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Authors: Theodoros G. Chatzimitakos, Stephen A. Pierson, Jared L. Anderson, Constantine D. Stalikas

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Enhanced magnetic ionic liquid-based dispersive liquid-liquid microextraction of triazines and sulfonamides through a one-pot, pH-modulated approach

Theodoros G. Chatzimitakos[1], Stephen A. Pierson[2], Jared L. Anderson[2], Constantine D. Stalikas[1*]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

[2]Department of Chemistry, Iowa State University, Ames, IA, 50010 United States

Corresponding author: Constantine Stalikas, e-mail: cstalika@cc.uoi.gr

Highlights

- A magnetic ionic liquid-based dispersive liquid-liquid microextraction is presented.
- Quartz silica was used as a solid support for the magnetic ionic liquid.
- A pH-modulated approach was employed to extract sulfonamides and triazines.
- Sulfonamides and triazines were determined in environmental water using HPLC-DAD.

Abstract

In this study, an enhanced variant of magnetic ionic liquid (MIL)-based dispersive liquid-liquid microextraction is put forward. The procedure combines a water insoluble solid support and the $[P_{66614}^{+}][Dy(III)(hfacac)_4^{-}]$ MIL, in a one-pot, pH-modulated procedure for microextraction of triazines (TZs) and sulfonamides (SAs). The solid supporting material was mixed with the MIL to overcome difficulties concerning the weighing of MIL and to control the uniform dispersion of the MIL, rendering the whole extraction procedure more reproducible. The pH-modulation during extraction makes possible the one-pot extraction of SAs and TZs, from a single sample, in 15 min. Overall, the new analytical method developed enjoys the benefits of sensitivity (limits of quantification: 0.034-0.091 μg L^{-1}) and precision (relative standard deviation: 5.2-8.1%), while good recoveries (i.e., 89-101%) were achieved from lake water and effluent from a municipal wastewater treatment plant. Owing to all of the above, the new procedure can be used to determine the concentrations of sulfonamides and triazines at levels below the maximum residue limits.

Keywords

Enhanced magnetic ionic liquid-based microextraction, sulfonamides, triazines, pH-modulated procedure, HPLC-DAD

1. Introduction

An ongoing trend in microextraction in chemical analysis is the use of ionic liquids (ILs). Commonly, ILs are molten salts at temperatures below 100°C. They are composed of organic or inorganic ions, the wide variety of which can result in approximately 10^{18} ionic liquids when diverse cations and anions are combined [1, 2]. So far, ILs have been employed for the separation of various compounds using dispersive liquid-liquid microextraction, single drop microextraction, hollow fiber membrane liquid-phase microextraction and solid phase microextraction, among others [3-9].

A more advanced, interesting concept of IL-based microextraction is the magnetic separation of the ILs from the analyzed matrix. To achieve separation and circumvent the laborious harvesting of ILs, magnetic ILs (MILs) have been developed by incorporating paramagnetic components in the IL chemical structure. Such MILs retain the advantageous properties of ILs and concurrently they strongly respond to external magnetic fields [10, 11]. Owing to this improvement, the employment of MILs in microextraction has been rendered easier and new microextraction modes have become available, such as dispersive liquid-liquid microextraction with magnetic retrieval and stir-bar dispersive liquid microextraction [12, 13]. MILs based on the tetrachloroferrate anion were among the first classes for rendering the ILs magnetic [14]. However, the applicability of tetrachloroferrate-based MILs in microextraction is limited, due to hydrolysis of the anion which gives rise to low harvest efficiency of MILs [15]. As an alternative, MILs with transition or rare-earth metals have been developed and are less prone to hydrolysis while possessing increased magnetic moments [16, 17]. Despite the improvements in the paramagnetic components of the MILs which are aimed at improving their magnetic properties, MILs have some drawbacks when they are considered for analytical methodologies. For example, the hydrophilic nature of MILs limits their potential for aqueous-based applications. Increasing the alkyl-chain length of the components or introducing alternative ions (e.g., trihexyl(tetradecyl)phosphonium and Aliquat 336) addresses this issue and improves their extractive potential towards different groups of analytes, resulting in more use in hydrophobic MILs [11, 15]. However, the high viscosity of MILs intended for dispersive liquid-liquid microextraction is another drawback, due to their poor dispersibility and tendency to tightly adhere to the surface of the vessel walls [13, 18].

Typical dispersive liquid-liquid microextraction procedures that employ MILs as extractants are based on vigorous stirring of the MIL drop to many smaller dispersed droplets. However, the phenomenon of MIL drop breakage is uncontrolled and the density and size of the formed droplets is random, or widely distributed. This has an impact on the reproducibility/repeatability and efficiency of the microextraction method employed. Another factor that can affect the analytical figures of merit of a relevant analytical method is the viscosity of the MIL employed. The direct addition of an exact amount of a viscous MIL is a tricky task, resulting in variations of the MIL amount added between samples due to the uncontrolled size of the drop that is formed on a pipette tip.

Water pollution is a matter of high concern due to the increasing number of organic pollutants with adverse health effects detected in aquatic environments. The overuse and improper discharge of agricultural pesticides and veterinary drugs can lead to contamination of surface waters with relevant compounds [19]. Triazines (TZs) constitute a major class of herbicides that have been used for more than 50 years in weed control. Due to their high water solubility and persistence in water and organisms, they are invariably an environmental safety concern [20]. Moreover, owing to their endocrine-disrupting, teratogenic and carcinogenic effects, they pose a threat for human and animal health [21, 22]. Sulfonamides (SAs) is a class of broad-spectrum antibacterial compounds that are widely administered in livestock animals and are among the most commonly used classes of antibiotics in Europe [23, 24]. They are harmful or highly toxic compounds (according to different risk assessment criteria), which can potentially cause cancer to humans, while their presence in the environment can also promote the development of antibiotic resistance [24-26]. The hazardous nature of the above classes of compounds has led regulatory agencies to establish maximum residue limits at 0.1 μg/L for each herbicide and 100 μg L^{-1} for SAs [23, 27].

In this study, we report an enhanced variant of MIL-based dispersive liquid-liquid microextraction which combines a water insoluble solid support and the $[P_{66614}^{+}][Dy(III)(hfacac)_4^{-}]$ MIL (trihexyl(tetradecyl)phosphonium tetrakis (hexafluoroacetylaceto)dysprosate(III)) in a one-pot, pH-modulated procedure for the microextraction of triazines and sulfonamides. The solid supporting material was mixed with the MIL to overcome difficulties regarding weighing of the MIL and to assist in the control of uniform dispersion of the MIL, thus rendering the whole extraction procedure more reproducible. The employed pH-modulation during the microextraction procedure makes feasible the one-pot extraction of SAs and TZs from a single sample.

2. Materials and methods

2.1 Chemicals and reagents

Manganese(ll) chloride tetrahydrate was purchased from Alfa Aesar (Ward Hill, MA, USA). Nickel(ll) chloride (98%), ammonium hydroxide (28-30% solution in water), and 1,1,1,5,5,5-hexafluoroacetylacetone (99%) were purchased from Acros Organics (Morris Plains, NJ, USA). Anhydrous diethyl ether (99.0%) was purchased from Avantor Performance Materials Inc. (Center Valley, PA, USA). Trihexyl(tetradecyl) phosphonium chloride (97.7%) was purchased from Strem Chemicals (Newburyport, MA, USA). Cobalt(ll) chloride hexahydrate (98.0%), dysprosium(lll) chloride hexahydrate (99.9%), and gadolinium(lll) chloride hexahydrate (99.9%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Quartz silica (50-70 mesh particle size), silica (35-70 mesh), sodium chloride, sodium sulfate, trisodium citrate, sodium hydroxide, hydrochloric acid, all SAs and TZs standards (purities >99%) and solvents (at least of analytical grade) were purchased from Aldrich (Sigma–Aldrich–Hellas, Greece). Stock standard solutions of each compound were prepared in acetonitrile (ACN) at concentrations of 1.0 mg mL^{-1}. All solutions were stored in screw-capped, amber-glass vials at −18°C.

2.2 Instrumentation

Chromatographic separation and analysis was carried out on a Shimadzu HPLC system coupled to a Diode Array Detector (DAD). The system consisted of a LC20AD pump, a CTO 10AS column oven, a SPD-M20A DAD and a Hypersil ODS column (250 × 4.6 mm, 5 μm) kept at 30°C. Sample was injected using a Rheodyne injector and the injection volume was 20 μL. The mobile phase consisted of water (A) and ACN (B), containing 0.1% (v/v) formic acid. The analytes were separated following a gradient elution program from 10% to 55% B (the MIL is completely soluble in this range), in 50 min. The flow rate of the mobile phase was set at 1.0 mL min^{-1}. The detector was set at a wavelength range of 220–360 nm. Data acquisition and processing were carried out using an LC-solution software version 1.21. Peak identification was based on the comparison of retention times and UV spectra with those of the authentic compounds.

2.3 MIL synthesis

The five MILs investigated in this study were synthesized and characterized using a previously reported procedure [15]. All MILs were purified using diethyl ether and water and subsequently dried in a vacuum oven overnight. When not in use, the MIL solvents were stored in a desiccator.

2.4 Sample preparation

Water samples from Pamvotis Lake (Ioannina, Greece) and effluents of the municipal treatment plant of Ioannina were collected and filtered (to remove particulate matter). Finally, the pH was adjusted to 9.0 through the addition of NaOH solution.

2.5 Microextraction procedure

An aliquot of 75 mL of a sample was transferred to a glass beaker and 15 g of trisodium citrate was added. After complete dissolution, 500 mg of a $[P_{66614}^{+}][Dy(III)(hfacac)_4^{-}]$-quartz silica mixture (1:20 w/w) was added under stirring, at ~700 rpm, resulting in the formation of tiny droplets. After 10 min, the pH was adjusted to 3.0 using hydrochloric acid and the mixture was stirred for an additional 5 min. Then, the MIL droplets were harvested using a neodymium cylinder magnet and the MIL was diluted to 300 μL with acetonitrile. Finally, the solution was filtered through a 0.20 μm syringe filter (Corning®) and injected into the HPLC system for further separation and analysis.

3. Results and discussion

3.1 Selection of the solid supporting material

In dispersive liquid-liquid microextraction the formation of as small as possible droplets is highly favorable to achieve maximum performance of the extraction procedure [28]. To overcome hindrances regarding the manipulation and dispersibility of the MIL (as mentioned in introduction), solid supporting materials were examined, which were mixed together with the MIL prior to microextraction. By mixing the MIL with the solid support, the weighing of the whole mixture was easier than weighing the neat viscous MIL. Thus, it is ensured that always the same exact amount of MIL is used for the microextraction procedure. Ideally, the MIL should be physically deposited on the solid support since strong interactions are not favorable. Moreover, the solid support should separate fast from the MIL so that all droplets progressively formed would be available for extraction in a reasonable length of time. Finally, it should not be able to adsorb the desired analytes at the expense of MILs, thus lowering the achieved recoveries.

In our case, the solid supports which were mixed with the MIL included soluble inorganic salts and insoluble silica and quartz silica microparticles. For inorganic salts, it is conceivable that they possess a dual role: first to assist in the dispersion and secondly to enhance the extraction in case salting out plays a key positive role. Similarly, silica microparticles were examined since they could also assist in the dispersion, while they could also adsorb potential interfering compounds due to their surface chemistry. At first, sodium chloride and sodium sulfate were tested. Although the produced MIL-salt mixture seemed homogenous, aggregates were formed when it was added to the water requiring more time to dissolve and, as a consequence, a low amount of dispersed MIL in the form of droplets was observed. Subsequently, silica microparticles were tested.. The mixture was "sticky", not homogenized completely with the silica and most of the MIL remained on the walls of the mixing glassware. When added to water, the MIL could not easily be released and part of it was retained on the silica microparticles. Moreover, part of SAs and TZs were adsorbed by silica microparticles. To avoid laborious deactivating procedures, quartz silica was further employed. When transferred to an aqueous sample under stirring, quartz silica particles carrying the MIL as extraction phase were dispersed homogenously in the bulk phase and the MIL was released easily (in less than 1 min) with the aid of stirring resulting in the formation of tiny droplets. In this manner, the droplets were dispersed in the bulk of the sample, while quartz silica settled at the bottom. Additionally, in the optimum conditions for the extraction (as will be explained later on) it was found that quartz silica cannot adsorb either SAs or TZs Quartz silica was finally selected as the most suitable solid supporting material. Visual inspection during microextraction experiments revealed that droplets were more homogenous, reproducible and smaller compared to those without the use of solid support. Therefore, the available interface is higher when a solid material is used while the dispersion phenomenon is less random and more controlled. Moreover, the size of the droplets was dependent on the ratio of quartz silica to MIL. Taking advantage of this, we examined different ratios in order to identify the optimal one that yielded the highest efficiency and most reproducible results. The ratios examined were: 1:5, 1:10, 1:20, 1:30 and 1:40 (MIL:quartz silica w/w), using two different sample volumes (i.e., 25 and 75 mL). Ratios of 1:5 and 1:10 resulted in decreased extraction yields due to the large-size droplets formed in the solution. In the case of ratios of 1:30 and 1:40, the droplets formed were so tiny that the extraction yields were decreased due to the high number of droplets that adhered to the beaker wall, resulting in lower overall extraction yields. The ratio 1:20 yielded the highest yield (almost 15% higher). Therefore, this ratio was used for further experiments. To test the superiority of the procedure using the solid support over traditional MIL dispersive microextraction [12], both procedures were applied under the same conditions (i.e., sample volume: 20 and 75 mL, amount of MIL: 25 mg, stirring rate: 700 rpm and stirring time: 15 min, using the pH-modulated approach, *vide infra*) and were compared. The results were conclusive for the superiority of the quartz silica-MIL over the bare-MIL dispersive microextraction procedure, since the former was found to be nearly 20% more efficient with regard to the extraction of TZs and almost 13% for SAs. Moreover, the reproducibility of microextraction, when the solid support was used was higher compared to the other method (the average relative standard deviation of five experiments for all analytes was 4.9 and 8.6 for the proposed and MIL dispersive microextraction procedure, respectively).

Before studying other parameters that affect the microextraction procedure, we made a comparison with other MILs for their extraction potential. For this study, another rare earth based MIL (i.e. $[P_{66614}^{+}][Gd(III)(hfacac)_4^{-}]$) and some transition metal based MILs ($[P_{66614}^{+}][Co(II)(hfacac)_3^{-}]$, $[P_{66614}^{+}][Mn(II)(hfacac)_3^{-}]$ and $[P_{66614}^{+}][Ni(II)(hfacac)_4^{-}]$) were used. All five tested MILs had the same extraction behavior for both classes of compounds. Since the transition-based MILs possess three hexafluoroacetylacetonate ligands coordinated to the metal instead of four and present the same adsorption efficiency, it can be deduced that the anion does not play any role in the extraction of the analytes. Therefore, the selection of $[P_{66614}^{+}][Dy(III)(hfacac)_4^{-}]$ was based solely on its effective magnetic moment, which is higher than the rest of the tested MILs [15]. Due to this, it could be harvested more easily and efficiently than the other studied MILs.

3.2 Optimization of extraction

Parameters affecting the extraction were optimized to achieve maximum efficiency. In all cases, distilled water spiked with 100 µg L^{-1} of each analyte was used to assess the performance of the extraction procedure as a function of several tested parameters. The criterion used for the evaluation of the different parameters was the average extraction yield of the total SAs and TZs content. The parameters studied were the pH, ionic strength, stirring time and rate, sample volume, and the amount of extracting phase.

3.2.1 pH-modulation for extraction

Due to the ionizable nature of SAs and TZs, pH is expected to play a significant role in their extraction. By properly modulating the pH in a one-pot experiment both classes of analytes can be extracted efficiently in a single MIL dosage. To further explore the applicability of this concept, we initially examined the extraction efficiency in the pH range 2-10 for both classes of compounds. As expected, in more alkaline conditions, the transfer of TZs is favored (optimum pH=9.0); on the contrary, SAs are extracted more efficiently under acidic conditions (optimum pH=3.0) (Figure 1). In both cases, it can also be seen that the extraction yield decreases significantly as the pH either decreases (in the case of TZs) or increases (in the case of SAs), resulting in less than 5% extraction yield. Generally, the adsorption of SAs is favored under acidic conditions, where the neutral or deprotonated species dominate [26]. However, it is known that TZs hydrolyze in strongly acidic environment [21, 22] and, therefore, they are commonly extracted under neutral or alkaline conditions.

The next step was to test the concurrent extraction of SAs and TZs in two ways: (I) by initially adjusting the pH to 3.0 and then increasing the pH of the solution to 9.0 and (II) by performing the opposite procedure of (I). The results demonstrate that the first (I) approach results in poor extraction of TZs while for SAs the extraction yield was satisfactory. This can be explained by the following. Firstly, the TZs studied herein have a pK_α between 1.0 and 4.3 and at pH 3.0 they co-exist in their neutral and protonated form. Thus, it can be deduced that their protonated form is extracted less efficiently than their neutral form, which dominates in the alkaline environment. Secondly and more importantly, TZs hydrolyze in strongly acidic environment, as mentioned above; this accounts for their decreased extraction yield at low pH. Due to this, TZs cease to exist in the working pH, in their native form and this accounts for the negligible extraction yield recorded. On the contrary, when the second way (II) was employed, TZs were extracted efficiently in the alkaline pH, while the subsequent decrease in the pH resulted in a satisfactory extraction of SAs. Moreover, the decrease in the pH was not accompanied by desorption of TZs from the MIL. This hints towards a mechanism which is not dependent upon the ionization of TZs and MIL. We have already concluded (section 3.1) that the anion of the MIL does not play any role in the extraction. It is most likely that the procedure proceeds through interactions with the cation. Considering the hydrophobic nature of the cation (due to alkyl chains), hydrophobic interactions arise, mainly, between the cation of the MIL and TZs. Therefore, the extraction of both classes of compounds from a single sample, with a single MIL dosage is possible, without loss of efficiency for either class.

3.2.2 Ionic strength

One of the most exploited parameters during the optimization of a microextraction procedure is the ionic strength due to the so-called salting out effect. On the other hand, as the ionic strength of a solution increases along with the favorable salting-out effect, secondary phenomena occur such as the increase in the viscosity of the solution, which often hinders the process. In our case, three different salts, namely sodium chloride, sodium sulfate and trisodium citrate were employed to increase the ionic strength of the solution up to 30% w/v. For the sake of simplicity, the results depicted in Figure 2 represent the average extraction yield of both SAs and TZs. As it can be seen, the higher amount of each of the three salts produced an increase in the extraction efficiency. This increase is more pronounced with trisodium citrate followed by sodium sulfate and sodium chloride. This is due to the different ionic strength that the salts exhibit. Apparently, the increase in extraction efficiency is attributed to the salting out effect, which lowers the solubility of organic compounds in aqueous media, thus, favoring their extraction [29, 30].

Another secondary effect concomitant of the presence of high salt content is the reduction of the diffusion rate of the analytes, especially for less polar ones. Due to the polar to intermediate polar nature of the target analytes, this effect does not significantly affect the extraction efficiency [31]. Aside from the salting-out effect on the extraction yield, the same experiments showed that as the ionic strength increases, the magnetic retrieval of the MIL was rendered easier and the tendency of the MIL droplets to adhere to the beaker wall was significantly lower. Although this does not affect the extraction yield, it favors the magnetic retrieval and thus, the reproducibility/repeatability of the procedure. Based on the results above, the addition of 20% w/v trisodium citrate was chosen in conducting further experiments, as a compromise of maximum efficiency and less consumption of salt.

3.2.3 Other extraction parameters

Extraction experiments were conducted at three different temperatures (i.e., 25, 35 and 45°C) to assess the effect of temperature on the extraction efficiency. The results showed that as temperature increases, there is a trivial increase (<5%) in the extraction efficiency of only TZs. Hence, no temperature control was used for further experiments. Stirring rate was set to a predetermined value without being optimized in relation to the other parameters. It was observed that stirring rates < 500 rpm resulted in poor extraction yields, due to the partial attachment of droplets on the magnetic stirring bar and rates > 900 rpm caused the formation of unfavorable bubbles in the solution that assisted in the MIL droplets adhering to the beaker walls. Thus, a moderate-high stirring rate (i.e., 700 rpm) was found to be optimum and was employed for all experiments.

The next parameters optimized were the volume of the sample and the amount of the extracting phase. With regard to sample volume, the volumes 25, 50, 75 and 100 mL were initially tested by spiking with the same amount of analytes. Results showed a minor decrease in the extraction efficiency (<7%) up to 75 mL of sample, while a more pronounced decrease (~25%) was noticed for 100 mL. Subsequently, sample volumes of 25, 50 and 75 mL at the same concentration of analytes and sorbent amounts of 150, 300 and 500 mg were examined and assessed. From Figure 3, it can be seen that 500 mg of the MIL-quartz silica mixture was needed in all three tested sample volumes to achieve total extraction of the analytes. Therefore, this amount along with 75 mL of sample was selected to achieve high enrichment factors.

An extraction time up to 30 min in increments of 5 min was studied separately for both SAs and TZs. The results showed that complete extraction of TZs and SAs can be achieved within 10 min and 5 min, respectively. Prolonged extraction times resulted in yields that were neither improved nor lessened for any of the tested compounds. Thus, the overall procedure can be completed in 15 min, which is a rather short period of time for analysis of two classes of compounds.

3.3 Analytical figures of merit

After optimizing all parameters that affect the extraction, an analytical method was developed for the determination of SAs and TZs. The solutes selected herein are representative and the method can be used for other compounds of the same category (e.g. sulfathiazole, simazine, etc.). As a proof-of-concept, the method was used to determine the concentration of the compounds in lake water and effluent from a municipal wastewater treatment plant. A chromatogram of spiked and non-spiked effluent can be seen in Figure 4. The analytical characteristics of the developed procedure are listed in Tables 1 and 2. In all cases, SAs were quantified at the absorption maxima of 270 nm and TZs at 260 nm. The calibration curves were prepared using water spiked with the analytes in the range 0.2-75 μg L^{-1} and 0.1-75 μg L^{-1} for TZs and SAs, respectively. For both classes of compounds, the coefficients of determination (R^2) were higher than 0.9970, suggesting good linearity. The limits of quantification (achieved by decreasing the analyte concentration up to a signal-to-noise ratio =10) ranged between 0.034 and 0.088 μg L^{-1} for SAs and 0.041 and 0.091 μg L^{-1} for TZs. The LOQs were lower than the maximum residue levels established for these analytes. The enrichment factors (EF) (calculated according to our previous study [13]) were found to be between 51 and 71 for SAs and between 20 and 41 for TZs. The extraction percentage (E%) (calculated according to our previous study [13]) was higher than 98% and 95% for SAs and TZs, respectively. The precision of the method was calculated as the relative standard deviation of five different samples, analyzed on the same day and three different samples on five consecutive days. The values were in the range of 5.2-7.3% (within-day) and 6.0-8.1% (between-day). Since no residues of the analytes were detected, relative recoveries of the examined compounds were calculated from the two water samples that were both spiked at two concentration levels (i.e., 0.2 and 1.0 μg L^{-1} of each analyte). For municipal treatment plant water, recoveries were in the range of 89-96 % and 91-101% for 0.2 and 1.0 μg L^{-1}, respectively. Likewise, recoveries from lake water were between 94 and 99% for the low concentration and 95 and 99% for the high concentration.

As it can be seen from Table 3, the proposed procedure is advantageous in terms or (relative) recoveries and repeatability (expressed as relative standard deviation), highlighting the superiority for the determination of both classes of compounds. Most importantly, the proposed procedure can be used, simultaneously, for the extraction of both classes, compared to the other methods which are specific for only one class of them.

4. Conclusions

In this study, an advanced dispersive liquid-liquid microextraction method using MILs was developed. One major improvement was the use of quartz-silica as a solid supporting material for the MIL microextraction mode. The use of the solid support, renders handling of the MIL easier as well as significantly increases the reproducibility and efficiency of the method. Using a pH-modulated approach, the extraction of SAs and TZs could be performed in a one pot procedure from the same sample in a short period of time allowing each class to be extracted separately at different sample pH. The enhanced method has suitable precision, good recovery and sensitivity and the achieved LOQs make feasible the determination of the compounds at levels below the maximum residue limits, as defined by regulatory agencies.

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Figure captions

Figure 1. Effect of sample pH on the extraction of a mixture of SAs and TZs, containing 100 µg L^{-1} of each (number of replicate analysis = 3).

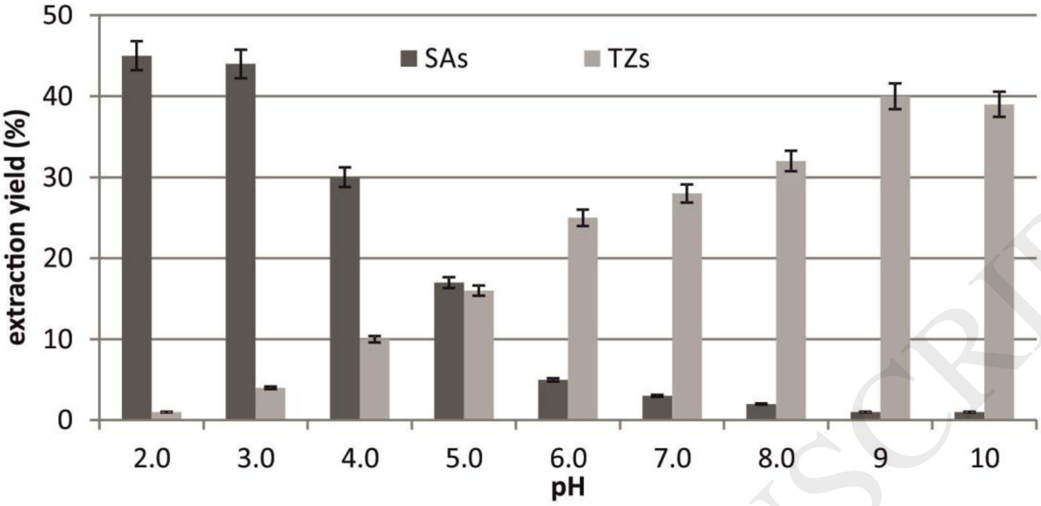

Figure 2. Addition of different salts to increase the ionic strength of the solution and the respective extraction efficiency for a mixture of SAs and TZs, containing 100 µg L^{-1} of each (number of replicate analysis = 3).

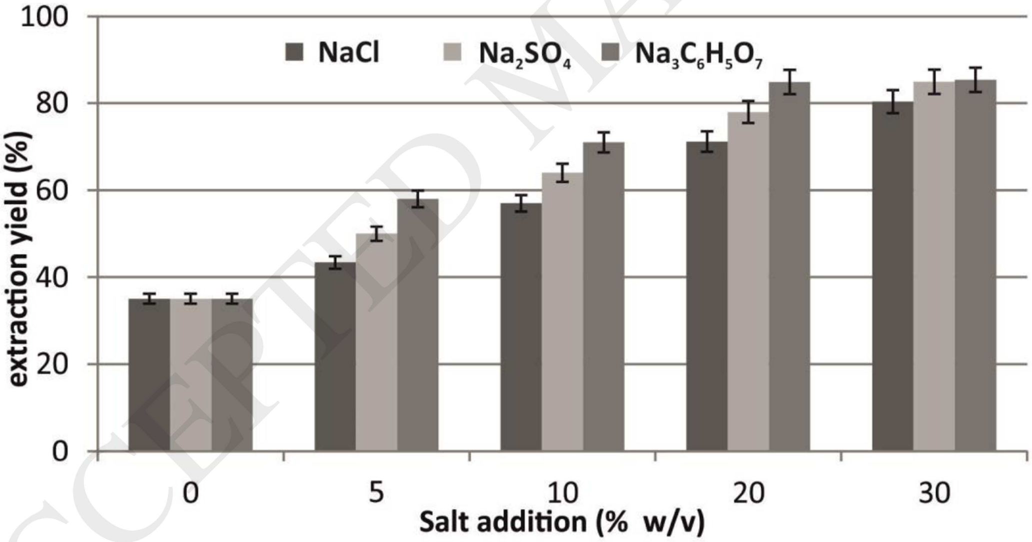

Figure 3. Effect of sample volume and amount of extracting phase on the efficiency of the method (number of replicate analysis = 3).

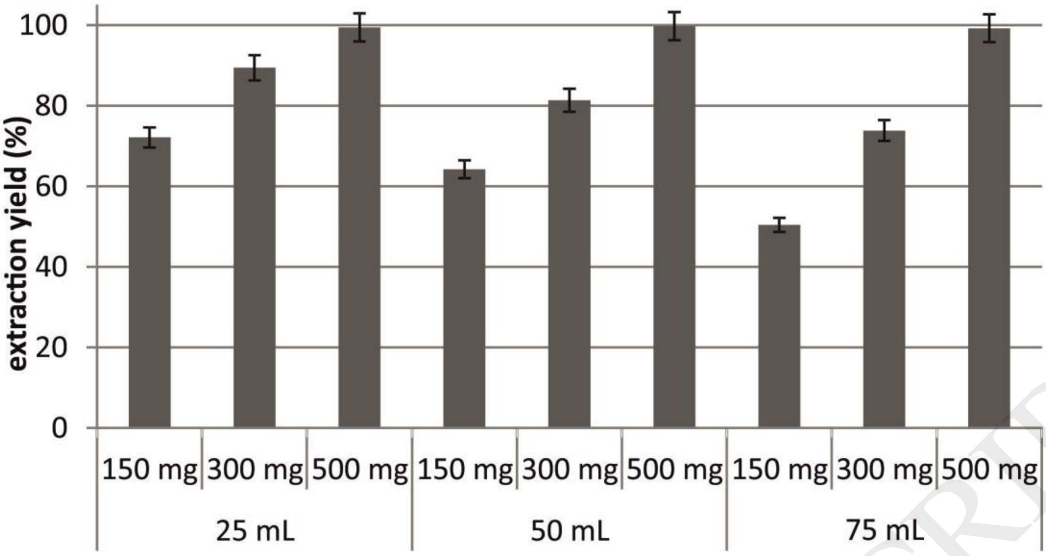

Figure 4. Chromatograms of the extract (obtained with the proposed procedure) of an effluent from municipal treatment plant, spiked with 50 µg L^{-1} SAs and TZs (two upper) and non-spiked (two lower), at two different wavelengths. Peak assignment: 1. sulfadiazine, 2. sulfapyridine, 3. sulfamerazine, 4. sulfamethazine, 5. sulfamethoxypyridazine, 6. sulfachloropyridazine, 7. sulfamethoxazole, 8. sulfisoxazole, 9. sulfadimethoxine, 10. terbuthryn, 11. atrazine, 12. propazine, 13. terbuthylazine

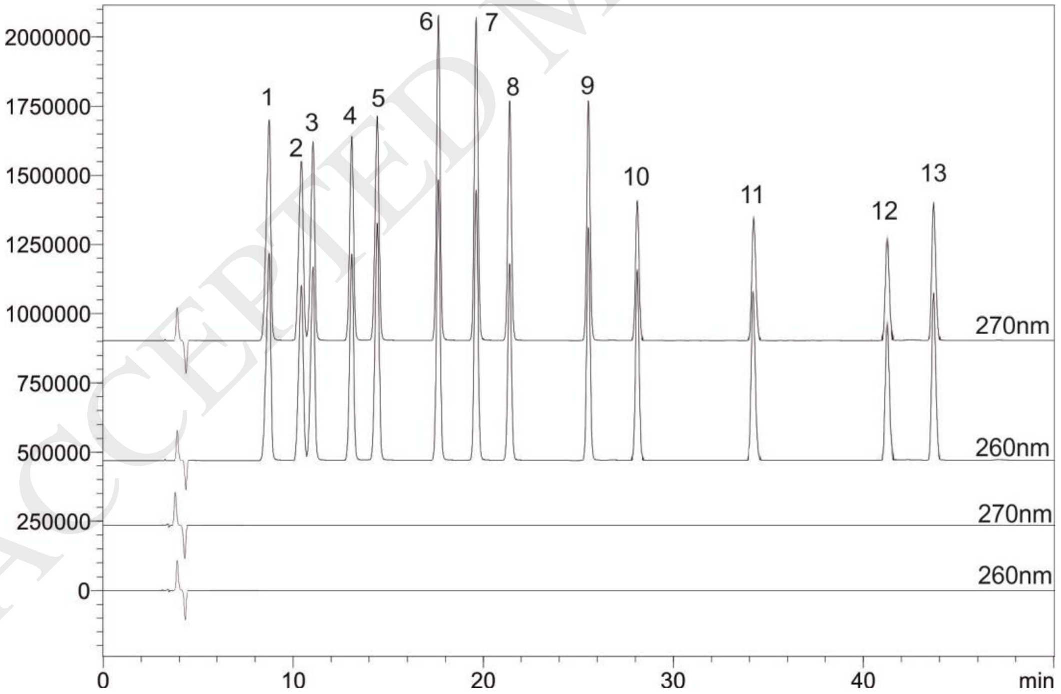

Table 1. Analytical figures of merit of the developed MIL-based microextrction procedure.

Compound	**Slope ± error**	**Intercept ± error**	**Standard error of the regression**	**Coefficient of determination (R^2)**	**LOQ (μg L^{-1})**
sulfadiazine	28983 ± 755	11735 ± 3458	7979	0.9973	0.054
sulfapyridine	12406 ± 237	11394 ± 1843	2488	0.9975	0.088
sulfamerazine	22967 ± 587	11510 ± 2688	6548	0.9984	0.054
sulfamethazine	22279 ± 460	14255 ± 2167	4838	0.9970	0.063
sulfamethoxypyridazine	25021 ± 563	15331 ± 2578	5933	0.9985	0.057
sulfachloropyridazine	33142 ± 560	30116 ± 2576	5931	0.9980	0.036
sulfamethoxazole	34189 ± 730	22849 ± 3346	7659	0.9988	0.034
sulfisoxazole	23989 ± 578	22985 6465	6599	0.9970	0.042
sulfadimethoxine	23148 ± 485	39335 ± 2222	5838	0.9969	0.045
terbuthryn	8368 ± 154	23333 ± 5473	7792	0.9983	0.041
atrazine	6845 ± 136	21602 ± 4829	9521	0.9980	0.051
propazine	6480 ± 195	17088 ± 6957	3717	0.9975	0.091
terbuthylazine	6841 ± 187	22427 ± 6671	3153	0.9973	0.044

Table 2. Enrichment factors (EF), extraction percentages (E%), relative standard deviations (RSD) and relative recoveries of the developed MIL-based microextrction procedure.

Compound	**EF**	**E%**	**RSD (%)**		**Relative Recovery (%)**[A]		**Relative Recovery (%)**[B]	
			within-day (n=5)	**between-day (n=3×5)**	**0.2 µg L^{-1}**	**1.0 µg L^{-1}**	**0.2 µg L^{-1}**	**1.0 µg L^{-1}**
sulfadiazine	71	99	5.2	7.2	95	97	99	99
sulfapyridine	68	99	7.3	7.9	93	95	94	95
sulfamerazine	69	99	5.4	6.0	95	101	94	95
sulfamethazine	71	99	6.6	8.1	92	98	96	98
sulfamethoxypyridazine	71	99	6.0	6.4	90	94	97	99
sulfachloropyridazine	68	99	7.0	8.1	95	100	96	97
sulfamethoxazole	68	99	5.3	7.0	96	99	94	96
sulfisoxazole	65	99	6.0	7.6	94	97	95	99
sulfadimethoxine	51	98	5.0	6.5	92	94	94	97
terbuthryn	41	97	5.1	6.4	92	97	94	97
atrazine	37	97	5.5	7.3	92	95	94	95

propazine	20	95	6.9	7.7	89	91	96	98
terbuthylazine	40	98	5.5	6.9	89	94	94	98

[A] effluent from municipal wastewater treatment plant

[B] lake water

Table 3: Comparison of the developed procedure with other analytical methods.

Analytes	**Method**	**Extractant**	**Matrix**	**Linear range (µg/L or µg/Kg)**	**LOD (µg/L) (S/N = 3)**	**RSD (%)**	**(Relative) Recovery (%)**	**Reference**
STZ, SMX, SDM and trimethoprim	bar adsorptive microextraction and HPLC-DAD	polystyrene-divinylbenzene polymer coated stir bars	Tap, estuarine and wastewater	0.16-8.00	0.08-0.16	<15.2	63.8-84.2	[32]
SMP, SMZ, SMX and SCP	magnetic solid-phase extraction and HPLC-Amperometric detector	magnetic hypercrosslinked polystyrene	water	2.0-200	0.21-0.33	3-10	84-105	[33]
SP, SM, SMR, SDX, SCP and SMM	magnetic dispersive solid phase extraction and HPLC-UV	$Fe_3O_4@SiO_2@G$	Lake, sewage and waste water	0.5-100	0.09-0.16	<10.7	74.2-104.1	[34]
SA, SD, SP, SM, SMZ, SMP, SCP, SMX and SDM	extraction and HPLC-DAD	Graphene-functionalized melamine sponges	lake water	1-200	0.03-0.09	2.7-4.2	96-105	[35]
cyanazine, atrazine and simazine	ionic liquid dispersive liquid-phase microextraction and HPLC-UV	1-Octyl-3-methylimidazolium hexafluorophosphate ([C8MIM][PF6])	river, underground, drainage and	0.5-80 for cyanazine and 1.0-100 for simazine and atrazine	0.05-0.06	4.8-8.9	85.1-100	[36]

			wastewater					
ametryn, atrazine, cyanazine, prometryn, propazine, simazine, simetryn, terbuthylazine and terbutryn	solid-phase extraction and HPLC-DAD	Oasis HLB	tap water	0.02-0.1	0.010-0.023	3.8-11.7	86-110	[37]
atrazine, ametryn, simetryn, propazine	solid-phase extraction and HPLC-DAD	double water compatible molecularly imprinted polymers	tap and river water	50-1000	3.2-8.6	1.33-4.73	69.2-95.4	[38]
SD, SP, SM, SMZ, SMP, SCP, SMX, SIX, SDM, terbuthryn, atrazine, propazine, terbuthylazine	magnetic ionic liquid-based dispersive liquid-liquid microextraction using a one-pot, pH modulated approach and HPLC-DAD	$[P66614^+][Dy(III)(hfacac)_4^-]$	lake water and effluent from a municipal wastewater treatment plant	0.1-100 for SAs and 0.2-75 for TZs	0.011-0.029 for SAs and 0.013-0.030 for TZs	5.2-7.3	90-101 for SAs and 89-98 for TZs	This work

Sulfamethoxazole (SMX), sulfadiazine (SD), sulfamethazine (SMZ), sulfadimethoxine (SDM), sulfameter (SMR), sulfamerazine (SM), sulfadoxine (SDX), sulfisoxazole (SIX), sulfamonomethoxine (SMM), sulfathiazole (STZ), sulfamethoxypyridazine (SMP), sulfachloropyridazine (SCP), sulfapyridine (SP), sulfacetamide (SA)