



ASSESSING STIR BAR SORPTIVE EXTRACTION FOR TRIAZINE HERBICIDES EXTRACTION BY USING A CENTRAL COMPOSITE DESIGN APPROACH

(Penilaian Pengekstrakan Erapan Bar untuk Pengekstrakan Herbisid Triazin Menggunakan Pendekatan Reka Bentuk Komposit Berpusat)

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Abstract

A (PDMS)-coated stir bar was prepared for a glass jacket-free stir bar sorptive extraction (SBSE) configuration by adhesion technique for the extraction of triazine herbicides prior to quantification using a gas chromatography-flame ionization detector (GC-FID). A central composite design (CCD) was used in the optimization of extraction and desorption conditions. At optimum conditions, values of factors were set as pH 8.5, with no addition of NaCl, for 25 minutes of extraction time, and 24 minutes of desorption time. Under optimal experimental conditions, the proposed method has linear ranges at 0.1 – 100 $\mu\text{g L}^{-1}$ with correlation of determination (R^2), ranging from 0.9991 – 0.9995, respectively. The limit of detection (LODs) and limit of quantification (LOQs) of three triazines were found to be ranging from 0.015 – 0.023 $\mu\text{g L}^{-1}$ and 0.047 – 0.060 $\mu\text{g L}^{-1}$, respectively.

Keywords: stir bar sorptive extraction, triazine herbicides, central composite design, partition coefficient

Abstrak

Bar berputar yang disalut dengan polidimetilsiloksana (PDMS) telah disediakan untuk pengekstrakan erapan bar berputar (SBSE) tanpa jaket kaca melalui teknik lekatan untuk dianalisa sebelum kuantifikasi racun herbisid triazin dengan menggunakan kromatografi gas-pengesan ionisasi nyala (GC-FID). Reka bentuk komposit berpusat (CCD) telah digunakan untuk proses pengoptimuman keadaan pengekstrakan dan nyahjerapan. Pada keadaan optimum, nilai faktor adalah pH 8.5, tanpa penambahan NaCl, 25 minit masa pengekstrakan, dan masa nyahjerapan 24 minit. Kajian berdasarkan julat kelinearan antara 0.1 – 100 $\mu\text{g L}^{-1}$

telah mencapai kelinearan yang baik dengan pekali R^2 di rekod antara 0.9991 – 0.9995. Had pengesanan (LODs) dan kuantifikasi (LOQs) bagi tiga jenis triazin tersebut masing-masing dihitung antara 0.015 – 0.023 μgL^{-1} dan 0.047 – 0.060 μgL^{-1} .

Kata kunci: pengekstrakan erapan bar berputar, herbisid triazin, reka bentuk komposit berpusat, pemalar pemisahan

Introduction

Since their introduction, triazine herbicides have been widely used in agriculture as selective herbicides in many parts of world. These herbicides and their degradation products are highly persistent and hence their analysis in environmental samples is important [1]. The concentration of triazines in aquatic environments like ground water, rivers and estuaries is often found to be close to the lower detection limits of most elaborate analytical procedures [2]. Therefore, in order to protect human health and the environment, it is significantly important to monitor their levels in environmental waters. This has increased the demand for the development of simple, reliable, sensitive and rapid analytical methods. Sample preparation is considered as the most critical step in the overall analytical process since it plays a key role in analyte extraction, pre-concentration, and cleanup [3].

Conventional liquid-liquid extraction (LLE) and solid-phase extraction (SPE) have been used for pre-concentration and cleanup before analysis. LLE is time-consuming and hazardous to health due to the high volume of toxic solvents used [4]. SPE needs less solvent but it is still time consuming, and often requires a concentration stage that presents disadvantages such as loss in the evaporation step [5].

However, modern trends in analytical chemistry are moving towards the simplification and miniaturization of sample preparation, as well as the minimization of organic solvent used. Stir bar sorptive extraction (SBSE), as a microextraction method, was first introduced by Baltussen et al. in 1999 [6]. This technique has gained wide acceptance as a highly efficient sample preparation method for enrichment of solutes from aqueous samples [7]. The extraction is controlled by the solutes partitioning coefficient between the polymer coating and the sample matrix and by the phase ratio between the polymer coating and the sample volume. For a polydimethylsiloxane coating and aqueous samples, this partitioning coefficient resembles the octanol-water partitioning coefficient. In comparison to solid phase micro-extraction, a larger amount of sorptive extraction phase is used, and consequently, very high sensitivities in environmental, food and biomedical fields trace analysis. SPME and SBSE have been compared for the analysis of different compounds, as organochlorine pesticides [8] and organophosphorus insecticides [9]. All the studies reached the same conclusion, whereby the SBSE concentration capability was better than those presented by SPME because of polydimethylsiloxane (PDMS) film phase that covers the bar is thicker.

In the SBSE technique, the sample is stirred with a glass enclosed magnetic stir bar coated with a layer of PDMS, resulting in a distribution of analytes between the aqueous sample matrix and the PDMS layer [3]. The glass jacket is useful to immobilize sorbents onto the stir bar but it may lead to low stability and reproducibility because the glass jacket is relatively fragile. In this work, we introduced a glass jacket-free SBSE configuration by introducing a low cost hollow glass cylinder as a template for coating the SBSE polymeric phase. This template is important for reproducing the same bar characteristics from batch to batch.

Thus, this work aims to develop the prepared homemade glass jacket-free SBSE using PDMS sorbent for the determination of the selected triazine herbicides at trace levels from water samples prior to their determination by gas chromatography-flame ionization detector (GC-FID). An experimental design was used to investigate the influence of the principal parameters affecting glass jacket-free SBSE extraction of triazines. Thus, for determining the best experimental conditions, a central composite design (CCD) was applied. The developed method was then tested using different quality control approaches including detection limit and recovery assay.

Materials and Methods

Chemicals and reagents

Triazines namely atrazine, cyanazine, and ametryn, were purchased from Dr. Ehrenstorfer (GmbH, Germany). A standard compound solution at 1000 mgL^{-1} each were prepared in methanol. The mixture of all the compounds was prepared by diluting the standard solution in ultrapure water. All standard stock solutions were kept in a refrigerator

at 4 °C. HPLC-grade methanol, acetonitrile, acetic acid and hydrochloric acid were purchased from Merck (Darmstadt, Germany). Sodium chloride and sodium hydroxide were of analytical grade and obtained from R & M (Essex, UK). Ultrapure water was purified by Milli-Q EasypureRodi system (Barnstead, USA). PDMS Sylgard 184 silicone elastomer kit, which comprised base/curing agent to be mixed in a ratio of 10 (base) to 1 (curing agent) was obtained from Sigma Aldrich (St. Louis, USA).

Gas chromatographic analysis

A gas chromatography (GC) model HP 5890 Series II system equipped with a flame ionization detector (FID) (Hewlett-Packard) was used in this work. An Agilent DB-5 capillary column (30 m x 0.32 mm i.d. x 1.50 µm film thickness) was employed for the chromatographic separation. Helium was used as carrier gas at a flow rate of 1.0 mL min⁻¹. The GC oven temperature was programmed as follows: initial temperature was held at 120 °C for 1 min, programmed at 30 °C min⁻¹ to 180 °C and kept at this temperature for 1 min, then 10 °C min⁻¹ to 250 °C and kept at this temperature for 3 min. The total run time was 15.00 min. The injection port and detector temperature were both set at 250 °C and 280 °C, respectively. Sample (1 µL) was manually injected into the injection port under the splitless mode.

Experimental design of PDMS stir bar sorptive extraction procedure

The glass jacket-free SBSE conditions were optimized by using a CCD (with $\alpha = 2.000$), based on 2⁴ factorial design plus eight axial points plus six replicates in the centre of the design. The variables chosen for SBSE optimization were pH of the sample solution, ionic strength, extraction time, and desorption time. The factors, their levels, and symbols that were investigated by CCD are shown in Table 1. 30 experiments were generated by CCD and executed in a randomized order. The data were processed using Minitab version 17 (Minitab Inc. USA).

Table 1. Design matrix for central composite design

Factors	Levels				
	- α (-2)	Low (-1)	Central (0)	High (+1)	+ α (+2)
(A) pH of sample solution	3.5	5.0	6.5	8.0	9.5
(B) Ionic strength (NaCl % (w/v))	0.0	1.0	2.0	3.0	4.0
(C) Extraction time (min)	5.0	10.0	15.0	20.0	25.0
(D) Desorption time (min)	10.0	15.0	20.0	25.0	30.0

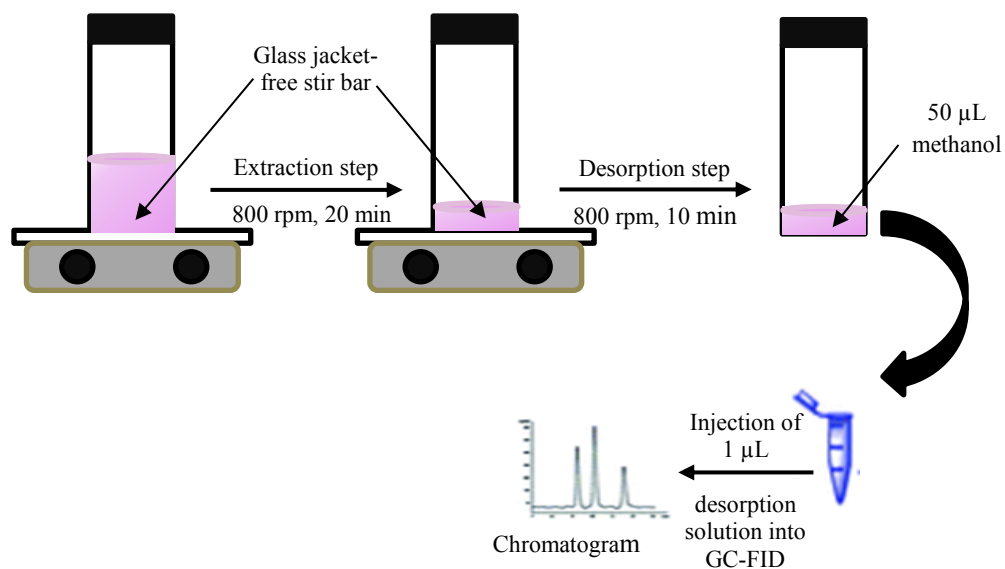


Figure 1. Schematic illustration of glass jacket-free SBSE process

In principle, the extractions were carried out with the homemade PDMS stir bar in a 25-mL amber glass vial, containing 10 mL standard solution of three selected triazines, and according to the experimental factorial design matrix. The vial was placed on the constant temperature magnetic stirrer. The stir bar was immersed into the standard solution and stirred at 800 rpm for 20 minutes. After extraction, the modified stir bar was removed, dried on a clean lint-tissue and transferred into a cylindrical glass desorption vial containing 50 μ L methanol to desorb the targeted triazines under a magnetic stirring rate of 800 rpm for 10 minutes. Then, 1 μ L of desorption solution was injected to the GC-FID injection port for analysis. The stir bar was regenerated in 0.5 μ L methanol under ultrasonication for 15 minutes before the next use. Finally, a numerical data analysis resulting from CCD suggested that the optimum conditions were set as: 8.5 (pH), no addition of NaCl, 25 min (extraction time), and 24 min (desorption time).

Method validation

Analytical performance of the proposed stir bar was validated in terms of repeatability, linearity, limit of detection (LOD), and limit of quantification (LOQ) using the optimized extraction conditions. The linearity was obtained from the construction of calibration curve from 0.1 – 100 μ g/L⁻¹ with triplicate measurements. LOD was determined at signal-to-noise ratio (S/N = 3) whilst the LOQ was determined at signal-to-noise ratio (S/N = 10). Repeatability of the methods was evaluated by performing nine measurements (three concentrations/three replicates) encompassing the concentration range, and calculating the relative standard deviations (RSD).

Quantification of partition coefficient and enrichment factor

At equilibrium, the partition coefficient for the analyte is dependent upon the phase ratio, and thus on the amount of extraction phase used as shown in equation 1.

$$K = \frac{C_{e,eq}}{C_{s,eq}} = \frac{m_e}{m_s} \times \frac{V_s}{V_e} = \frac{m_e}{m_s} \times \beta \quad (1)$$

The distribution coefficient between the extraction phase used and the sample is defined as the ratio between the analyte concentrations in the extraction phase ($C_{e,eq}$) over the concentration of the analyte in the sample ($C_{s,eq}$) at equilibrium. This ratio is equal to the ratio of the mass of the analyte in the extraction phase (m_e) over the mass of the analyte in the sample (m_s) times the phase ratio β , which is defined as the ratio between the volume of the sample (V_s) over the volume of the extraction phase (V_e). According to the mass balance relationship (equation 2):

$$C_t \cdot V_s = C_{e,eq} \cdot V_e + C_{s,eq} \cdot V_s \quad (2)$$

where C_t is the original concentration of analytes. The enrichment factor, EF, can be defined as the ratio of the equilibrium concentration of analytes in the extraction phase to the original concentration of analytes in the sample. EF can be calculated from equation 3:

$$EF = \frac{C_{e,eq}}{C_t} = \frac{1}{\left(\frac{V_e}{V_s} + \frac{1}{K}\right)} \quad (3)$$

Results and Discussion

Central composite design

Based on the above results, a 2^4 of CCD was performed at five levels to optimize the factors pH, ionic strength, extraction time, and desorption time in order to improve the extraction recovery (ER%) percentage of triazines. The stirring speed and volume of desorption solvent were held constant at 800 rpm and 300 μ L. The CCD was used not only to evaluate the variables significance, but also to analyze the interaction among them. A quadratic regression model, on the basis of a multiple linear regression (MLR), should be applied to relate the responses and the variables. The second order polynomial equation obtained using coded value is given in regression in Equation 4:

$$ER = 66.44 + 6.865 A - 5.512 B + 10.674 C + 5.396 D - 6.880 A^2 - 1.768 B^2 - 3.568 C^2 - 4.226 D^2 + 4.12 AB + 6.07 AC - 5.49 BC \quad (4)$$

where, A, B, C and D are the pH, ionic strength, extraction time and desorption time, respectively. As shown in the equation, the developed model consisted of four main effects, four curvature effects, and three interaction effects. Variables A, C, D, and interaction effects of AB and AC had positive linearity toward the fitted model.

To evaluate the significance of each factor and interaction terms, analysis of variance (ANOVA) was used and the obtained results are presented in Table 2. The quality of fit of the model equation was represented by the coefficient of determination (R^2 and adjusted- R^2). R^2 of 0.9651 and adjusted- R^2 of 0.9538 showed a good relationship between the experimental data and fitted model, as well as the high potential of model in prediction of response. The P-values were used to check the statistical significance of each coefficient, which in turn was necessary to understand the pattern of the mutual interactions between the test variables. Furthermore, P-value lower than 0.05 indicates the statistical significance of an effect at 95% confidence level. In this study, all individual experimental factors were significant with P-value < 0.05.

The other criterion for evaluating the model is the lack of fit (LOF) test which was performed by comparing the residual with the pure error achieved from the replicated design points at the central level of variables. In this case, if the P-value was greater than 0.05 (at the significance level of 95%), the regression will be significant. Considering the ANOVA results from Table 3, the P-value of the LOF test was 0.799, which confirms the lack of fit insignificance.

Table 2. Analysis of variance (ANOVA) for the developed models

Source	Df ^a	Sum of Square	Mean Square	F-value	P-value
Model	11	8365.69	760.52	45.25	0.000
Blocks	1	64.0	64.0	4.77	0.043
A	1	1131.17	1131.17	67.30	0.001
B	1	729.30	729.30	43.39	0.000
C	1	2734.22	2734.22	162.67	0.002
D	1	698.76	698.76	41.57	0.000
A ²	1	1298.39	1298.39	77.25	0.001
B ²	1	85.71	85.71	5.10	0.037
C ²	1	349.13	349.13	20.77	0.003
D ²	1	489.86	489.86	29.14	0.000
AB	1	271.43	271.43	16.15	0.001
AC	1	590.09	590.09	35.11	0.000
BC	1	482.17	482.17	28.69	0.000
LOF ^b	13	202.86	14.49	0.58	0.799
Pure error	4	99.69	24.92		
Total	29	8668.24			

^a Degree of freedom, ^b Lack of fit, and bold value is significant at p < 0.05

Effect of variables on extraction efficiency

The matrix pH and ionic strength variables affect the extraction thermodynamics, so influencing the interaction between the analytes and the PDMS phase. The pH of the sample solution plays an important role for ionizable compounds such as triazines. Triazines are basic herbicides, and it is assumed that at a basic pH condition, better extraction recovery will be obtained.

In this work, pH values ranging from 3.5 to 9.5 were investigated. Triazine compounds contain amino groups and their existing forms will be affected by medium pH. It can be seen from the figure that at low pH values, the extraction efficiencies are low because the nitrogen atoms of triazines were protonated. Therefore, the molecules of triazines were in ionic form, resulting in only π - π interaction that contributed to the extraction. With the increase of pH value, hydrophobic interaction also contributed to the extraction because triazines existed in a neutral form. According to the polynomial equation (equation 1) and response surface plot (Figure 2 (a)), the pH variables were significant with a positive sign, showing an increase of extraction recovery due to the increase in pH value, reaching the maximum at pH 8.5 and then decreasing after that. Lei et al. [10] applied polydimethylsiloxane (PDMS)/MIL-100(Fe) coated stir bar for the determination of six triazines (simazine, atrazine, prometon, ametryn, prometryne and prebana) and observed that pH 8 was the optimum pH for their study.

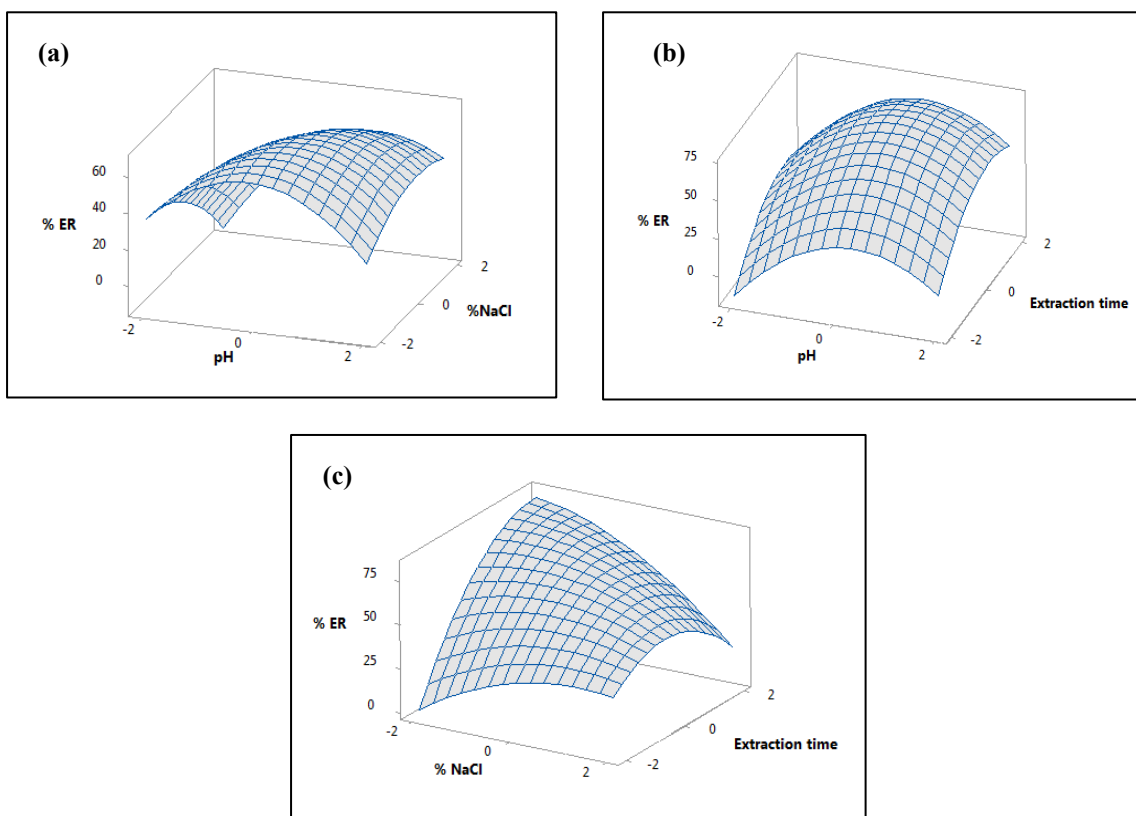


Figure 2. Response surface plots of total extraction recovery as a function of (a) pH vs NaCl, (b) pH vs extraction time and (c) extraction time vs NaCl

However, inert salts, such as sodium chloride, were added during SBSE in order to modify the ionic strength of the sample solution. It has been observed that the addition of inert salt does not improve, but even reduce, the extraction efficiency for hydrophobic analytes ($\log K_{o/w} > 3$) [11]. In contrast, for polar analytes ($\log K_{o/w} < 3$), the extraction efficiency increased with the addition of salts. Since the $\log K_{o/w}$ for atrazine, ametryn, and cyanazine was 2.61, 2.98, and 2.22, respectively, they can be considered as semi polar analytes and the addition of the inert salt was

investigated. Apart from pH adjustment, salt addition showed a significant effect ($P < 0.05$) with a negative sign which indicated the reduction of extraction efficiency with an increase of salt content.

Extraction time is one of the parameters that impact the extraction efficiency. A range of extraction time varying from 5 – 25 min has been studied in this SBSE and the results are shown in Figure 2 (b) and Figure 2 (c). The extraction time has a positive effect upon extraction and increasing the extraction time caused the increase of the extraction recovery of the target triazines.

The multi-response optimization process was done by selecting the Minitab software profile for the selection of optimum conditions of the SBSE. Based on the optimization plot in Figure 3, the suggested optimum conditions suggested were set as: 8.5 (pH), no addition of NaCl, 25 min (extraction time), and 24 min (desorption time). Three additional experiments were carried out under the optimal conditions, in which a good agreement between the calculated and experimental responses was obtained (97.5 % ER) with 3.8% of RSD value.

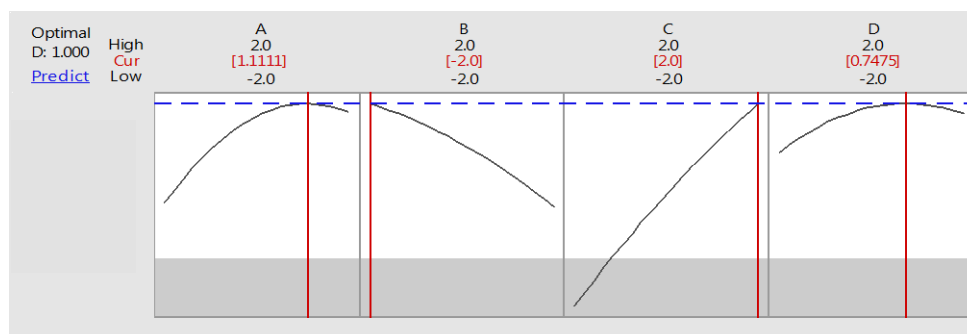


Figure 3. The optimization plots for the central composite design.

Method validation

Under the optimized conditions, analytical performance of the proposed method was evaluated and the results are summarized in Table 3. A good linearity was obtained in a concentration range of 0.10 – 100 μgL^{-1} with correlation of determination (R^2) ranging from 0.9991 – 0.9995. The LODs and LOQs were calculated as the concentration corresponding to signal-to-noise ratios of 3 and 10 respectively. The LODs and LOQs of three triazines were found to be ranging from 0.015 – 0.023 μgL^{-1} and 0.047 – 0.060 $\mu\text{g L}^{-1}$, respectively, which were lower than the maximum residue limit (MRL) set by European Union (EU) for triazines (a maximum level of 0.10 μgL^{-1} of a pesticide in water samples). The RSDs for three target analytes were in the range of 4.1 – 7.5% ($c = 10 \mu\text{gL}^{-1}$).

Pan et al. [1] used stir bar sorptive extraction (SBSE) coupled with pulse glow discharge-ion mobility spectrometry (PGD-IMS) for the analysis of triazine herbicides in water samples. The LODs ranged from 0.006 to 0.015 μgL^{-1} . Wu et al. [12] used solid-phase microextraction with graphene-coated fiber for the analysis of triazine herbicides in water samples. The LODs ranged from 0.05 to 0.2 μgL^{-1} . Liu et al. [13] used effervescent tablet assisted on-site liquid phase microextraction for the determination of five triazine herbicides in water by an ultra-high pressure liquid chromatography tandem mass spectrometer. The LODs ranged from 0.002 to 0.008 μgL^{-1} . It is important to note that the detection limits achieved by the proposed method are better than or comparable to those reported previously using different extraction techniques.

Table 3. Analytical performance of the proposed PDMS coated stir bar for the analysis of triazines

Analytes	Linear Equation	Linear Range ($\mu\text{g L}^{-1}$)	Correlation Coefficient (R^2)	Limit of Detection ($\mu\text{g L}^{-1}$)	Limit of Quantification ($\mu\text{g L}^{-1}$)	Repeatability (%RSD)
Atrazine	$y = 2.34x + 3.24$	0.1 - 100	0.9991	0.015	0.047	7.5
Ametryn	$y = 1.05x + 3.50$	0.1 - 100	0.9995	0.023	0.060	4.1
Cyanazine	$y = 1.23x + 8.01$	0.1 - 100	0.9993	0.018	0.055	5.0

Quantification of partition coefficient and enrichment factor

SBSE is a sample preparation technique based on sorptive extraction. The sorptive extraction process is by nature an equilibrium technique, where the extraction of solutes from the liquid sample phase into the extraction medium is controlled by the partition coefficient (K). This coefficient is dependent upon the phase ratio, and thus on the amount of extraction phase used.

The coefficient, K shows that to obtain high EF, a low V_e/V_s ratio and high partition coefficient are required. SBSE may be applied to medium polarity and non-polar analytes and to those whose polarities can be reduced before extraction. The major factor affecting EF was the partition coefficient. The EF was directly related to K .

In the present study, the amount of atrazine, cyanazine, and ametryn in the PDMS sorbent were calculated using the peak area ratio measurements and the calibration curves of the standards only. Data of the enrichment factor for the target analytes were determined and presented in Table 4 which indicates the correlations between the enrichment factor and partition coefficient. The enrichment factor of cyanazine was slightly lower as compared to atrazine and ametryn. This was due to the higher solubility of cyanazine in the sample aqueous phase thus reducing its partition into the extraction phase.

Table 4. Analytical performance in term of enrichment factor and partition coefficient

Triazines	Enrichment factor, EF ^a	Partition coefficient, K
Ametryn	334	614
Atrazine	316	581
Cyanazine	281	511

^a Enrichment was determined at concentration of $5.0 \mu\text{g L}^{-1}$ for all analytes

Analysis of real samples

In most microextraction techniques, the efficiency of extraction by SBSE can be affected by the composition of the matrix. High levels of dissolved or suspended organic matter contained in real water samples may disrupt analytes from extraction to the stir bar, thus the extraction performance changes from sample to sample.

The relative recovery (RR) was investigated to study the matrix effect towards the extraction efficiency of respective devices [14]. To further evaluate the practical applicability of the proposed method, extraction and analysis were performed on six water samples that were collected from paddy fields (three stations from organic plots and three stations from conventional plots). In order to identify the influence of matrix, the extraction recovery of triazines from real samples were compared with the extraction recovery from ultrapure water sample. The proposed method achieved relative recoveries in the range of 95–98% with RSD values between 3% and 6%.

Conclusion

A study on the extraction of triazines by using a homemade PDMS-coated stir bar was successfully carried out. By applying the experimental design, behaviour of each variable and their interaction during the extraction and

desorption procedures were discriminated using the ANOVA test. In this study, the SBSE parameters affecting the extraction recovery have been optimized as follows: sample at pH 8.5, no addition of NaCl, 25 minutes of extraction time, and 24 minutes of desorption time. A low V_E/V_S ratio and high partition coefficient offered a high enrichment factor. The enrichment factor was directly related to the partition coefficient. Overall, the proposed procedure was proven to be a good alternative methodology for the determination of selected triazine residues in environmental samples, being a simple, fast, reproducible, effective and an environmentally-friendly analytical method.

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