



Determination of Triazine Herbicides in Environmental Water Samples by Acetonitrile Inorganic Salt Aqueous Two-Phase Microextraction System

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Abstract

Acetonitrile inorganic salt aqueous two-phase extraction method was established for the determination of triazine herbicides (simeton, cyanazine, desmetryn, terbumeton, terbuthylazine and dimethametryn) in environmental water samples by high-performance liquid chromatography (HPLC). The extraction solvents types and volume of acetonitrile, the inorganic salt types and amount of $(\text{NH}_4)_2\text{SO}_4$, extraction time and pH of sample solution were optimized by single-factor experiment and central composite design. Under the optimum extraction conditions, all linear ranges were obtained with coefficients of determination (r) ≥ 0.9993 . The limits of detection for this proposed method were in the range of 0.16–0.28 $\mu\text{g/L}$ for six triazine herbicides. The developed method has been successfully applied to the analysis of target triazine herbicides from lake, canal and moat in real-world water samples. The recoveries of target analytes were in the range from 87.0 to 110.9% and the relative standard deviation was lower than 7.3%.

Keywords Acetonitrile inorganic salt · Aqueous two-phase microextraction · Triazine herbicides · Environmental water samples · High-performance liquid chromatography

1 Introduction

Triazine herbicides are ascribed to triazole pesticides, which have been widely used as selective herbicides to control broadleaf and grassy weeds in many agricultural crops [1].

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Due to the excessive use of triazine herbicides in agricultural, the residues of these herbicides have been continuously monitored in soils, groundwater [2], surface water [3] and food [4, 5] in recent years. They are considered one of the most important classes of persistent organic pollutants (POPs) because of the environmental persistence, bioaccumulation, semi-volatility and high toxicity. Among them, the atrazine has been listed as a human carcinogen [6]. With the increase of production and usage, the environmental hazard of triazine herbicides is paid great attention. The US EPA has stipulated that the content of atrazine may not be more than 3.0 $\mu\text{g/L}$ and simazine should not exceed 4.0 $\mu\text{g/L}$ in drinking water [7]. The European Union (EU) has banned its use in agricultural production in 2007 and stipulated that single pesticide in drinking water should not exceed 0.1 $\mu\text{g/L}$ [8, 9]. The Ministry of Health [10] and environmental quality standard of China for surface water (GB3838-2002) have specified the limits of triazine herbicides, for instance, the standard limit of atrazine in surface water is 3.0 $\mu\text{g/L}$. For the sake of protecting the human health and controlling the environmental pollution, the analytical methods are required to detect the triazine herbicides with high sensitivity and selectivity in different sample matrix.

However, the trace amount of POPs is difficult to directly detect due to the strong interference of coexisted contaminant and matrices in untreated environmental media. Therefore, the pretreatment process of matrix sample was unable to avoid before analysis. Several useful sample preparation methods have been developed for the determination of triazines residues, including liquid–liquid extraction (LLE) [11], solid-phase extraction (SPE) [12], solid-phase microextraction (SPME) [13] and liquid–liquid microextraction (LLME) [14]. For the analysis of triazine herbicides residues in water, the traditional chromatographic analysis models are generally adopted, such as gas phase chromatography–mass spectrometry (GC–MS) [15], high-performance liquid chromatography (HPLC) [16] and high-performance liquid chromatography–mass spectrometry (HPLC–MS) [17].

Aqueous two-phase system (ATPS) is ascribed to the dispersive liquid–liquid microextraction (DLLME) [18], which consisted of hydrophilic organic solvents or polymers with inorganic salts in aqueous solution. Meanwhile, the research shows that some hydrophilic small organic molecules, such as acetonitrile [19], isopropanol, acetone with a suitable inorganic salt and water mixed to form ATPS, and the material transfer and the phase separation are realized quickly. The microemulsion is formed when the concentration of extraction solvent exceeded the critical concentration. The inhomogeneous interphase system was obtained by high speed centrifugation or heating, and the target analytes were concentrated to the organic phase based on the difference of partition coefficients. ATPS has been widely used for the determination of organic pollutants and metal ions, which is attributed to the advantages of mild condition, low cost and solvent consumption [20].

In the study, ATPS was formed in the presence of acetonitrile and $(\text{NH}_4)_2\text{SO}_4$. Compared with acetonitrile, the inorganic salt has a stronger affinity for water molecules. Therefore, water molecules migrated from acetonitrile into the inorganic salt and lead to a decrease in hydration, thus resulting in a decrease in the solubility of acetonitrile in water [21]. Therefore, the phase rich in acetonitrile is separated from the rest of the solution. When the ATPS is formed, the upper and lower phases are acetonitrile and inorganic salt, respectively. Furthermore, the analytes are extracted into the acetonitrile-rich phase based on the distribution coefficients in the two phases. Compared with traditional LLE, the purification and concentration of target analytes in environmental water were carried out simultaneously in a short time [22].

The small molecule organic solvent–inorganic salt ATPS was developed for the simultaneous analysis of simeton, cyanazine, desmetryn, terbumeton, terbuthylazine and dimethametryn by HPLC in the environmental water samples. In order to achieve the effective extraction and analysis of target analytes, the extraction parameters were optimized

by single factor and central composite design. In addition, the precision and reproducibility of analytical methods were validated, respectively. Finally, the suitable pretreatment technique was applied to the determination of triazine herbicide in actual water samples for the trace POPs removal, and reference to other related research.

2 Experiment

2.1 Reagents and Solutions

The triazine herbicides (simeton, cyanazine, desmetryn, terbumeton, terbuthylazine and dimethametryn) were obtained from Dr. Ehrenstorfer (Augsburg, Germany). The purity of all the compounds was higher than 99.0%. The individual stock solution of each analyte (500.0 $\mu\text{g/mL}$) was prepared by dissolving 5 mg of the analyte in 10 mL of acetonitrile and stored at 4 °C. The mixed stock solution (10.0 $\mu\text{g/mL}$) was prepared with individual stock solutions by diluting with acetonitrile and stored at 4 °C. The mixed working standard solution was prepared by diluting the mixed stock solution with acetonitrile.

Chromatographic grade acetonitrile was purchased from Tedia Co., Ltd. (Tedia, USA). NaOH, HCl, KCl, K_2HPO_4 , $(\text{NH}_4)_2\text{SO}_4$, NaCl and K_2CO_3 were of analytical grade and purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). All environmental water samples were filtered through a filter (0.22 μm) and stored at 4 °C. 0.22 μm and 0.45 μm organic filters were purchased from Tianjin Jinteng Experimental Equipment Co., Ltd. (Tianjin, China).

2.2 Instruments

All analyses were performed on an HPLC system (Shimadzu, Japan) equipped with two delivery pumps (Model LC-20AT), an automatic sampler (SIL-10AF) and a UV/Vis detector (model SPD-20A). The analytical separation was accomplished on a Shim-pack GTST/GISS- C_{18} , 4.6 mm \times 250 mm column with 5 μm particle diameter. The chromatographic mobile phase contained acetonitrile (A) and water (B). The gradient program was as follows: 0–5 min, 40–60% (A), 5–15 min, 60–80% (A), 15–20 min, 80–40% (A). The injection volume of analytical solution was 10.0 μL . The flow rate of mobile phase was kept at 1.0 mL/min and column temperature was kept at 30 °C. The detection wavelength was 228 nm. The KQ-100DE ultrasound cleaner was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasound cleaner were 40 kHz and 100 W, respectively. The centrifuge was purchased from Shanghai Jingke Industrial Co., Ltd. (Shanghai, China).

2.3 Aqueous Two-Phase Extraction Procedure

5 mL of the water sample containing the target analytes was transferred to a 10 mL centrifuge tube. 2.78 g of $(\text{NH}_4)_2\text{SO}_4$ was accurately weighed and added to the sample solution and shaken for 1 min until the inorganic salt was completely dissolved. 0.46 mL of acetonitrile was added to the mixture, then the mixture was ultrasound extraction for 9.5 min and centrifuged at 4000 rpm for 5 min, the ATPS was formed. The upper and lower phase was acetonitrile and inorganic salt, respectively. The analytes were extracted into the acetonitrile-rich phase. 100 μL of the upper organic phase was collected and filtrated with 0.22 μm organic membrane filter for HPLC analysis.

3 Results and Discussion

3.1 Optimization of Extraction Condition

To obtain high extraction efficiency, the effects of experimental parameters, including the extraction solvents types and volume of acetonitrile, the inorganic salt types and amount of $(\text{NH}_4)_2\text{SO}_4$, extraction time and pH of sample solution were investigated.

3.1.1 Optimization of the Extraction Solvents Type

The molecular structure and $\log K_{ow}$ of extraction solvent have significant effects on the extraction recovery. The $\log K_{ow}$ of methanol, acetone, ethanol, and acetonitrile is -0.63 , -0.24 , -0.14 and -0.34 , respectively. In this experiment, the ability of the four organic solvents for the target analytes was investigated when the amount of $(\text{NH}_4)_2\text{SO}_4$ was fixed at 2.80 g. As can be seen in Fig. 1, methanol did not form ATPS with $(\text{NH}_4)_2\text{SO}_4$, and the extraction effect of acetonitrile is better than ethanol and acetone. The recoveries of the analytes were the best when acetonitrile was used as an extraction solvent. It is because of the strong acting force between acetonitrile and the hydrogen bond of triazine herbicides, which enhance the interaction between acetonitrile and the analytes, making the analytes more easily soluble in acetonitrile. Therefore, acetonitrile was selected as the extraction solvent in the following experiment.

3.1.2 Optimization of the Acetonitrile Volume

To obtaining the optimum extraction efficiencies, the volume of acetonitrile were investigated. ATPS was not easily formed when the volume of acetonitrile was lower than 0.3 mL. The effects of acetonitrile on the recoveries of target analytes were investigated by the volume of 0.30, 0.35,

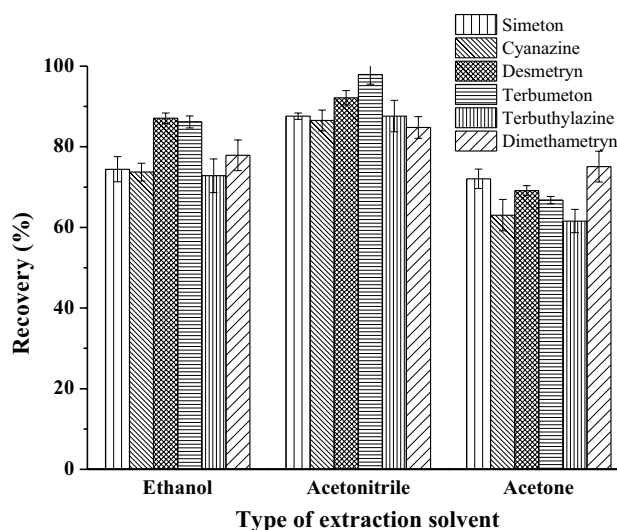


Fig. 1 Effect of extraction solvent types on the recoveries of triazine herbicides. Water sample volume, 5 mL, $(\text{NH}_4)_2\text{SO}_4$ amount, 2.80 g, extraction time, 10 min, pH 7.0

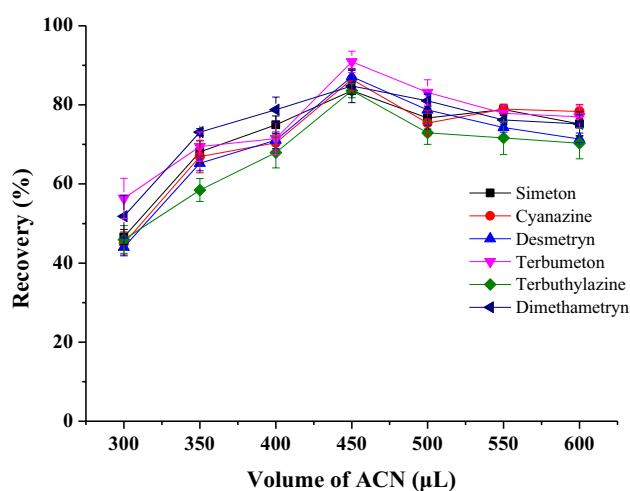


Fig. 2 Effect of the acetonitrile volume on the recoveries of triazine herbicides. Water sample volume, 5 mL, amount of $(\text{NH}_4)_2\text{SO}_4$, 2.80 g, extraction time, 10 min, pH 7.0

0.40, 0.45, 0.50, 0.55 and 0.60 mL. As shown in Fig. 2, the recoveries of the analytes increase with the increase of the volume of acetonitrile from 0.30 to 0.45 mL. When the volume of acetonitrile exceeded 0.45 mL, the recoveries of analytes were decreased. The intervention of $(\text{NH}_4)_2\text{SO}_4$ was benefit to enhanced the intermolecular interactions between the organic and water, which resulted in the separation of organic phase. As the amount of acetonitrile are up to 0.45 mL, the amount of the analytes was gradually stabilized in the upper phase. Based on the result, the volume of acetonitrile was set at 0.45 mL in all subsequent experiments.

3.1.3 Optimization of the Inorganic Salt Type

The addition of salt is beneficial to the phase separation, which is due to the electrostatic interaction of electrolytes and ionic salivation. Therefore, the effect of phase separation with different salts was investigated. When the volume of acetonitrile was 0.45 mL, KCl and NaCl were of no avail to form the aqueous two-phases system. On the contrary, K_2CO_3 , $(NH_4)_2SO_4$ and K_2HPO_4 were helpful for the formation of stable ATPS, which was attributed to the ionic radius of NH_4^+ (148pm) larger than Na^+ (95pm) and similar to K^+ (133pm). As shown in Fig. 3, the recovery of $(NH_4)_2SO_4$ was superior to that of K_2CO_3 and K_2HPO_4 . The hydrated layer of SO_4^{2-} and NH_4^+ are tightly bounded while the hydrogen-bonded association between them was greatly weakened due to the increase of H-O-H bond angles. The distance between the S atom and O atoms of water molecules gradually tends to increase with the increase of water molecules number, which lead to the weakening of hydrogen bond strength. The charge of S atoms and H increases gradually and the charge of atom O of SO_4^{2-} and water decreases. The hydration of ion was stronger than the hydrogen-bonding interaction between acetonitrile and water. Thus, $(NH_4)_2SO_4$ was selected as the inorganic salt for further experiments.

3.1.4 Optimization of the $(NH_4)_2SO_4$ Amount

With the amount of salt increases, the volume of upper phase increases and the concentration of target analytes in the upper phase decreases [23], which was beneficial to the improvement of the extraction efficiency. The effect of the amount of $(NH_4)_2SO_4$ on the target analyte recoveries

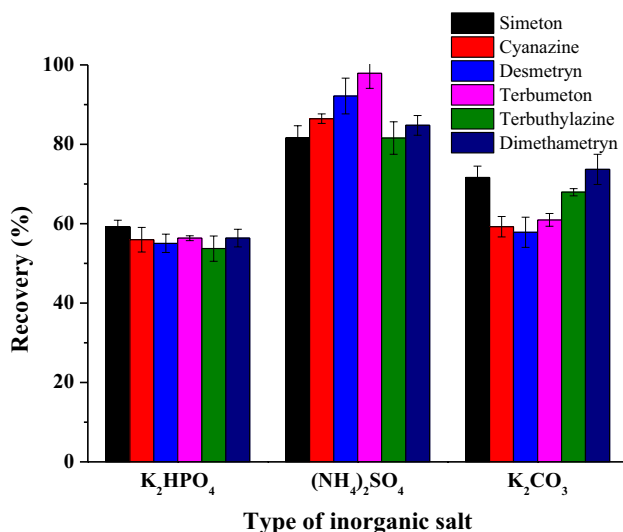


Fig. 3 Effect of inorganic salt types on the recoveries of triazine herbicides. Water sample volume, 5 mL, volume of acetonitrile, 0.45 mL, extraction time, 10 min, pH 7.0

experiment was investigated (2.2, 2.4, 2.6, 2.8, 3.0, 3.2 and 3.4 g). Figure 4 shows that when the amount of $(NH_4)_2SO_4$ increased to 2.80 g, the recoveries of the target analytes reached the maximum. The amount of $(NH_4)_2SO_4$ was continued to increase and the recovery was decreased slightly. The intermolecular force of the $(NH_4)_2SO_4$ with water was greater than that of acetonitrile, which resulted in the separation of organic phase. As the amount of $(NH_4)_2SO_4$ increased continuously, the ionic forces of the inorganic salt placed in advantage in competition, and thus the recoveries of the target analytes decreased slightly. Hence, 2.80 g of $(NH_4)_2SO_4$ was chosen in the subsequent experimental.

3.1.5 Optimization of the Extraction Time

Ultrasound cavitation and emulsification can refine the material, improve the extraction efficiency and accelerate the phase separation of the system. Therefore, ultrasound-assisted extraction was used and the effect of ultrasound time on extraction efficiency was investigated in the range of 0–14 min. As shown in Fig. S1, the recoveries of triazine herbicides increased steadily within 10 min. The recoveries decreased slightly when the ultrasound extraction time was longer than 10 min. The extraction equilibrium can be achieved in a short time and the phase transfer speed of the analyte was fast. Finally, 10 min was selected for the ultrasound extraction time.

3.1.6 Optimization of the pH

The pH of the sample solution plays an important role in the extraction of analytes, because it affects the existing forms of the analyte [24] and its partitioning in the ATPS.

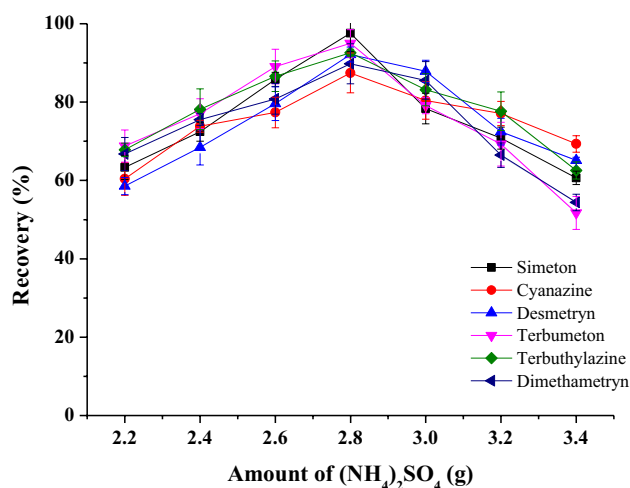


Fig. 4 Effect of $(NH_4)_2SO_4$ amount on the recoveries of triazine herbicides. Water sample volume, 5 mL, volume of acetonitrile, 0.45 mL, extraction time, 10 min, pH 7.0

Theoretically, the maximum extraction efficiency can be achieved when the analytes exist in the uncharged form. The effect of pH of the sample solution in the range of 3–11 on the extraction recoveries of the triazine herbicides was studied. 1 mol/L of HCl solution and 1 mol/L of NaOH solution were used to adjust the pH value. As shown in Fig. S2, when the pH of the sample solution is the range of 6.0–8.0, there is no significant change in the extraction efficiency of individual target analytes. The highest extraction recoveries were obtained at pH 7; the extraction efficiency under acidic and alkaline conditions was inferior to that under the neutral pH conditions, which is ascribed to the neutral characteristics of target analytes. Meanwhile, the strong acid or alkali environments were not beneficial to the formation of ATPS. Therefore, the adjustment of pH was unnecessary and set at 7.0.

3.2 Response Surface Optimization Experiment Design

After a series of single factor data analysis, the optimal ATPS conditions for extracting triazine herbicides was 0.45

mL acetonitrile, 2.80 g $(\text{NH}_4)_2\text{SO}_4$, pH at 7.0 and ultrasound extraction time at about 10 min, the obtained recoveries of 6 triazine herbicides reached 83.6–97.6%. In order to achieve better extraction efficiency, the three single factors of acetonitrile volume, $(\text{NH}_4)_2\text{SO}_4$ amount and ultrasound extraction time in the experiment were combinatorial optimized through a response surface model. According to the principle of central composite design (CCD) experimental design, response surface experimental analysis of 20 experimental points (6 central points) with five levels and three factors was designed. The acetonitrile volume (A), amount of $(\text{NH}_4)_2\text{SO}_4$ (B) and ultrasound extraction time (C) were used as independent variables; the recovery of triazine herbicides was the response value and the experimental design matrix is shown in Table 1. The optimum recoveries of the 6 triazine herbicides ranged from 90.6 to 99.8%. Applying a multiple linear regression data analysis program, the second-order polynomial equation associated with the experimental response and experimental variables is shown in Table S1.

The significant differences of the regression model were tested by *F* value and *P* value, and the results of the fitting model for the 6 triazine herbicides (Table S2) showed that

Table 1 Variables and experimental results of the CCD design matrix

No.	X_1	X_2	X_3	Y_1 (%)	Y_2 (%)	Y_3 (%)	Y_4 (%)	Y_5 (%)	Y_6 (%)
1	-1	1	-1	74.9	76.8	68.1	69.8	67.2	64.5
2	-1	-1	-1	89.8	87.8	76.4	84.7	86.5	84.1
3	0	0	0	97.2	98.2	94.5	93.2	97.1	96.5
4	0	0	0	98.9	99.4	96.2	92.8	97.0	95.1
5	0	0	0	96.8	92.6	98.8	97.5	91.2	90.6
6	1	1	-1	78.2	70.8	72.5	74.0	83.8	81.5
7	0	0	2	62.4	69.1	61.6	65.8	62.4	70.1
8	2	0	0	75.4	67.2	63.1	73.8	76.1	77.8
9	0	-2	0	70.9	74.1	68.2	74.8	71.6	67.3
10	0	0	2	50.5	72.7	64.8	55.5	60.8	61.4
11	-1	1	1	74.9	77.8	80.1	79.4	86.2	72.8
12	0	0	0	98.0	94.8	97.1	99.8	97.2	99.1
13	0	0	0	96.4	98.8	95.4	92.7	98.9	97.5
14	0	2	0	64.2	57.8	60.7	64.8	58.4	56.7
15	0	0	-2	82.6	84.1	77.2	81.8	84.6	77.8
16	-2	0	0	78.4	76.1	64.8	70.9	78.6	79.3
17	-1	-1	1	82.0	84.1	79.8	78.4	86.2	77.8
18	1	-1	-1	76.8	74.3	84.5	83.2	87.4	88.2
19	1	1	1	74.9	65.7	67.8	72.3	70.1	77.7
20	0	0	0	91.8	94.1	93.2	97.6	96.8	94.4

X_1 was the volume of acetonitrile; the value for each level (-2, -1, 0, 1, 2) was 0.43, 0.44, 0.45, 0.46, 0.47 (mL), respectively

X_2 was the amount of $(\text{NH}_4)_2\text{SO}_4$; the value for each level (-2, -1, 0, 1, 2) was 2.7, 2.75, 2.8, 2.85 and 2.90 (g), respectively

X_3 was the extraction time; the value for each level (-2, -1, 0, 1, 2) was 8, 9, 10, 11 and 12 (min), respectively

$Y_1, Y_2, Y_3, Y_4, Y_5, Y_6$ were the recovery of simeton, cyanazine, desmetryn, terbumeton, terbuthylazine and dimethametryn

the quadratic regression equation model was significant; the P values were all less than 0.05. The unrealistic terms are not significant and their P values are all greater than 0.05, indicating that the model used can be well fitted to the experiment. The coefficient of determination (R^2) is 0.9843, the degree to which the experimental value of the reaction was close to the predicted response value indicates that the predicted results of this model can represent the actual experimental results. Through the analysis of variance in this model, the extraction efficiency of X_1 , X_2 , and X_3 was not significant under single factor conditions and the extraction efficiency was extremely significant under the conditions of X_{12} , X_{22} , and X_{32} (P value less than 0.05 is significant).

As can be seen from Table S3, the volume of acetonitrile and the amount of $(\text{NH}_4)_2\text{SO}_4$ were the main factors within the range selected by each factor. To further illustrate the interaction between experimental variables and independent variables, two independent variables were used as research factors and the other was a three-dimensional response surface map for independent variables. The extraction efficiency of target analytes under interaction was investigated (Fig. S3 and Fig. S4). According to the software Design-Expert, the optimal experimental conditions were as follows: the volume of acetonitrile was 0.46 mL, the amount of $(\text{NH}_4)_2\text{SO}_4$ was 2.78 g, the ultrasound extraction time was 9.5 min, and the recoveries of simeton, cyanazine, desmetryn, terbumeton, terbuthylazine and dimethametryn were 97.61, 97.2, 96.4, 97.1, 96.9 and 98.2%, respectively.

3.3 Matrix Effect

The determination of trace target analytes in real-world water sample was interfered because of the influenced significant effect of the matrix, which lead to the decrease of accuracy and precisions. Matrix effect (ME) could be calculated by the following Eq. (1):

$$\text{ME (\%)} = \frac{\Delta A}{A} \times 100\% \quad (1)$$

where ΔA was the peak area of matrix-matched standard – peak area of solvent standard, and A was the peak area of matrix-matched standard. The result was shown in Table 2.

The average matrix effect at different concentrations of six analytes ranged from – 8.4 to 17.3%, which indicated that the inexistence of the matrix interfered the determination.

3.4 Method Validation

To investigate the applicability of the proposed method for the determination of triazine herbicides in water samples, several factors including linear range, calibration equation, correlation coefficients of determination (r), the residual standard deviations ($S_{y/x}$), limits of detection (LODs), limits of quantification (LOQs) and relative standard deviations (RSDs) were evaluated under optimum conditions. The calibration curves of the six triazine herbicide were established by plotting the peak area versus the concentration of spiked samples ($n = 5$).

The characteristic calibration data listed in Table 3 are obtained under optimized conditions. Good linear relationships were obtained for the terbuthylazine and dimethametryn in the concentration range of 3.0–200.0 $\mu\text{g/L}$; meanwhile, the other four chemicals were in the range of 2.0–200.0 $\mu\text{g/L}$. The correlation coefficients (r) ranged from 0.9993 to 0.9998, suggesting that the linearity is satisfactory in the linear range of the analytes. The LODs and LOQs of the proposed method were 0.18–0.28 and 0.53–0.84 $\mu\text{g/L}$, respectively.

The repeatability was assessed by means of the intra-day and inter-day RSDs at the concentration of 5.0, 10.0 and 100.0 $\mu\text{g/L}$ (Table 4). The intra-day precisions were measured for five replicate procedures in a single day and the RSDs ranged from 2.1 to 5.7%. The inter-day precisions were calculated on five consecutive days and the RSDs ranged from 1.8 to 6.9%. These results demonstrated a high sensitivity and excellent repeatability of this proposed method.

3.5 Analysis of Environmental Water Samples

To further confirm the reliability of this method for the analysis of triazine herbicides in real samples, it was applied to the determination of analytes in Tai lake, moat and canal water. The recoveries of triazine herbicides were assessed

Table 2 Matrix effects of 6 triazine herbicides ($n = 6$)

Compound	10.0 $\mu\text{g/L}$		50.0 $\mu\text{g/L}$		100.0 $\mu\text{g/L}$	
	Matrix effect (%)	RSD (%)	Matrix effect (%)	RSD (%)	Matrix effect (%)	RSD (%)
Simeton	– 14.5	5.7	– 12.7	4.7	– 8.4	4.2
Cyanazine	– 16.2	8.9	– 14.8	5.5	– 10.4	4.4
Desmetryn	– 10.9	6.4	– 9.4	4.9	– 13.5	3.5
Terbumeton	17.3	7.3	11.4	6.8	6.8	4.6
Terbuthylazine	14.9	6.4	10.3	5.2	9.3	3.9
Dimethametryn	– 15.7	7.1	– 14.2	6.5	– 7.9	5.7

Table 3 Linear ranges, correlation coefficients, detection limits, quantitative limits and RSDs of 6 triazine herbicides ($n=5$)

Analytes	Regression equation	Correlation coefficients (r)	Linear ranges ($\mu\text{g/L}$)	Sy/x	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)	RSD %
Simeton	$y=(1.05x \pm 0.018^a) + (9.47 \pm 1.98^b)$	0.9994	2.0–200	3.14	0.18	0.60	4.5
Cyanazine	$y=(0.93x \pm 0.011^a) + (8.12 \pm 1.23^b)$	0.9997	2.0–200	1.96	0.16	0.53	5.5
Desmetryn	$y=(1.03x \pm 0.008^a) + (8.66 \pm 1.46^b)$	0.9999	2.0–200	1.34	0.17	0.54	6.7
Terbumeton	$y=(1.06x \pm 0.011^a) + (8.46 \pm 1.27^b)$	0.9998	2.0–200	2.01	0.19	0.60	4.1
Terbuthylazine	$y=(1.48x \pm 0.028^a) + (5.72 \pm 3.08^b)$	0.9993	3.0–200	4.90	0.25	0.84	4.5
Dimethametryn	$y=(1.63x \pm 0.020^a) + (9.50 \pm 2.18^b)$	0.9997	3.0–200	3.46	0.28	0.74	5.2

^aStandard deviation of slope

^bStandard deviation of intercept

Table 4 Intra-day and inter-day precision at low, medium and high concentration of analyte

Triazine herbicides	Intra-day precision (RSD %, $n=5$)			Inter-day precision (RSD %, $n=5$)		
	Low (5.0 $\mu\text{g/L}$)	Medium (50.0 $\mu\text{g/L}$)	High (100.0 $\mu\text{g/L}$)	Low (5.0 $\mu\text{g/L}$)	Medium (50.0 $\mu\text{g/L}$)	High (100.0 $\mu\text{g/L}$)
Simeton	4.0	4.7	2.7	4.3	3.4	6.0
Cyanazine	2.5	2.1	3.1	6.9	5.5	4.0
Desmetryn	4.1	4.2	2.9	5.0	3.8	1.8
Terbumeton	5.7	2.3	4.1	5.6	3.2	3.7
Terbuthylazine	4.5	2.1	3.0	1.9	6.3	2.1
Dimethametryn	2.8	3.4	3.6	4.7	4.3	6.0

by spiking the analytes into water samples with three known concentrations of 5, 50 and 100 $\mu\text{g/L}$. Each water sample was measured in parallel five times. Triazine herbicides were not detected in any of the three water samples. The results (Table 5) showed that the recovery of standard addition was ranged from 87.0 to 110.9% with a relative standard deviation of less than 7.3%. As a result, the recovery and precision of this method were satisfactory, which could meet the requirements for the determination of actual environmental samples. HPLC chromatograms of black and spiked (10.0 $\mu\text{g/mL}$) 6 triazine herbicides in environmental sample are listed in Fig. 5.

3.6 Comparison with Other Methods

This method was compared with the other reported methods for determination of herbicides in samples. The optimal extraction of the parameters was shown in Table 6. It can be seen that consumption of extraction solvent was relatively lower than that in other methods. The LODs obtained by the present method are similar to or lower than these obtained by the reported methods. In addition, it was simple in operation and extraction time was shorter as compared with other methods. The results indicate that

the present method was suitable for the determination of triazine herbicides in water samples.

4 Conclusion

In the present work, the triazine herbicides in water samples were concentrated and determined by acetonitrile– $(\text{NH}_4)_2\text{SO}_4$ ATPS coupled with HPLC. The target analytes were extracted rapidly into the upper phase, and the organic solvent amount was significantly lower than that of traditional liquid-liquid extraction, which devotes to a relatively eco-friendly method. The results demonstrate that the method has good linear range, low detection limit, satisfactory precision and reproducibility. According to the results of the measurement, it can be concluded that the amount of triazine herbicide residues in real-world environmental water was lower than that of EU standard. The proposed method was simple equipment, convenient operation, fast phase separation and high extraction efficiency sample pretreatment method. As expected, this method can be applied to analyze the trace residue of triazine herbicides in environmental water samples.

Table 5 Recoveries of the triazine herbicide in lake water, canal water and moat water samples ($n=5$)

Triazine herbicides	Spiked ($\mu\text{g/L}$)	Tai lake water			Moat water			Canal water		
		Found ($\mu\text{g/L}$)	Recovery (%)	RSD (%)	Found ($\mu\text{g/L}$)	Recovery (%)	RSD (%)	Found ($\mu\text{g/L}$)	Recovery (%)	RSD (%)
Simeton	5.0	4.6	91.9	5.2	4.9	97.2	2.7	4.51	90.2	6.8
	50.0	49.1	98.1	3.8	46.8	93.6	4.4	48.05	96.1	7.3
	100.0	102.0	102.0	4.1	93.5	93.5	4.8	93.5	93.5	1.3
Cyanazine	5.0	4.6	92.8	1.3	4.92	98.3	5.4	4.86	97.1	1.9
	50.0	43.5	87.0	1.6	46.55	93.1	4.2	45.2	90.4	3.3
	100.0	92.2	92.2	5.3	100.4	100.4	2.7	98.4	98.4	3.4
Desmetryn	5.0	4.8	95.0	5.1	5.02	100.3	2.8	4.96	99.3	3.2
	50.0	46.15	92.3	5.0	54.5	109.0	6.2	47.65	95.3	2.5
	100.0	88.8	88.8	5.5	95.1	95.1	3.1	109.7	109.7	5.1
Terbumeton	5.0	4.97	99.4	3.6	4.76	95.2	5.2	4.4	87.9	6.2
	50.0	43.3	86.6	7.1	44.15	88.3	6.2	45.45	90.9	5.7
	100.0	92.4	92.4	2.1	94.2	94.2	6.4	91.6	91.6	2.5
Terbutylazine	5.0	4.8	96.7	7.3	5.105	102.1	5.7	4.98	99.5	5.8
	50.0	45.4	90.8	3.7	49.6	99.2	4.8	51.05	102.1	6.1
	100.0	90.7	90.7	4.9	96.5	96.5	6.9	110.9	110.9	3.5
Dimethametryn	5.0	5.1	101.5	6.8	4.88	97.5	4.1	4.94	98.8	2.6
	50.0	52.9	105.7	5.1	52.6	105.1	7.1	52.6	105.2	4.3
	100.0	99.8	99.8	4.5	100.1	100.1	6.2	106.2	106.2	5.2

Fig. 5 HPLC chromatograms of blank and spiked (10 $\mu\text{g}/\text{mL}$) in environmental sample. 1. Sime-ton, 2. Cyanazine, 3. Desmetryn, 4. Terbumeton, 5. Terbutylazine, 6. Dimeth-ametryn. Environmental water sample volume, 5 mL, Volume of acetonitrile, 0.45 mL, amount of $(\text{NH}_4)_2\text{SO}_4$, 2.80 g, extraction time, 10 min, pH, 7.0

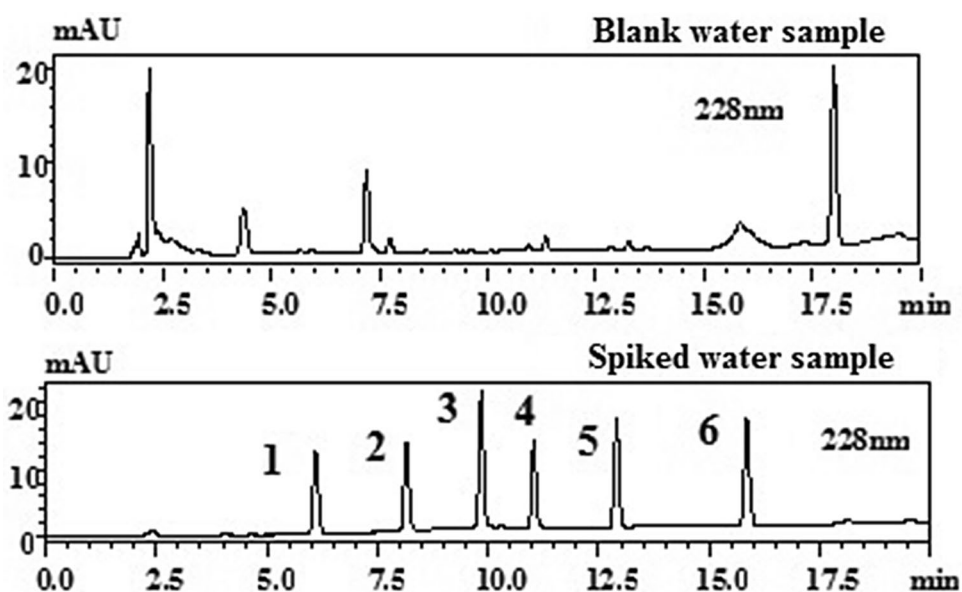


Table 6 Comparison of the proposed method with reference methods

Method	Detection	Sample type	Sample volume (mL)	Extraction solvent type	Extraction solvent volume (mL)	LOD ($\mu\text{g}/\text{L}$)	Extraction time (min)	References
CPE ^a	HPLC–UV	milk	10	Glacial acetic acid	0.157	6.79–11.19	30	[4]
SPME ^b	HPLC–DAD	water	10	Acetone	50	0.05–0.20	30	[5]
HILME–MHFBC ^c	HPLC–DAD	water	10	Methanol	0.8	0.14–0.48	/	[25]
HF–LPME ^d	HPLC–UV	water	200	di- <i>n</i> -hexylether	1.0	0.03–1.12	300	[26]
ATPS	HPLC–UV	water	5	Acetonitrile	0.45	0.16–0.28	10	This work

^aCloud point extraction

^bMagnetic solid-phase extraction

^cHomogenous ionic liquid microextraction-magnetical hollow fiber bar collection of extraction

^dHollow fiber-based liquid phase microextraction

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