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ORIGINAL ARTICLE

Determination of melamine in soil samples using surfactant-enhanced hollow fiber liquid phase microextraction followed by HPLC–UV using experimental design

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ABSTRACT

Surfactant-enhanced hollow fiber liquid phase (SE-HF-LPME) microextraction was applied for the extraction of melamine in conjunction with high performance liquid chromatography with UV detection (HPLC–UV). Sodium dodecyl sulfate (SDS) was added firstly to the sample solution at pH 1.9 to form hydrophobic ion-pair with protonated melamine. Then the protonated melamine–dodecyl sulfate ion-pair (Mel–DS) was extracted from aqueous phase into organic phase immobilized in the pores and lumen of the hollow fiber. After extraction, the analyte-enriched 1-octanol was withdrawn into the syringe and injected into the HPLC. Preliminary, one variable at a time method was applied to select the type of extraction solvent. Then, in screening step, the other variables that may affect the extraction efficiency of the analyte were studied using a fractional factorial design. In the next step, a central composite design was applied for optimization of the significant factors having positive effects on extraction efficiency. The optimum operational conditions included: sample volume, 5 mL; surfactant concentration, 1.5 mM; pH 1.9; stirring rate, 1500 rpm and extraction time, 60 min. Using the optimum conditions, the method was analytically evaluated. The detection limit, relative standard deviation and linear range were 0.005 μg mL^{-1}, 4.0% (3 μg mL^{-1}, $n = 5$) and 0.01–8 μg mL^{-1}, respectively. The performance of the procedure in extraction of melamine from the soil samples was good according to its relative recoveries in different spiking levels (95–109%).

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Introduction

Melamine, 1,3,5-triazine-2,4,6-triamine, is a triazine-based chemical containing high nitrogen level (66.7 g nitrogen in 100 g). This chemical is used widely in production of melamine resins which has a broad range of industrial uses, including manufacture of industrial coating, components of paper and

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paperboards, white boards, dishware, kitchenware, plastics, flame retardant fibers, electrical equipment, adhesives, laminates, permanent-press fabrics [1–3]. Melamine is also added to crop fertilizer for its high *N* content to act as a slow nitrogen release source [4–6]. It may also be a by-product when triazine-based pesticides such as cyromazine are used [7].

Melamine contamination has been detected in both environmental and food samples. The primary source of food contamination with melamine was resulted from using melamine-tainted milk or other protein sources such as wheat gluten as one of food ingredients [8,9].

The stimulus for addition of melamine as adulteration to food products is its high nitrogen content that increases the apparent protein content measured by standard protein analysis tests, such as Kjeldahl or Dumas [10].

Apart from adulterated products, migration of melamine from kitchenware in contact with food content at higher temperatures or acidic conditions [11,12] was known as another source of melamine contamination.

Environmental melamine contamination has also detected due to its huge consumption in industry and also its application in agriculture. As evidence, detection of melamine in waste water [13], water and sediment [14], soil [15] and as a consequence crops [16] can be mentioned.

The maximum level allowed for melamine residue has regulated and set 1 mg kg^{-1} for powdered infant formula and 2.5 mg kg^{-1} for other foods and animal feed (FAO/WHO 2010) [17].

Melamine can cause tissue injury, such as acute kidney failure, urolithiasis, bladder cancer, and even death above the safety regulation level [18].

There are several analytical methods reported for quantitative determination of melamine in different matrices, including: high performance liquid chromatography with UV detection (HPLC–UV) [19–21], liquid chromatography–tandem mass spectrometry (LC/MS/MS) [22–24], gas chromatography–mass spectrometry (GC/MS) [25–27,9], gas chromatography–tandem mass spectrometry (GC/MS/MS) [28,29], capillary zone electrophoresis [30], and enzyme-linked immunosorbent assay (ELISA) [31]. Different samples require especial pretreatment before analysis depending on their matrices. However, most of the reported methods have applied for determination of melamine in food samples, especially dairy product and milk while few studies have reported melamine analysis in soil samples [15,16,32,33].

The present study utilized surfactant-enhanced two-phase hollow fiber liquid phase microextraction in combination with HPLC–UV for determination of melamine in soil samples. Sodium dodecyl sulfate (SDS) was employed to form an extractable ion-pair with aqueous protonated melamine in acidic solution. Firstly melamine was converted to a protonated species in the presence of acid in aqueous sample solution. Then the positively charged analyte formed an ion-pair with sulfate group of SDS. Hydrocarbon tail of SDS in the formed ion-pair enhanced the extraction efficiency of melamine—that is known as a polar compound by itself—into an organic phase. The effects of different parameters on extraction efficiency of the protonated melamine–dodecyl sulfate ion-pair (Mel–DS) were evaluated by a multivariate strategy based on an experimental design. Firstly, a fractional factorial design was employed for screening the main parameters affecting the extraction efficiency and then a central composite design was performed to optimize the significant variables involved in the procedure. The model can predict mathematically how a response relates to the values of various factors [34] moreover, allows optimization with a minimum number of experiments compared to a one-at-a-time procedure.

Experimental

Reagents and material

The hollow fiber polypropylene membrane support Q 3/2 Accurel PP (200 μm thick wall, 600 μm inner diameter and 0.2 μm average pore size) was obtained from Membrana (Wuppertal, Germany). 1-Decanol, 1-octanol, isooctane, toluene and butyl acetate were purchased from Merck (Darmstadt, Germany) and were used as extraction solvents. Hydrochloric acid, trifluoroacetic acid (TFA), sodium chloride and methanol were also supplied by Merck (Darmstadt, Germany). Melamine was purchased from Fluka (Sigma–Aldrich, St. Louis, MO, USA) and was used as standard. These materials are all of analytical grade.

Stock solution of melamine (500 μg mL^{-1}) was prepared by dissolving it in 50% aqueous methanol. The stock standard solution was kept in 4 °C and protected from light. It was stable at least for one year [35]. Aqueous working solutions were prepared daily by dilution of stock solution with double distilled water.

Deionized water was prepared by Millipore Q 5 instrument (Millipore Corp., Billerica, MA, USA).

Apparatus

The experiment was carried out using a Shimadzu HPLC system comprising a micro-volume double plunger pump connected with a manual injector with a 100 μL sample loop, solvent delivery module LC-20AD, on-line degasser DGU-$20A_5$ and column oven CTO-20AC.

The UV detector SPD-20A with wavelength of 240 nm was used for detection of melamine. The pump and detector were controlled by the Shimadzu LC solution software. A Nucleodur C_{18} HPLC column (150 × 4.6 mm I.D., 5 μm particle size) from Machery–Nagel, Germany was used for chromatographic separation. This was preceded by a Nucleodur guard cartridge (8 × 4 mm) with the same material of the analytical column. The mobile phase was consisted of 0.1% (pH 2) TFA/methanol (90:10) pumped at flow rate of 1 ml/min. All chromatographic analyses were done at room temperature. A Multi-Hotplate Stirrer (0–1500 rpm, Witeg, Germany) was used to stir three sample solutions simultaneously.

Surfactant-enhanced hollow fiber liquid phase microextraction

The extraction was performed using the polypropylene hollow fiber pieces with the practical length of 2.5 cm. The approximate internal volumes of these segments were 7 μL. The hollow fiber segments were sonicated for 2 min in acetone to remove any possible contaminants and then allowed to dry completely in air. 1-Octanol was used for both impregnation of the pores and also filling the lumen of the hollow fiber. Organic solvent was drawn into the micro-syringe before a hollow fiber affixed onto the tip of the micro-syringe's needle, then the hollow fiber immersed

into the organic solvent for 10 s. Subsequently, the syringe plunger was depressed and 1-octanol injected into the lumen of the hollow fiber. The surface of the hollow fiber was cleaned with distilled water to remove any residual organic solvent present on the fiber surface. Then, the prepared fiber was placed in a sample-vial with 5 ml of sample solution containing 1.5 mM SDS that its pH was adjusted at 1.9. The sample was stirred with 1500 rpm during the extraction with a magnetic stirrer. After 60 min. extraction time, the analyte enriched 1-octanol was withdrawn into the syringe and the hollow fiber was discarded. The analyte enriched 1-octanol was injected into the HPLC and diluted with mobile phase to 100 µL in the loop.

Design of experiments

Preliminary, univariate design was used to select the extraction solvent. In the next step the other parameters which may affect the surfactant-enhanced hollow fiber liquid phase microextraction procedure including surfactant and salt concentrations, pH, sample volume, time of extraction and stirring rate were evaluated. A fractional factorial design with resolution IV (2^{6-2}) was used for this purpose. Afterward, a central composite design was performed to optimize the values of the four significant variables obtained in the fractional factorial design, in order to improve the response. A 2^4 central composite design was performed, with eight star points and six center points, totaling 30 experiments ($2^4 + (2 \times 4) + 6$). The value of axial spacing (α) used was 2. The data were processed using Minitab 16.2.0 software.

Results and discussion

Extraction solvent selection

Choosing the most suitable extraction solvent is of primary importance for achieving good extraction efficiency of the target compounds. Therefore, some factors should be considered, i.e., the solvent must be immiscible with water, the solubility of the analytes should be higher in the organic phase than the donor phase to promote the extraction of the analytes and the density of the extraction organic solvent must be lower than water. Five organic solvents were investigated: 1-decanol, 1-octanol, isooctane, toluene and butyl acetate.

A series of sample solutions were studied by using 15.00 mL of 3 µg mL^{-1} aqueous solution of melamine with adjusted pH at 3, containing 1 mM SDS. These solutions stirred at 800 rpm during 20 min extraction time. As shown in Fig. 1 using different organic solvents resulted in different extraction efficiency and the highest response was obtained when using 1-octanol as extraction solvent. Therefore, 1-octanol was selected for subsequent experiments.

Screening by the fractional factorial design

The proposed SE-HF-LPME procedure is depending on several factors. The sequential study of all potential factors is being too complex and involving a prohibitive long experimental time [36].

Screening is the first step in the efficient assessment of the factors affecting an analytical system.

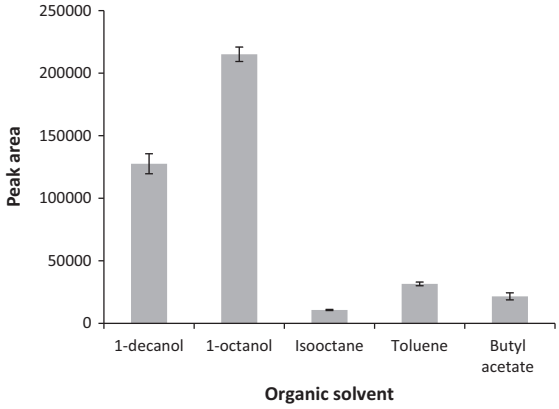

Fig. 1 Effect of type of extraction solvent on extraction.

Usually, factorial design is employed to reduce the total number of experiments. The design determines which factors have important effects on a response as well as how the effect of one factor varies with the level of the other factors. The principal steps of the statistically designed experiments are determination of response variables, factors, factor levels, choice of the experimental design and statistical analysis of the data. Today the most widely used kind of experimental design, to estimate main effect as well as interaction effects, is the 2^n (full) factorial design in which each variable is investigated at two levels [37].

Based on the preliminary experiments carried out in our laboratory, six factors may affect the experimental response of the SE-HF-LPME procedure. These factors are surfactant (S) and salt concentration (I), pH (P), sample volume (V), time of extraction (T) and stirring rate (R) that evaluated at two levels.

One of the disadvantages of a full factorial design is that the number of experimental runs required for estimating all the main effects and interactions increases rapidly as the number of factors increases (64 runs in this work) [38].

Consequently, an experimental fractionated factorial design (2^{6-2}) with resolution IV was built for the determination of the main and interaction factors affecting the extraction efficiency.

In order to evaluate the work, peak area of 3 µg mL^{-1} melamine standard solution in different runs was considered as the experimental response.

The overall design consisted of 16 experiments and each experiment was replicated two times. The experiments were carried out randomly in order to minimize the effect of unexplained variability in the observed responses due to systematic errors [39]. Design matrix and response are shown in Table 1.

Statistical model

Afterward, in order to determine whether main and two-way interaction between factors was statistically significant, the results were statistically analyzed and the main and interaction effects and other statistical parameters of the fitted model were determined. The effect of a factor is defined as the change in response produced by a change in the level of the factor [40] (two time of its coefficient in the fitted model).

The coefficients, standard error of the coefficients and effects are shown in Table 2. Where the standard error of

Table 1 Quarter-fractional design matrix and response of surfactant-enhanced HF-LPME procedure for extraction of melanin.

Experimental number	*S* (mM)	*P*	*T* (min)	*V* (μL)	*R* (rpm)	*I* (w/v%)	Response
1	0.5	1	15	4.5	200	0	5306
2	7	1	15	4.5	1500	0	31,485
3	0.5	6	15	4.5	1500	6	4331
4	7	6	15	4.5	200	6	917
5	0.5	1	60	4.5	1500	6	23,797
6	7	1	60	4.5	200	6	16,756
7	0.5	6	60	4.5	200	0	11,731
8	7	6	60	4.5	1500	0	38,445
9	0.5	1	15	9.5	200	6	1446
10	7	1	15	9.5	1500	6	10,368
11	0.5	6	15	9.5	1500	0	7923
12	7	6	15	9.5	200	0	13,450
13	0.5	1	60	9.5	1500	0	28,467
14	7	1	60	9.5	200	0	37,677
15	0.5	6	60	9.5	200	6	2492
16	7	6	60	9.5	1500	6	14,886

the coefficient is a measure of the variation in estimating the coefficient and *T*-value is the ratio of the coefficient to the standard error.

The coefficient of determination (R^2) of 99.48% shows a good fit of the experimental data.

Student t-test

Student's *t*-test was applied to determine whether calculated effects were significantly different from zero. The *t*-value for a 99% confidence level and 15 degrees of freedom is equal to 3.71. The Pareto chart of standardized effects at *P*-value = 0.01 is presented in Fig. 2.

The vertical line on the plot judges the effects that are statistically significant. The bars, extending beyond the line, correspond to the effects that are statistically significant at the 99% confidence level. Furthermore, the positive or negative sign (corresponding to a black or white) response can be enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific factor [41].

Analyzing Fig. 2 infers salt addition was the most significant variable with negative effect, followed by extraction time, surfactant concentration and stirring rate all with positive effect and lastly, pH with negative effect. The interaction between salt and surfactant concentration was important, too.

According to the Pareto diagram sample volume and the other interaction effects were not statistically significant.

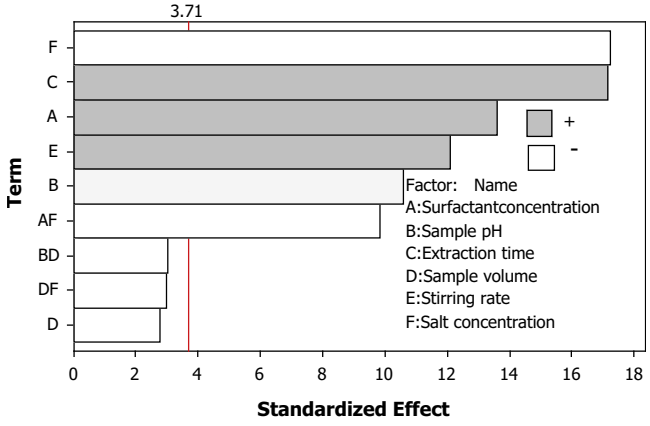

Fig. 2 Standardized main and two way interaction effects Pareto for quarter-fractional factorial design (*p*-value = 0.01).

Optimization using central composite design

In the following step, a central composite design (CCD) combined with the desirability function was applied for simultaneous optimization of the four factors (surfactant concentration, sample pH, extraction time and stirring rate) that influenced the surfactant-enhanced HF-LPME procedure. Those were chosen from the first screening design. As it is evident salt addition was neglected in this part, due to its great

Table 2 Estimated parameters of the polynomial model (coded unit).

Term	Effect	Coefficient	Standard error of coefficient	*t*-value	*P*-value
Constant		15,592	360.6	43.24	0.000
Surfactant concentration	9811	4906	360.6	13.60	0.000
Sample pH	−7641	−3820	360.6	−10.6	0.000
Extraction time	12,378	6189	360.6	17.16	0.000
Sample volume	−2007	−1004	360.6	−2.78	0.032
Stirring rate	8741	4370	360.6	12.12	0.000
Salt concentration	−12,436	−6218	360.6	−17.24	0.000
Surfactant concentration * salt concentration	−7096	−3548	360.6	−9.84	0.000
Sample volume * salt concentration	−2145	−1072	360.6	−2.97	0.025
Sample pH * sample volume	−2161	−1080	360.6	−3.00	0.024

negative effect on extraction efficiency. Furthermore, SDS in the presence of high concentration of salt formed a cloudy state that would cover the pores in the surface of the hollow fiber and as a consequence interfere the mass transfer of the analyte.

The factorial design allowed the investigation only of linear relationships between parameters and response variables because only two levels were tested [42]. For closer investigation of the factors, the central composite design is an effective alternative to the factorial design, because five different levels are examined for each factor. This design originally developed by Box and Wilson [43] and improved by Box and Hunter [44].

The desirability function is based on the search for a global optimum [$D = f(Y_1, Y_2, \ldots, Y_n)$] by the transformation of the measured property to a dimensionless scale for each criterion [45]. The search for desired goals, achievement of maximum peak area, was found by mean of the desirability function D.

A rotatable central composite design permitted to be modeled by fitting a second-order polynomial with the number of experiments equal to ($2^F + 2F + N$), where F is the number of factor and N is the number of center runs [38]. In this work F and N were set at 4 and 6, respectively, which meant that 30 ($2^4 + 2 \times 4 + 6$) experiments had to be run. The 30 experiments were performed in three blocks and in random manner to minimize the effect of uncontrolled variables on the response [46].

Eq. (1) was used to calculate axial spacing (α) for a rotatable design [47].

$$\alpha = (f)^{1/4} \tag{1}$$

where f is the number of factorial points in the design.

Using Eq. (1), the axial spacing of $\alpha = \pm 2$ was calculated to satisfy the rotatability of the design. The factors and their levels used in the CCD and the corresponding design matrix with three blocks and responses are shown in Tables 3 and 4, respectively.

The mathematical relationship between the response Y and four significant independent variables, T, S, R and P can be initially, approximated by a nonlinear polynomial mode including 4 squared terms, 6 two way factor interaction terms, 4 linear terms and 1 intercept term as shown below:

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 T + \beta_2 S + \beta_3 R + \beta_4 P + \beta_{11} T^2 + \beta_{22} S^2 \\ & + \beta_{33} R^2 + \beta_{44} P^2 + \beta_{12} TS + \beta_{13} TR + \beta_{14} TP + \beta_{23} SR \\ & + \beta_{24} SP + \beta_{34} RP \end{aligned} \tag{2}$$

where β_0 is the average of the results of the replicated center point or intercept [48]. β_1, β_2, β_3 and β_4 are the main half-effects of the coded variables including T, S, R and P, respectively; β_{11}, β_{22}, β_{33} and β_{44} are squared half-effects; β_{12}, β_{13}, ... and β_{34} are two factor interaction half-effects and Y is the peak area.

Table 3 Factor level used in the central composite design.

Factor notation	Levels				
	−2	−1	0	+1	+2
S	0.5	2.125	3.75	5.375	7
P	1	2.25	3.5	4.75	6
T	15	26.25	37.5	48.75	60
R	200	525	850	1175	1500

Table 4 The matrix of the central composite design experiments and the responses.

Experimental number	Blocks	p	R	S	T	Response[a]
1	1	1	−1	−1	−1	292,010
2	1	−1	1	−1	−1	242,930
3	1	−1	−1	1	−1	336,364
4	1	1	1	1	−1	241,352
5	1	−1	−1	−1	1	120,464
6	1	1	1	−1	1	106,279
7	1	1	−1	1	1	127,277
8	1	−1	1	1	1	84,372
9	1	0	0	0	0	330,437
10	1	0	0	0	0	280,970
11	3	−1	−1	−1	−1	199,963
12	3	1	1	−1	−1	201,088
13	3	1	−1	1	−1	410,775
14	3	−1	1	1	−1	211,396
15	3	1	−1	−1	1	123,758
16	3	−1	1	−1	1	135,123
17	3	−1	−1	1	1	103,092
18	3	1	1	1	1	73,877
19	3	0	0	0	0	376,489
20	3	0	0	0	0	328,081
21	2	−2	0	0	0	217,009
22	2	2	0	0	0	335,535
23	2	0	−2	0	0	214,043
24	2	0	2	0	0	136,782
25	2	0	0	−2	0	274,888
26	2	0	0	2	0	283,852
27	2	0	0	0	−2	165,339
28	2	0	0	0	2	32,961
29	2	0	0	0	0	336,228
30	2	0	0	0	0	312,807

[a] The mean of two replicates.

Analysis of variance (ANOVA) and estimated response surface model

In the next step, the regression method was used to find a satisfactory response model with the reasonable statistics (Table 5).

As shown in Table 5, effects of the linear terms, two-way factor interactions and squared terms were statistically significant whereas the blocks were insignificant. As can be seen in Table 6, the p-value of the lack-of-fit is $p = 0.265 > 0.01$ that indicates the fitted model is satisfactory at a 99% confidence level, on the other hand, the R^2 value indicated that the fitted model explains 92.2% of the variability in the peak area.

The coefficients of the nonlinear polynomial model, p-values and other statistical parameters were shown in Table 6.

Model validation

Fig. 3 represents the residual plots for Y (Peak area) in the model (Table 6). It shows that the distribution of the residuals for the response approximately follows the fitted normal distribution and the residuals of the response randomly scatter in the residual plots.

Table 5 Analysis of variance for central composite design (coded units).

Source	Degree of freedom (d.f.)	Sum of squares (seq. SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	*F*-value	*p*-Value
Blocks	2	1,428,846,610	1,428,846,610	714,423,305	0.4	0.679
Regression	14	2.73111×10^{11}	2.73111×10^{11}	19,507,927,136	10.90	0.000
Linear	4	1.18134×10^{11}	1.18134×10^{11}	29,533,492,868	16.51	0.000
Square	4	1.30104×10^{11}	1.30104×10^{11}	32,525,917,816	18.18	0.000
Interaction	6	24,873,337,163	24,873,337,163	4,145,556,194	2.32	0.096
Residual error	13	23,257,740,910	23,257,740,910	1,789,056,993		
Lack of fit	10	20,588,310,013	20,588,310,013	2,058,831,001	2.31	0.265
Pure error	3	2,669,430,897	2,669,430,897	889,810,299		
Total	29	2.97798×10^{11}				

Table 6 Estimated regression coefficients of *Y* (peak area) for central composite design (coded units).

Term	Coefficient	Standard error of coefficient	*t*-value	*P*-value
Constant	327,502	17,268	18.966	0.000
Block 1	−4939	10,921	−0.452	0.659
Block 2	−4821	10,921	−0.441	0.666
T	15,824	8634	1.833	0.090
S	−23,825	8634	−2.760	0.016
R	7701	8634	0.892	0.389
P	−63,600	8634	−7.366	0.000
$T \times T$	−16,044	8076	−1.987	0.068
$S \times S$	−41,259	8076	−5.109	0.000
$R \times R$	−15,269	8076	−1.891	0.081
$P \times P$	−60,324	8076	−7.469	0.000
$T \times S$	−15,323	10,574	−1.449	0.171
$T \times R$	5838	10,574	0.552	0.590
$T \times P$	−10,402	10,574	−0.984	0.343
$S \times R$	−19,734	10,574	−1.866	0.085
$S \times P$	16,713	10,574	1.581	0.138
$R \times P$	−22,556	10,574	−2.133	0.053

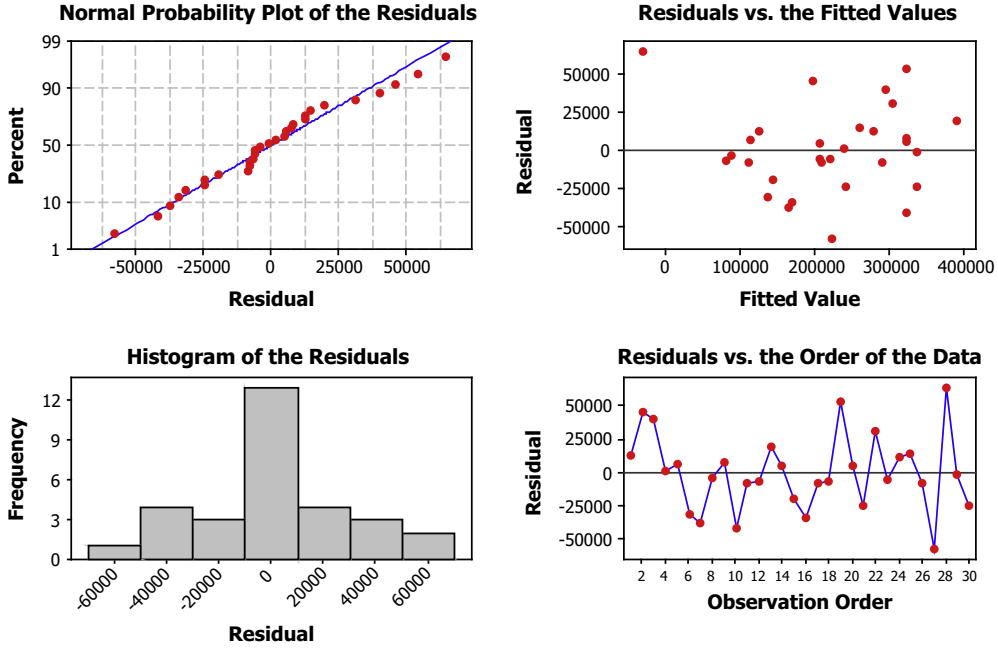

Fig. 3 Residual plots for *Y* (peak area) in the model.

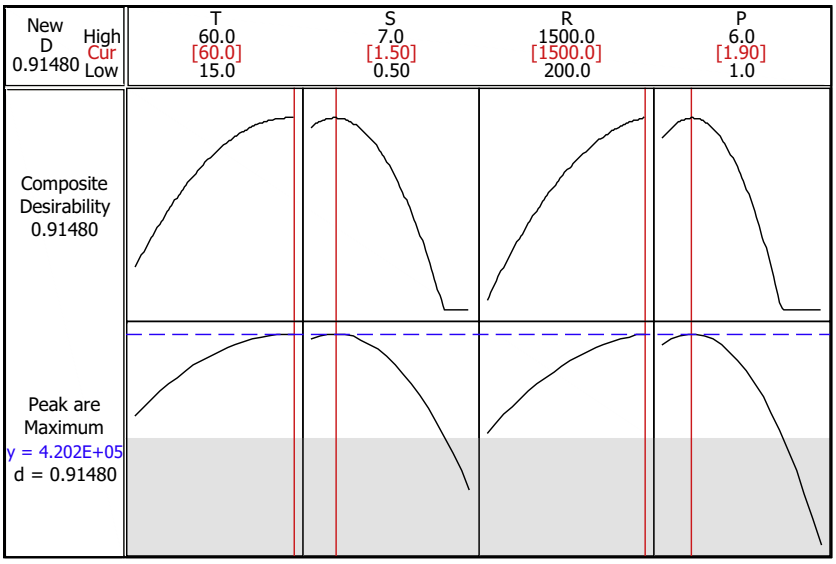

Fig. 4 The optimization plots for the central composite design.

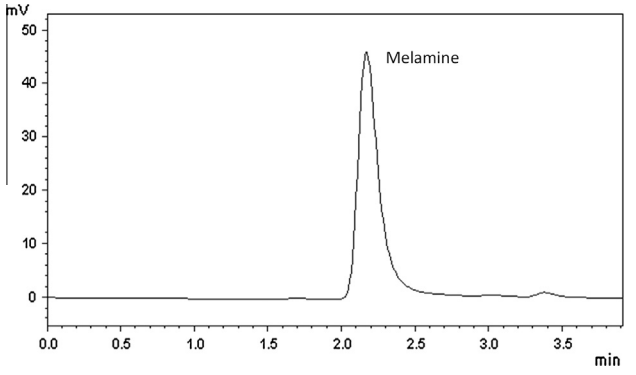

Fig. 5 Chromatogram of 3 μg mL^{-1} melamine standard solution obtained after surfactant-enhanced HF-LPME procedure under optimum conditions.

Response optimization

The optimization plot (Fig. 4) indicates the predicted conditions for the optimum point and the desirability of the prediction. Each individual plot in the figure shows the way each factor influences the response (peak area). According to the overall results of the optimization study the following experimental conditions were chosen: extraction time, 60 min; surfactant concentration, 1.5 (mM); stirring rate, 1500 (rpm); pH, 1.9.

Fig. 5 represents the chromatogram of 3 μg mL^{-1} melamine standard solution obtained after surfactant-enhanced HF-LPME procedure under optimum conditions.

Analytical performance

The figures of merit in the proposed surfactant-enhanced hollow fiber liquid phase microextraction method including dynamic linear range (DLR), limit of detection (LOD) based on signal-to-noise ratio (S/N) of 3 and relative standard deviation (RSD) for the extraction of melamine from 5 ml of 3 μg mL^{-1} aqueous solutions were investigated under optimum conditions and were 0.01–8 μg mL^{-1}, 0.005 μg mL^{-1} and 4.0% (n = 5), respectively. Calibration equation of y = 155,615 x + 7388 with correlation coefficient (R^2) of 0.998 was obtained by plotting the calibration curve using 8 spiking levels.

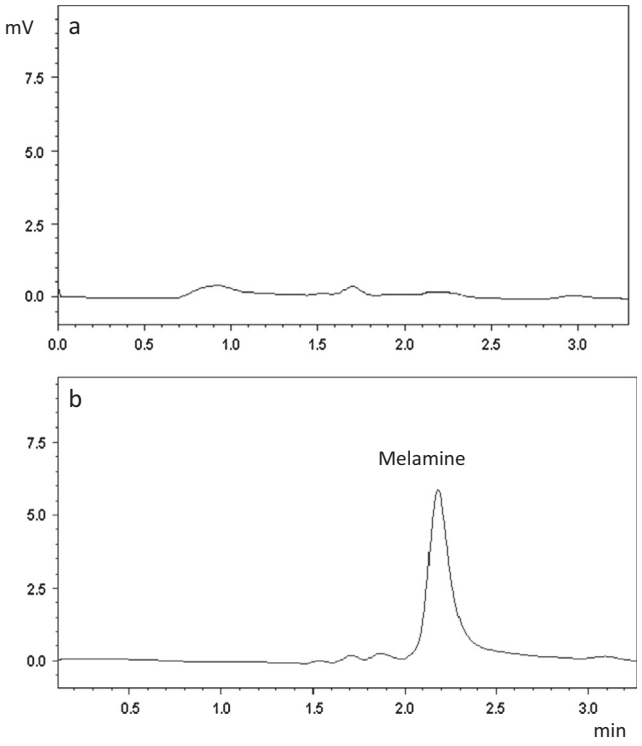

Fig. 6 Chromatograms after surfactant-enhanced HF-LPME procedure under optimum conditions from (a) soil sample, (b) soil spiked sample (0.6 mg kg^{-1}).

Table 7 Relative recoveries and relative standard deviations of melamine for three different spiked soil samples.

Sample	Added concentration (mg kg^{-1})	Founded concentration (mg kg^{-1})	RSD (%) (n = 3)	Relative recovery (%)
Kang soil	0	–	–	–
	0.1	0.109	5.2	109
	0.6	0.570	4.5	95
Zoshk soil	0	–	–	–
	0.1	0.102	5	102
	0.6	0.594	4.3	99
Shandiz soil	0	–	–	–
	0.1	0.095	4.5	95
	0.6	0.630	4.7	105

A preconcentration factor of 50 was achieved by considering the sample volume of 5 mL and the final diluted octanol phase of 100 μL. The enhancement factor based on the slope ratio of the calibration curves for the preconcentrated samples and the ones not submitted to preconcentration was 25.

Real sample analysis

Although field samples are the best choice for analytical works but in our city, we could not find melamine resin manufacturing factory that would lead to soil contamination in neighbor lands. So we used spiked soil samples as an alternative. Soil samples were collected from three villages near Mashhad, Iran. It was grinded and then sieved using a sieve with mesh number 30.6 g of the sieved soil was mixed completely with 12 mL of double distilled water in a test tube and spiked with melamine. The test tube was centrifuged for 10 min at 6000 rpm. After centrifugation, 7 mL of the supernatant was diluted three times and its pH adjusted to 1.9 with some drops of 2 M HCl. 5 mL of the prepared solution was transferred to a sample-vial and then the required amount of SDS was added to make the final concentration of 1.5 mM. Finally, the proposed surfactant-enhanced HF-LPME was carried out on the sample solution. Fig. 6 represents the chromatograms obtained from soil sample extracted with and without spiking. The relative recoveries along with respective relative standard deviation (RSD)% (n = 3) were calculated to assess sample matrix effects on extraction efficiency in two concentration levels (0.1 and 0.6 mg kg^{-1}). The calculated data were shown in Table 7.

Conclusions

In the present study, surfactant-enhanced HF-LPME method was used for extraction and determination of melamine. The effects of different parameters on extraction yield were investigated using a fractional factorial design for screening and a central composite design for optimization of the significant factors. This technique represents a simple, easy, free of cross contamination and inexpensive sample preparation method. Under optimum condition, it provides low detection limit, wide linear range and reasonable RSD% for extraction of melamine. The current HF-LPME technique benefits from advantageous of miniaturization and also excellent clean up in complex matrix using hollow fiber membrane [49]. Furthermore, two individual steps of extraction and clean up can be performed simultaneously. Therefore, the pretreatment procedure was much easier and faster comparing with the existing methods of determination of melamine in soil samples that applied extraction and clean up steps, separately [15,32]. Moreover, the proposed method provides lower detection limit (0.005 μg mL^{-1}) than the other methods reported elsewhere for melamine determination in soil, e.g. HPLC–UV (0.05 μg mL^{-1}), an enzyme-linked immunosorbent assay (ELISA) (0.15 μg mL^{-1}) and an enzyme-linked rapid colorimetric assay (RCA) (0.2 μg mL^{-1}) method [33]. Finally the optimized procedure was applied successfully for determination of melamine in soil samples with acceptable relative recoveries (95–109%).

Conflict of Interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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