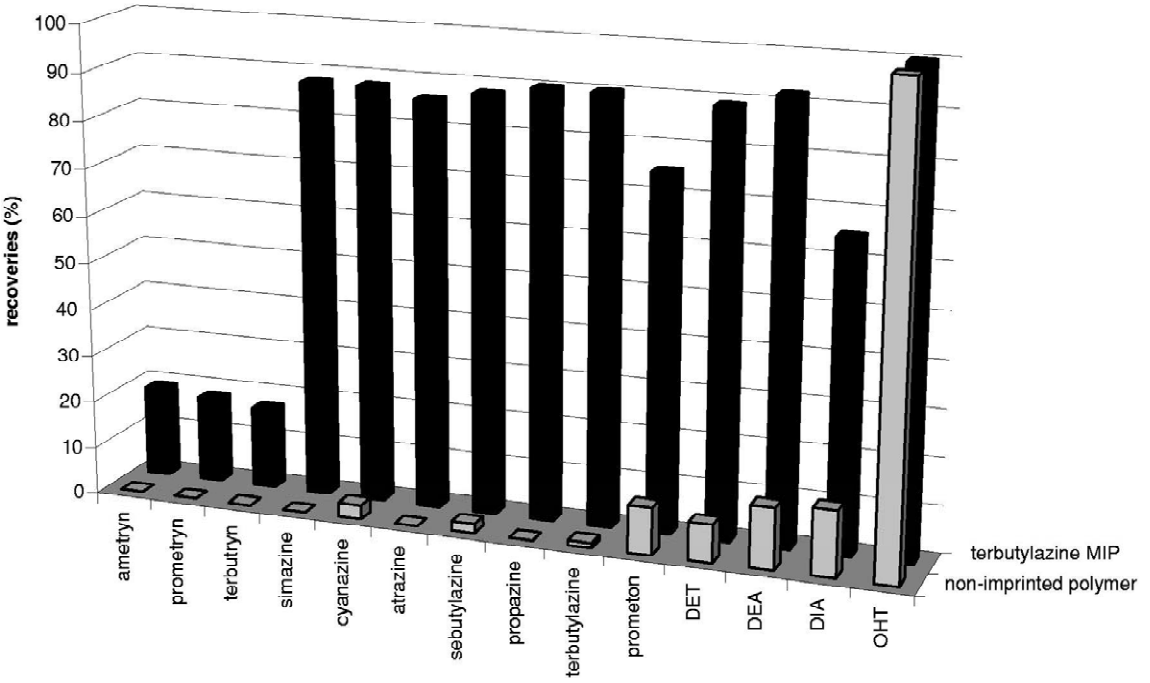

Fig. 3. Extraction recoveries (%) obtained by applying the same conditions as in Fig. 2 but with 5 ml dichloromethane for the washing step.

size of this compound that allows it to reach the specific cavities and by the presence of a methoxy group in the molecule (see Fig. 1). This group can develop hydrogen bonds with the polymer more readily than an alkyl group or a chlorine atom. Difenoxuron also possesses a methoxy group but it is larger than the template thus preventing its access to the cavities. Consequently, this procedure permits selective extraction of triazines even if few analytes can interfere with the specific cavities.

3.2. Effect of the structure of molecules on their retention

The MIP has been synthesized for molecular recognition of terbutylazine, so it is not surprising to obtain different extraction recoveries within the triazine group. The recovery differences can be explained by the interaction energies between the molecules and the recognition sites of the polymer. The end of the common names of triazines describes the substituent in the 2-position in the heterocycle (see Fig. 4). Compounds ending in ‘‘-ine’’ possess a chlorine atom (chlorotriazines), those ending in ‘‘yn’’ and ‘‘on’’ a thiomethyl group (thiotriazines) and a methoxy group (methoxytriazines), respectively. The hydroxy metabolite (OHT) possesses a hydroxy group. Different behaviours were observed for these

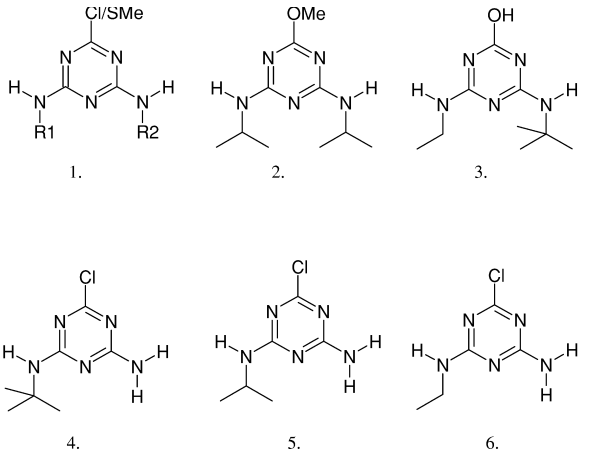

Fig. 4. Chemical structure of triazines and metabolites. (1) Chloro- and thiotriazines, R1, R2: H, alkyl groups, CN, (2) prometon, (3) OHT, (4) DET, (5) DEA, (6) DIA.

sub-classes of triazines. The chlorotriazines, including their dealkylated metabolites, i.e. deethylterbutylazine (DET), deethylatrazine (DEA) and DIA, are extracted with high recoveries, thus indicating a high affinity for the MIP, compared to thiotriazines, which have a poor affinity for the MIP. The hydroxy metabolite was strongly retained on the MIP but non-selective interactions could be involved in its retention.

In order to understand the effect of structure on the retention mechanism on the MIP during percolation of dichloromethane, the electric charge of atoms and the molecular volume were calculated for each triazine by molecular modeling [28].

Chlorotriazines, including the template, are extracted with 85% recoveries vs. 15% for thiotriazines. Thiotriazines possess a thiomethyl group in the 2-position that is larger than the chlorine atom of the template, limiting the access to the cavities. In addition, distribution of the electric charges in the molecules can contribute to poor retention of thiotriazines. Molecular modeling shows that all nitrogen atoms in triazines contribute to a negative charge and therefore, are able to form hydrogen bonds with the hydrogen of carboxylic acid functions of the MIP. Nitrogen atoms located in the *para* position of the substituent in the 2-position and nitrogen atoms of both amine functions were better able to create hydrogen bonds [29]. The chlorine atom and the thiomethyl group were positively charged, but the thiomethyl group was more positive than the chlorine atom rendering hydrogen bonds less favourable.

The high affinity of OHT for the non-imprinted polymer can be explained by the presence of a hydroxyl group in the 2-position. By its negative charge, this group is both a donor and an acceptor of hydrogen bonds, causing strong retention on the non-imprinted polymer. The dealkylated degradation products, DET, DIA and DEA, possess a chlorine atom in the 2-position and a primary amine function. Consequently, steric hindrance caused by alkyl groups on the nitrogen atom is reduced, leading to hydrogen bonds with the non-imprinted polymer that explain their partial retention (10%). The lower extraction recovery (65%) for DIA on the MIP compared to the other degradation products can be explained by its higher polarity (log K_{ow}=1.1). During percolation of the water sample, DIA develops weaker hydrophobic interactions which lead to its loss during this step.

3.3. Matrix effects

A series of experiments was carried out with mineral and tap water samples spiked with three triazines and two metabolites by applying the previous procedure. The extraction recoveries, reported in Fig. 5, are lower than 20% for the tap and the mineral water samples indicating a matrix effect. This loss of retention can be explained by the presence of cations in these water samples. In order to confirm this hypothesis, extraction recoveries were measured using pure water spiked with triazines and containing 0.15 *M* NaCl or 0.004 *M* $CaCl_2$, close to the amount of Ca^{2+} in a mineral water. With NaCl in pure water, the compounds are retained as in pure water. Na^+, at this concentration, has no effect on retention. In contrast, Ca^{2+}, at a lower concentration level, dramatically decreases the extraction recoveries to levels as low as for tap or mineral water, indicating an ion-exchange mechanism. Methacrylic acid, used as monomer for the synthesis, possesses a carboxylic acid function with a pK_a value of 4.65. During percolation of the water sample, ion-exchange between the proton of the carboxylic acid of the polymer and the divalent cations can take place, removing the hydrogen bond donor groups necessary for selective retention on the MIP.

This matrix effect was eliminated by regenerating the interaction sites before the dichloromethane washing step: 1 ml of 0.1 *M* hydrochloric acid solution was percolated through the MIP after percolation of the water sample to exchange the divalent cations by protons, followed by a washing step of 1 ml of pure water before drying the MIP and the percolation of dichloromethane. Fig. 6 shows the extraction recoveries for mineral water and tap water using both procedures. With the HCl washing, triazines and metabolites are extracted with recoveries higher than 89% and no retention is observed on the non-imprinted polymer, except for DEA and DET (15% of recoveries).

3.4. Extraction of polar metabolites

The low recovery of 65% obtained for DIA (see

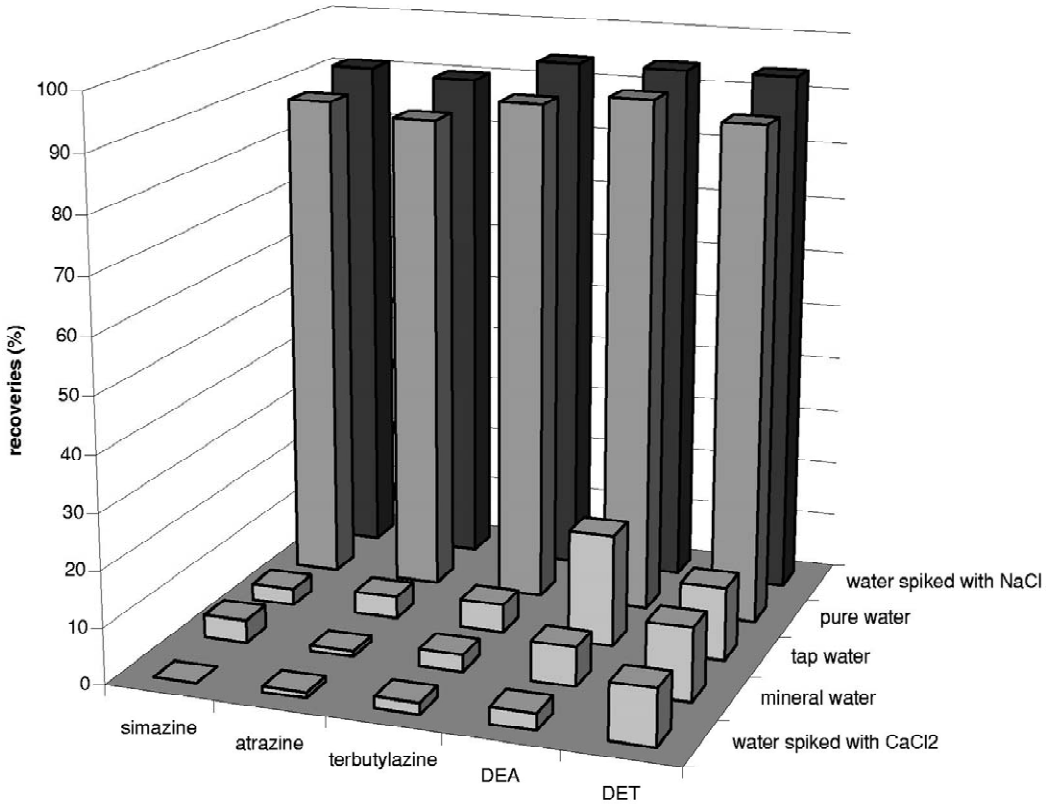

Fig. 5. Extraction recoveries (%) obtained by applying the procedure described in Fig. 3 to different kinds of water; mean value of two measurements.

Fig. 3) compared to other degradation products has been explained by a breakthrough occurring during percolation of the water sample. In order to confirm this hypothesis, didealkylatedatrazine (DDA, log $K_{ow}=0$) and other metabolites were added to the water sample. Fig. 7 shows that DDA is not retained with a sample volume of 50 ml and that the recoveries of DIA, DEA and DET decrease when the sample volume increases from 50 to 100 ml, in agreement with a retention mechanism based on hydrophobic interactions. Analyte recoveries are in the order of the analyte polarities and decrease with an increase of sample volume. HCl washing (1.5 ml) causes a loss of retention for DIA decreasing the recovery from 65% (Fig. 4) to 30% for a sample volume of 50 ml. This effect can be due to a partial ionization of DIA during the application of the acid solution at pH 1.

In order to increase the retention of these polar metabolites on the MIP, the compounds have to be more strongly retained by hydrophobic interactions during percolation of the water samples. This can be obtained using a mixed-mode sorbent that consists of a combination of a polymeric sorbent and the terbutylazine MIP. One hundred mg of PS–DVB sorbent with a specific surface area of 1080 m^2/g was selected to strongly retain the compounds during percolation of the water sample. The transfer of compounds to the MIP layer occurred by the 5 ml of dichloromethane that disrupted the hydrophobic interactions with the PS–DVB polymer and generated hydrogen bonds in the MIP. Extraction recoveries, shown in Fig. 7, are high for this mixed-mode sorbent: recoveries about 50% for the polar DDA and above 85% for DIA, DEA and DET were obtained for a 100-ml sample.

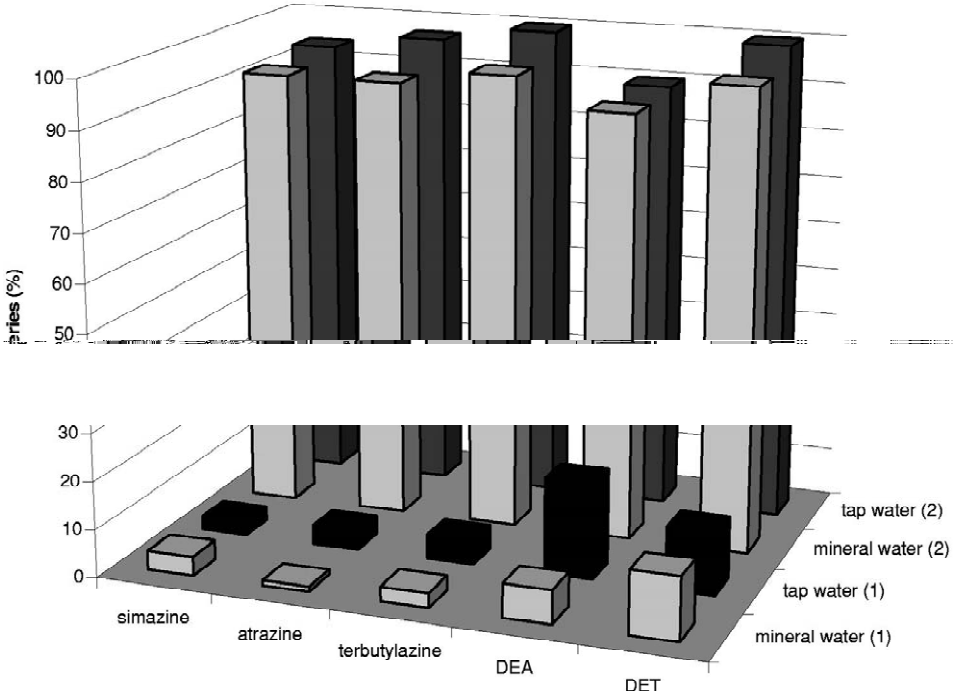

Fig. 6. Extraction recoveries (%) obtained by applying the procedure described in Fig. 3 (1) and by addition of a HCl washing (2) before the percolation of dichloromethane; mean value of three measurements, RSDs ranged between 0 and 8%.

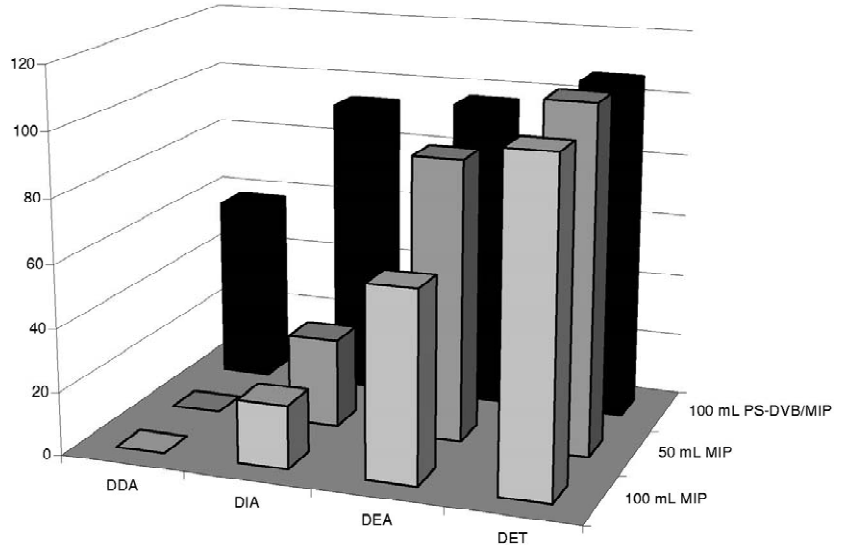

Fig. 7. Extraction recoveries (%) obtained for triazines and metabolites after the percolation of 50 and 100 ml on terbutylazine MIP and of 100 ml on the mixed sorbent. The sample was spiked with 500 ng and 100 ng of each compound for the extraction on the MIP and on the mixed sorbent, respectively; mean value of two measurements.

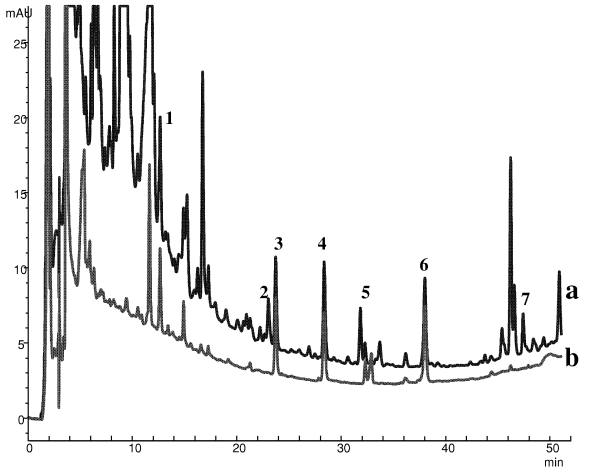

Fig. 8. Chromatograms obtained after the preconcentration of 50 ml of a diluted industrial effluent spiked at 1 μg/l with a mixture of triazines and phenylureas through the SDB support (a) and through the terbutylazine MIP cartridge (b). Compounds: (1) DEA, (2) monuron, (3) DET, (4) atrazine, (5) diuron, (6) terbutylazine, (7) neburon. UV detection at 220 nm.

3.5. Selective extraction of triazines from an industrial effluent

To illustrate the potential of MIP for the direct and selective extraction of compounds from aqueous media, an extraction of an industrial effluent from the textile industry was carried out on terbutylazine MIP and results were compared to those obtained using a classical PS–DVB sorbent. Fifty millilitres of a diluted industrial effluent were filtered and spiked with 1 μg/l of a mixture of triazines and phenylureas and extracted (see Section 2). The chromatograms obtained are presented in Fig. 8. Using a PS–DVB support, many interfering substances and the phenylureas have been retained and are present in the chromatogram (Fig. 8a). Using a MIP, a large portion of the interfering compounds has been removed and the phenylureas are not present demonstrating the high selectivity of the MIP (Fig. 8b). This improvement in selectivity is particularly interesting for the detection and the quantification of DEA that co-eluted with interfering compounds on the PS–DVB support.

4. Conclusion

This study has shown the potential of MIPs for the direct selective extraction of triazines and metabolites from water samples. The washing step that consists of removing the interfering compounds from the MIP and keeping the analytes specifically retained on it is crucial and has to be carefully optimized for good use of the MIP for the direct extraction of compounds from water samples. The matrix effects caused by the calcium ions in real water were eliminated by a simple acid washing. Molecular modeling provided a better understanding of the retention mechanism involved in the procedure. Compared to a classical sorbent, the MIP improved the selectivity. The use of the mixed-mode-sorbent based on PS–DVB and MIP allowed the development of a powerful selective extraction method for the polar metabolites of triazines in water samples.

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