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RESEARCH ARTICLE

Ultra-preconcentration of common herbicides in aqueous samples using solid phase extraction combined with dispersive liquid–liquid microextraction followed by HPLC–UV

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ABSTRACT

An analytical method, solid-phase extraction combined with dispersive liquid–liquid microextraction (SPE–DLLME), was established to extract and determine the herbicides in aqueous samples. In this method, herbicides were adsorbed from a large volume of aqueous samples (100 mL) into 500 mg functionalized octadecyl silica (C_{18}) sorbent. After the elution of the desired compounds from the sorbent by using acetone, DLLME technique was performed on the obtained solution. Under the optimum conditions, the calibration graphs are linear in the range of 0.02–10 $\mu g\ L^{-1}$ and limits of detection (LODs) are in the range of 0.003–0.006 $\mu g\ L^{-1}$. The relative standard deviations (RSDs, for 0.50 $\mu g\ L^{-1}$ of 2,4-D and alachlor, and 1.00 $\mu g\ L^{-1}$ of atrazine in water) are in the range of 6.1–8.1% ($n = 5$). The SPE–DLLME provided a high enrichment factor (1725–2065) for herbicides.

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Introduction

Sample preparation is one critical step of an analytical procedure and an integral part of any analysis. Optimized sample preparation is necessary, not only to reduce the time taken but because each step adds a potential source of error. The amount of sample preparation needed depends on the sample matrix and the properties and level of analyte to be determined. The determination of trace contaminants in complex matrices, such as biological samples and highly saline solutions, often requires extensive sample extraction and preparation regimes prior to instrumental analysis (Ma *et al*. 2018, 2019). Several techniques have been developed for the extraction and preconcentration of contaminants from aqueous samples, such as solid-phase extraction (SPE) (Rivoira *et al*. 2015, Wang *et al*. 2019), solid-phase microextraction (SPME) (Mirzajani *et al*. 2017, Pei *et al*. 2019), liquid–liquid extraction (LLE) (Duca *et al*. 2014), continuous sample drop flow microextraction (CSDFME) (Karimaei *et al*. 2017), homogeneous liquid–liquid extraction (HLLE) (Ebrahimzadeh *et al*. 2007), and liquid-phase microextraction (LPME) (Yilmaz and Soylak 2016, Reclo *et al*. 2017).

Dispersive liquid–liquid microextraction (DLLME) was introduced by Assadi and coworkers in 2006 (Rezaee *et al*. 2006). DLLME possesses very simple principles and it is based on a ternary component solvent system. In this method, an appropriate mixture of an extraction solvent and a disperser is rapidly injection into aqueous sample by a syringe, so a cloudy solution is formed. After centrifugation of the cloudy solution, a settled phase in the bottom of a conical tube is used with the most appropriate analytical technique. Rapidity, high enrichment factor (EF), high extraction recovery (ER), simplicity of operation, low cost, environmental benignity, and the consumption of the extraction solvent at the microlevel volume are some of the advantages of this method. So far, DLLME has been successfully used for the extraction and preconcentration of different organic and inorganic compounds from aqueous samples (Fattahi *et al*. 2007, Naseri *et al*. 2008, Anthemidis and Ioannou 2009, Mohammadi *et al*. 2009, Montes *et al*. 2009, Rezaee *et al*. 2009, Xiong *et al*. 2009, Farajzadeh *et al*. 2010, Othman *et al*. 2015, Sharafi *et al*. 2015, Akramipour *et al*. 2018). For complex matrices such as highly saline solution and savage, and biological

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samples as urine and blood DLLME cannot be used successfully. In these samples for the sake of the formation of probable precipitation and high density of solution the formation of sedimented phase confronts difficulty. Therefore, in the analysis of these samples, a clean-up step is necessary before DLLME. The best method for a fast cleaning-up of these samples is SPE. The principal goals of SPE are trace enrichment (concentration), matrix simplification (sample clean-up) and medium exchange.

In the previous study, we demonstrated a new combination of SPE and DLLME which was successfully used for the extraction and determination of chlorophenols (CPs) in the aqueous samples (Fattahi *et al.* 2007). Up to now, SPE–DLLME has been used for extraction and preconcentration of organic and inorganic compounds from different matrices (Liu *et al.* 2009, 2011, Han *et al.* 2013, Shamsipur *et al.* 2014). A combination of SPE and DLLME not only leads to high EF and low detection limit, but also can be used successfully in complex matrices like urine, blood, and highly saline solutions. In the present paper, DLLME after SPE combined with high performance liquid chromatography–ultraviolet detection (HPLC–UV) was studied for the analysis of three herbicides from different categories of organic compounds in aqueous samples. The practical applicability of the method was investigated for the herbicides extraction and determination in well, tap, and river water samples.

Experimental

Reagents and standards

Alachlor, 2,4-D and atrazine were supplied by Sigma Aldrich Co. (Seelze, Germany). Methanol (for spectroscopy), acetone (suprasolv for gas chromatography), acetonitrile (hyper grade for liquid chromatography), carbon disulfide (for spectroscopy), chlorobenzene, chloroform, hydrochloric acid, and sodium chloride were obtained from Merck (Darmstadt, Germany). The ultra-pure water (six times distillated) used was purchased from Shahid Ghazi Pharmaceutical Co. (Tabriz, Iran). Stock standard solution of herbicides was prepared in methanol (5.0 mL), with concentration levels of 1000 mg L^{-1} for alachlor and 2,4-D, and 2000 mg L^{-1} for atrazine and was stored in a freezer at −20 °C. The working solutions were prepared daily by appropriate dilution of the stock standard solution.

The well, tap and river water samples were collected from Kermanshah (Iran) in glass bottles, stored in the dark at 4 °C and analyzed within 24 h of collection without any previous treatment or filtration.

Instrumentation

The analysis of herbicides was performed by an HPLC Knauer with Chromgate software version 3.1 having binary pumps Smartline-1000-1 and Smartline-1000-2 and detector Smartline-UV-2500 variable wavelength programable (Berlin, Germany), an on-line solvent vacuum degasser and manual sample injector fitted with a 20 μL injection loop (model 7725i, Rheodyne, Cotati, CA). Separations were carried out on an H5-ODS C18 column (15 cm × 4.6 mm, with 5 μm particle size) from Anachem (Luton, UK). The mobile phase was a mixture of water–acetonitrile (30:70, v/v) and the flowrate was 1.0 mL min^{-1} in isocratic elution mode and the detection was performed at the wavelength of 220 nm. The Hettich Zentrifugen (EBA20, Tuttlingen, Germany) was used for centrifuging.

Extraction procedure

SPE of herbicides from the water samples was carried out using 500 mg of the C_{18} sorbent (6 mL syringe barrel, Varian, Harbor City, CA). The C_{18} cartridge was preconditioned with 4.0 mL of acetone, water and water at pH 3.0, respectively. The water samples (100 mL), containing 0.500 μg L^{-1} of alachlor and 2,4-D, and 1.00 μg L^{-1} of atrazine, were acidified with hydrochloric acid (37%) to pH 3.0 passed through the column at a flow rate of about 15 mL min^{-1} with the aid of a vacuum pump (Rotavac, Heidolph, Schwabach, Germany). The cartridges were rinsed with 5 mL of water at pH 3.0 to remove the matrix interferences. After drying the solid phase by passing air through it for several minutes, the target analytes were subsequently eluted with 1.00 mL acetone and were collected into the 10-mL screw cap glass test tubes with conical bottom. Twenty-eight microliters chlorobenzene (extraction solvent) was added to the acetone, which was used as disperser solvent in the subsequent DLLME procedures. Then, 5.0 mL aqueous solution (pH 3.0) was injected rapidly into the test tub with a 5.00-mL syringe (gastight, Hamilton, NV). A cloudy solution, resulting from the dispersion of the fine chlorobenzene droplets in the aqueous solution, was formed in the test tube. After extracting for a few seconds, the phase separation was performed by centrifugation at 5000 rpm for 3.0 min. The sedimented phase (20 ± 1 μL) was completely transferred into another test tube and concentrated under a gentle nitrogen flow. The residue was dissolved in 25 μL of mobile phase for further HPLC analysis.

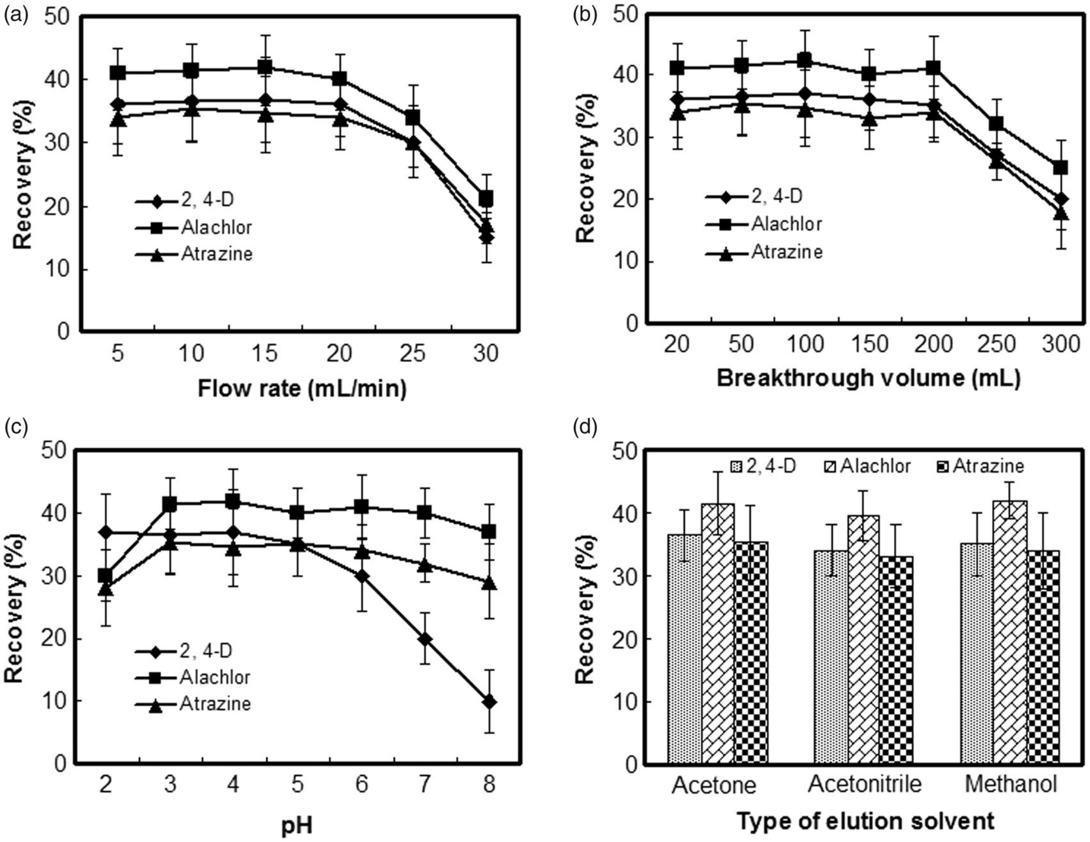

Figure 1. The effect of the flow rate (a), breakthrough volume (b), sample solution pH (c), and different elution solvents (d) on the herbicides recovery from SPE–DLLME.

Result and discussion

In this research, the combination of SPE and DLLME was employed for the extraction and preconcentration of organic compounds from water samples. To reach a high ER and EF with the proposed SPE–DLLME method, the SPE, and DLLME conditions were examined and optimized. Enrichment factor, %ER, and relative recovery (%RR) were calculated according to equations described in Rezaee *et al.* (2006).

Optimization of SPE parameters

Effect of flow rates

Two important factors for the quantitative recoveries and desorption of herbicides on the solid phase extraction studies are flow rates of the sample solution and elution solvent. The flow rate of the sample solution through C_{18} column controls the analytical time and affects the effective retention of the analytes. The flow rate of the sample solution must be high enough to shorten the analytical time and also, must be slow enough to perform an effective retention to analytes into the adsorbent. The effect of flow rate on recoveries of three herbicides was investigated in the flow rate range of 5–30 mL min^{-1}. As can be seen from Figure 1(a), it was found that in the range of 5–20 mL min^{-1}, the herbicides recovery by the cartridge was not affected considerably by the sample solution flow rate. As a result, 15 mL min^{-1} was used as the optimized sample flow rate.

The flow rate of elution solvent was investigated and quantitative desorption of analytes from the cartridge was achieved in a flow rate of 1 mL min^{-1}, using 1.00 mL of acetone. At higher flow rates, quantitative desorption of analytes needed larger volumes of acetone. Therefore, a flow rate of 1 mL min^{-1} was chosen for further studies.

Effect of the breakthrough volume

In order to study the influence of the breakthrough volume on the recovery of herbicides from water samples, different volumes of sample solution from 20 to 300 mL were passed from the solid phase column and then DLLME was performed as mentioned in the experimental section. The results in Figure 1(b) indicate that the recovery remained constant with the breakthrough volume increase from 20 to 200 mL, but then at higher sample volumes, not only was the recovery not satisfactory, but also the analysis time was too long. In order to shorten the analysis time, a sample volume of 100 mL was selected for the following tests.

Influence of the sample solution pH

The pH value plays an important role in adsorption of herbicides on the cartridge. The effect of pH on the extraction of herbicides from water samples was studied in the pH range of 2.0–8.0. The higher and lower pH values were not studied because solid phase in this pH values is not resistant. For the 2,4-D, when the pH is low, the acid–base equilibrium significantly shifts toward the neutral form. As sample pH increases, 2,4-D slowly changes into ionic form and ER decreases. Regarding alachlor and atrazine, it seems that in pH less than 3.0 they change into ionic form and in pH more than 3.0 they turn into neutral form. It can be seen from Figure 1(c) that the ER is best at pH 3.0. Hence, pH 3.0 was chosen in the following experiments.

Salt influence

Salt addition is frequently used to adjust the ionic strength, improve the extraction efficiency and reduce the detection limit. Depending on the nature of the target analytes, addition of salt to the sample solution can decrease the solubility of the analytes and therefore enhance extraction because of the salting-out effect. To study the ionic strength effect, the experiments were conducted at different sodium chloride concentrations of the sample solution, ranging from 0 to 5% (w/v). The EFs for herbicides obtained highest values when 1% of sodium chloride was added to the samples. Further addition of sodium chloride did not result in an increase in extraction efficiency. Therefore, subsequent experiments were carried out with adding 1% (w/v) salt.

Influence of the elution solvent type and volume

In SPE combined with DLLME, due to the eluent of SPE also played as the dispersant in the followed DLLME procedure, acetone, acetonitrile, and methanol as elution solvent were investigated. The solid phase was eluted using 1.00 mL of each elution solvent. The results illustrated in Figure 1(d) indicate that the recoveries by using acetone, acetonitrile, and methanol as elution solvent were 34.5–41.3, 33–39.5, and 34–42.1%, respectively. According to the results, variations of recoveries using different elution solvents are not remarkable, thus, acetone is selected because of low toxicity and cost. For the evaluation of the required acetone volume to elute all the herbicides from the solid phase, the elution was carried out three times with 1.00 mL of acetone. It was concluded that a volume of 1.00 mL was sufficient to desorb the trapped herbicides from the cartridge.

Optimization of DLLME parameters

Effect of type and volume of extraction solvent

In conventional DLLME, extraction solvent density should be higher than water. For this purpose, carbon disulfide, chloroform, and chlorobenzene were studied as extraction solvent. A series of sample solution were studied by using 1.0 mL acetone containing 43.0, 76.0, and 28.0 μL carbon disulfide, chloroform, and chlorobenzene, respectively. The volume of the sedimented phase for all extraction solvents was 20.0 μL. The results revealed that chlorobenzene possesses a higher ER and lower relative standard deviation (RSD) in comparison with the other tested solvents. This is most probably because of the interaction between benzene ring of the solvent and that presented in the herbicides structures. Therefore, chlorobenzene was selected as the extraction solvent.

To investigate the effect of extraction solvent volume on the ER, additional experiments were performed by using 1.0 mL acetone containing different volumes of chlorobenzene (i.e. 18.0, 28.0, 38.0, 48.0, and 58.0 μL). The ER increases with increasing volume of chlorobenzene up to 28.0 μL. However, because of dilution effect, a further increase in the extraction solvent resulted in a slight decrease of the ER. Thus, further experiments were carried out by using 28.0 μL of chlorobenzene as the extraction solvent.

Effect of type and volume of disperser solvent

When combining SPE with DLLME, the elution solvent of SPE should be used as disperser solvent in the DLLME stage. For this purpose, acetone, acetonitrile and methanol were used as disperser (elution) solvent. According to the results in Section "*Influence of the elution solvent type and volume*" acetone was selected as disperser solvent and 1.0-mL volume of acetone was selected as an optimum volume of disperser solvent.

Effect of extraction time

In DLLME, extraction time is defined as the time between injection of a mixture of disperser and extraction solvents into the sample solution and starting to centrifuge the resulting cloudy solution. The effect of extraction time was examined in the range of 0–30 min with other experimental conditions kept constant. The results showed that the extraction time has no significant effect on the extraction efficiency of the system. This is due to the fact that, after formation of cloudy solution, the surface area between chlorobenzene and aqueous phase is infinitely large so that the transfer of target analytes from aqueous phase into the extraction phase occurred rapidly and, subsequently, the equilibrium state is established very quickly.

Quantitative analysis

The calibration curves obtained under optimized conditions are summarized in Table 1. Linearity was observed in the range 0.02–5 μg L^{-1} for 2,4-D and alachlor, and 0.04–10 μg L^{-1} for atrazine. Correlation coefficient (r^2) ranged from 0.9988 to 0.9993. The precisions were studied by extracting the spiked water sample at the concentration of 0.50 μg L^{-1} for 2,4-D and alachlor, and 1.00 μg L^{-1} for atrazine. The RSDs were calculated to be in the range of 6.1–8.1% ($n = 5$). The limits of detection (LODs), based on signal-to-noise ratio (S/N) of three ranged from 0.003 to 0.006 μg L^{-1}. The EFs and recoveries of herbicides were from 1725 to 2065 and 34.5 to 41.3%, respectively.

Table 1. Quantitative results of SPE–DLLME and HPLC–UV for determination of herbicides in water sample.[a]

Compounds	RSD%[b] ($n = 7$)	EF	R (%)	LR (μg L^{-1})	r^2	LOD (μg L^{-1})
2,4-D	6.8	1840	36.8	0.02–5	0.9993	0.003
Alachlor	8.1	2065	41.3	0.02–5	0.9991	0.003
Atrazine	6.1	1725	34.5	0.04–10	0.9988	0.006

[a] Extraction conditions: water sample volume and its pH values, 100 mL, 3.0; eluent or disperser solvent (acetone) volume, 1.00 mL; extraction solvent (chlorobenzene) volume, 28.0 μL; sample solution flow rate, 15 mL min^{-1}; sedimented phase volume, 20.0 ± 1 μL; room temperature.

[b] RSD% at a concentration of 2,4-D and alachlor 0.50 μg L^{-1}, atrazine 1.00 μg L^{-1}.

EF: enrichment factor; R: recovery; LR: linear range; r^2: correlation coefficient; LOD: limit of detection for a $S/N = 3$.

Real water analysis

The proposed SPE–DLLME–HPLC–UV methodology was applied to the determination of herbicides in several water samples. River water was collected from Gharaso River (Kermanshah, Iran), tap water was collected from Kermanshah (Iran) and well water samples were collected from Mahidasht and Miandarband (Kermanshah, Iran). The results for river and tap waters showed that they were free of herbicides contamination. In the well water samples, 2,4-D and alachlor were detected and they were confirmed by spiking herbicides into the well water samples. The concentration of 2,4-D and alachlor in the well water samples are shown in Table 2. The accuracy of the method was verified by the analysis of the samples spiked with different levels of herbicides. The resulted relative recoveries (Table 2) are between 88.4 and 108.0%, which indicates that matrix had little effect on the extraction efficiency. Figure 2 shows the obtained chromatograms of well water and spiked well water at the concentration level of 0.50 μg L^{-1} for 2,4-D and alachlor, and 1.00 μg L^{-1} for atrazine.

Comparison of SPE–DLLME with other methods

This proposed SPE–DLLME technique was compared with our previous work (Shamsipur *et al.* 2012) and, also, with other published methods such as SPE–HPLC–UV, HS–SPME–IMS, SDME–GC–μECD,

Table 2. Relative recoveries and standard deviations of herbicides from spiked tap, well, and river water samples.[a]

Sample compound	Concentration, mean ± SD (μg L^{-1})	Added (μg L^{-1})	Found, mean ± SD (μg L^{-1})	Relative recovery (%)
Mahidasht well water				
2,4-D	0.07	0.5	0.558 ± 0.032	97.6
Alachlor	0.04	0.5	0.562 ± 0.040	104.4
Atrazine	n.d.	1.00	0.884 ± 0.060	88.4
Miandarband well water				
2,4-D	0.03 ± 0.002	0.25	0.295 ± 0.022	106.0
Alachlor	0.02 ± 0.004	0.25	0.265 ± 0.015	98.0
Atrazine	n.d.	0.5	0.453 ± 0.035	90.6
Tap water				
2,4-D	n.d.	0.5	0.486 ± 0.028	97.2
Alachlor	n.d.	0.5	0.516 ± 0.044	103.2
Atrazine	n.d.	1.00	0.887 ± 0.068	88.7
River water				
2,4-D	n.d.	0.25	0.235 ± 0.018	94.0
Alachlor	n.d.	0.25	0.270 ± 0.025	108.0
Atrazine	n.d.	0.5	0.443 ± 0.030	88.6

[a] Extraction conditions: water sample volume and its pH values, 100 mL, 3.0; eluent or disperser solvent (acetone) volume, 1.00 mL; extraction solvent (chlorobenzene) volume, 28.0 μL; sample solution flow rate, 15 mL min^{-1}; sedimented phase volume, 20.0 ± 1 μL; room temperature.

SD: standard deviation ($n = 3$); n.d.: not detected.

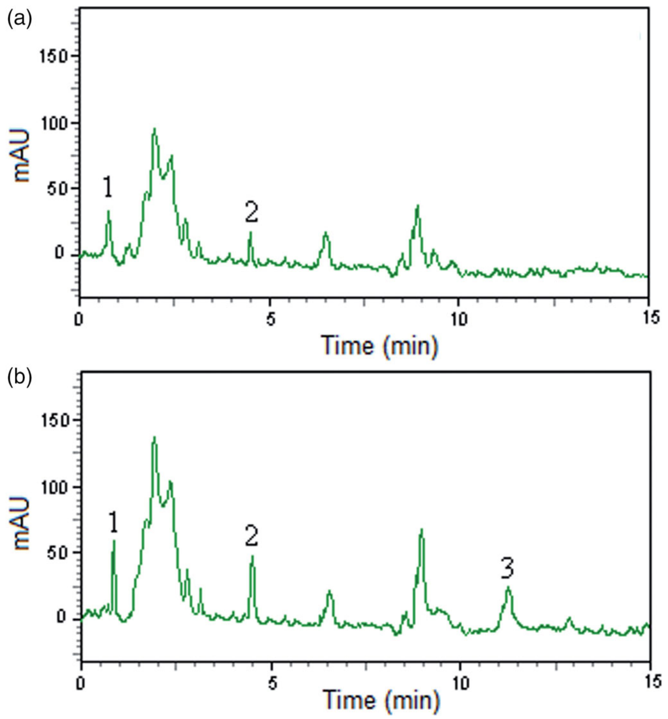

Figure 2. The chromatograms of the well water (A) and the spiked well water samples at the concentration level of 0.500 μg L^{-1} for 2,4-D and alachlor, and 1.00 μg L^{-1} for atrazine (B), obtained using SPE–DLLME combined with HPLC–UV. Extraction conditions: water sample volume, 100 mL; sample solution pH, 3; sample solution flow rate, 15 mL min^{-1}; eluent or disperser solvent (acetone) volume, 1.00 mL; extraction solvent (chlorobenzene) volume, 28.0 μL; volume of the aqueous solution for DLLME, 5.00 mL; sedimented phase volume, 20 ± 1 μL; room temperature. Peak identification: (1) 2,4-D, (2) alachlor, and (3) atrazine.

Table 3. Comparison of SPE–DLLME–HPLC–UV with other extraction methods for determination of herbicides.

Compound	Method	Sample volume (mL)	LOD (μg L^{-1})	RSD (%)	Extraction time (min)	References
2,4-D	SPE–UPLC–MS/MS	500	0.003	12.5	20	Gervais *et al.* (2008)
	DLLME–HPLC–UV	5	0.05	5.1	<4	Shamsipur *et al.* (2012)
	SPE–DLLME–HPLC–UV	100	0.003	6.8	≈.8	Represented method
Alachlor	SDME–GC–μECD	5	0.0025	6.8	15	Zhao *et al.* (2006)
	SPE–GC–MS	1000	0.01	5.0	200	Bruzzoniti *et al.* (2006)
	DLLME–HPLC–UV	5	0.05	6.2	<4	Shamsipur *et al.* (2012)
	SPE–DLLME–HPLC–UV	100	0.003	8.1	≈.1	Represented method
Atrazine	SPE–HPLC–UV	100	0.1	8.3	40	Zhao *et al.* (2008)
	HS–SPME–IMS	7	15	<10	10	Mohammadi *et al.* (2009)
	DLLME–HPLC–UV	5	0.1	4.5	<4	Shamsipur *et al.* (2012)
	SPE–DLLME–HPLC–UV	100	0.006	6.1	≈.1	Represented method

LOD: limit of detection; RSD: relative standard deviation.

SPE–GC–MS, and SPE–UPLC–MS/MS. The respective LOD, RSD, and sample volume and extraction time of each method are summarized in Table 3. The LODs values in SPE–DLLME were low and the extraction time was relatively short. As can be seen, the RSDs of SPE–DLLME are similar to other methods. Therefore, SPE–DLLME combined with HPLC–UV is a very simple and sensitive method for the extraction and determination of herbicides in real water samples.

Conclusions

Application of a DLLME after SPE, for the extraction of ultra trace concentrations of herbicides in water samples in combination with HPLC–UV has been developed and optimized. As compared with the other methods, the analytical technique offered numerous advantages such as high preconcentration factor, low detection limit, simplicity, ease of operation, and relatively short analysis time. The ultra preconcentration factor and the low detection limit were the major advantages of the technique. In this method, the sample preparation time (less than 10 min) as well as the consumption of the toxic organic solvents (at microliter level) was minimized without affecting the method sensitivity. As a conclusion, the proposed method possesses great potential in the analysis of ultra trace compounds in real water samples.

Disclosure statement

No potential conflict of interest was reported by the authors.

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