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Ultrasound-assisted surfactant-enhanced emulsification microextraction for determination of cadmium in water samples prior to analysis by flame atomic absorption spectrometry with the aid of experimental design

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ABSTRACT

Ultrasound-assisted surfactant-enhanced emulsification microextraction (UASEME) coupled with flame atomic absorption spectrometry (FAAS) was developed for preconcentration and determination of cadmium in tap and river water. The Plackett–Burman design was applied for effective variables screening such as volume of extraction solvent and surfactant, the pH and ionic strength of sample solution, speed and time of centrifuge, concentration of ligand (dithizone) and ultrasonic time. The obtained significant factors were optimized by using a Box–Behnken design and the response surface equations were derived. Under optimum conditions, relative standard deviation (RSD, n=5) of 50 μgL^{-1} Cd^{2+} and limit of detection (LOD) were 6.5% and 0.4 μgL^{-1} respectively. The method encompass linear response at 0.5 –94 μgL^{-1} with correlation coefficients (r^2) 0.9923.

Highlights

▶UASEME combined with Flame atomic absorption spectroscopy was used for extraction and determination of cadmium in water samples. ▶A multivariate strategy based on an experimental design using a Plackett–Barman design for screening and a Box–Behnken design is applied for optimization of significant factors. ▶pH value, Volume of Triton X-100, Volume of $CHCl_3$ were significant factors.▶Under optimum conditions, enrichment factors was 93 times. ▶UASEME was quantified successfully applied for analysis of cadmium in tap and river water samples.

KEYWORDS

Ultrasound-assisted surfactant-enhanced emulsification microextraction;
Flame atomic absorption spectrometry;
Plackett–burman design;
Box–behnken design;
Cadmium.

INTRODUCTION

Nowadays, study and analysis are of importance due to heavy metal ions in various samples, following industrial processes, have high toxicity and release to the environment, atmosphere, surface and ground water. Thus, Buildup of heavy metal levels in the water, air and soil occur particularly in industrial areas. However, different techniques for metal determination are available, and the atomic spectroscopy methods are applied widely[1-6].

Cadmium is considered to be highly toxicant, even at very low concentrations, it will cause damage to organs such as the kidneys, liver, lung, bone and blood[7]. Cadmium is used extensively in electroplating, some industrial colors, manufacturing some types of batteries. Due to low concentration of these elements in the majority of samples, direct determination of this element is difficult. Thus, sample preparation and preconcentration methods are required. The microextraction methods have been usually applied as a sample preparation technique. Different microextraction methods have been performed to determine cadmium in various samples including cloud point extraction (CPE)[8-10], single drop microextraction (SDME)[11, 12], Dispersive liquid–liquid microextraction (DLLME)[13-16], Dynamic ultrasound assisted extraction (DUAE)[17], hollow fiber supported liquid membrane extraction[18].

Dispersive liquid–liquid microextraction is recently ionized because the method has high advantages of simplicity, rapidity, low sample volume, low cost, high recovery and a high enrichment factor. In traditional DLLME method, a mixture including 20–100 μL of a water-insoluble extraction solvent, as extraction solvent, with a density higher than water (e.g., tetrachloroethylene or carbon tetrachloride) and 0.1–2 mL of a water-soluble solvent, as disperser agent, [e.g., methanol (MeOH), acetone or acetonitrile (ACN)] was rapidly injected with a syringe into 4–10 mL of the aqueous sample in a centrifuge tube and a stable emulsion formed. The emulsion is then centrifuged and the extraction solvent removed from the tube with a syringe and analyzed[19]. Ultrasound-assisted emulsiûcation microextraction (UAEME) was developed by coupling between DLLME and ultrasound-assisted LLE. In this method, the disperser solvent omits from the extraction procedure and ultrasonic energy is applied for dispersing of extraction solvent into sample solution[20].

Ultrasound-assisted surfactant-enhanced emulsiûcation microextraction (UASEME) was recently developed for improved traditional DLLME. In UASEME, ultrasound was used for extraction solvent dispersion, and surfactant was enhanced to this process. The molecular structure of surfactants is amphipathic because they contain both hydrophobic and hydrophilic groups. The hydrophobic is generally a hydrocarbon chain with different member of carbon atoms, which may be linear or branched, and also contains aromatic rings and the hydrophilic group contain polar group (nonionic surfactant) or ionic group (cationic surfactant and anionic surfactant)[21-23]. Surfactant reduces the surface tension of water by adsorbing at the liquid–gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid–liquid interface. Reducing of interfacial tension between two phases cause the droplet radius decrease. Thus, surface area between organic and aqueous phase and efficiency extraction increases[24]. Therefore, surfactant can enhance the higher dispersion of organic phase into aqueous phase than traditional disperser agent.

Chemometric as a powerful, practical and useful tool can use for screening and optimization of effective factor in analytical methods. The reagent consumption and analysis time decrease because the number of required experiments reduce. Unlike the traditional analytical methods that one factor at a time studies when the other factors is constant, chemometric enable the simultaneous study of several control factors and the development of mathematical models that permit assessment of the relevance and statistical signiûcance of the factors being studied. This method also can evaluate the interaction effects between the studied variables[25, 26].

In this study, UASEME combined with flame atomic absorption spectroscopy (FAAS) is used for extraction and determination of cadmium in water sample. A multivariate strategy based on an experimental design using a Plackett–Barman design for screening and a Box–Behnken design is applied for optimization of signiûcant factors such as Volume of extraction solvent (CCl_4), volume of surfactant (Triton X-100), pH, ionic strength (concentration of NaCl), concentration of ligand (dithizone), ultrasound time, speed and time of centrifuge. Finally, this method is successfully used for preconcentration and determination of Cd in water sample.

EXPERIMENTAL

Chemicals and solvents

Stock standard solution of Cadmium (II) with a concentration of 1000 mg L^{-1} was obtained by dissolving appropriate amount of Cadmium chloride (Merck, Darmstadt, Germany) in 1% HNO3. A solution of 10^{-2} mol L^{-1} dithizone (Merck, Darmstadt, Germany) was prepared by dissolving appropriate amounts of this reagent in $CHCl_3$. Triton X-100 (TX-100, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as emulsiûers. Ammonium acetate buffers (0.2mol L^{-1}) were prepared by adding anappropriate amount of acetic acid to ammonium acetate solutions resulting in solutions of pH 4-6. For pH 6.8, a phosphate (0.2mol L^{-1}) buffer solution was prepared by adding an appropriate amoun of disodiumhydrogenphosphate to sodium dihydrogenphosphate. Ammoniumchloride buffer solutions (0.2mol L^{-1}) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions, resulting in solutions of pH 9 and nitric acid (0.1mol L^{-1}) was used to adjust the pH 2. Other chemical reagents including ethanol, chloroform ($CHCl_3$) and acetic acid were all of analytical grade or better.

Instrumental

A Hitachi Z - 2000 (Hitachi, Japan) ûame atomic absorption spectrometer equipped with a 100 mm burner head, zeeman background correction and an air–acetylene ûame was utilized. A cadmium hollow cathode lamp (Hitachi, Japan) at a wavelength of 228.8 nm was used as a radiation source, operated at 7.5 mA with a monochromator slit width of 1.3 nm. The pH values were measured by a pH-meter Metrohm 691. A centrifuge Model Dynamica velocity 18h was used to assist phase separation. The extraction solvent ($CHCl_3$) was homogenized using a compact ultrasonic Hiescher up 100h (100W, 30 kHz) at 30 kHz for 3min.

UASEME procedure

A 10ml aqueous sample solution containing 50 µgL^{-1} of cadmium ion was placed in a screw cap glass test tube with conical bottom and 1.0 ml buffer, 5.0×10^{-5} mol.L^{-1} dithizone and 0.1 % NaCl were added. Subsequently, a mixture of 72 µl Triton X-100 (TX-100) and 137µl chloroform (as solvent extraction) were rapidly injected into sample solution by a syringe. The tube was homogenized using a compact ultrasonic at 30 kHz for 3min and the solution became turbid. Then, the solution was centrifuged for 4min at 6000 rpm. Fine droplets of the $CHCl_3$ sediment at the bottom of the test tube. After removing bulk aqueous phase by a syringe, these demented phase was allowed to evaporate at room temperature. Finally, the residue was dissolved in 200µl ethanol and the cadmium concentration was determined by ûame atomic absorption spectrometry.

RESULTS AND DISCUSSION

In order to evaluate main factors which affecting the efûciency of UASEME method, i.e. volume of extraction and emulsifier, pH, ionic strength, ultrasound time, centrifugation time and centrifugation speed, a design with two steps (screening and optimization) was used for searching the optimal experimental conditions.

Screening design

Screening design is used for examining different factors to reduce the number of effective factors in the extraction efûciency. A particular type of such designs is Plackett–Burman design[26]. This design is useful as with few experiments it is possible to detect the most important factors that affect signiûcantly the process[27].

Based on the preliminary experiments, at least eight factors might have affected the experimental response in the present work. The factors [volume of extraction solvent ($CHCl_3$), volume of surfactant (Triton X-100), pH, ionic strength (concentration of NaCl), concentration of ligand (dithizone), ultrasound time, speed and time of centrifuge were considered during the multivariable approach. The lowest and highest values for each factor are selected from the results of previous experiments. In total the design consists of 15 runs, consists of twelve experiments plus three central points (TABLE 1), to be carried out randomly in order to eliminate the effects of ex-

TABLE 1 : Experimental variables and levels of the plackett–burman design

Factors	level	
	Low(-1)	High(+1)
(X1) Volume of $CHCl_3$ (solvent extraction) (μL)	40	100
(X2) Volume of Triton X-100 (surfactant) (μL)	50	150
(X3) pH value	2	6
(X4) concentration of ligand(dithizone) (mol/l)	5×10^{-6}	1.0×10^{-4}
(X5) Ionic strength (NaCl concentration; w/v) (%)	0	0.5
(X6) Ultrasound time (min)	0	5
(X7) Centrifugation speed (rpm)	4000	6000
(X8) Centrifugation time (min)	4	6

Run	X1	X2	X3	X4	X5	X6	X7	X8
1	-1	+1	+1	-1	+1	-1	-1	-1
2	+1	-1	+1	+1	-1	+1	-1	-1
3	-1	-1	+1	+1	+1	-1	+1	+1
4	+1	-1	+1	-1	-1	-1	+1	+1
5	-1	+1	-1	-1	-1	+1	+1	+1
6	+1	-1	-1	-1	+1	+1	+1	-1
7	+1	+1	-1	+1	-1	-1	-1	+1
8	+1	+1	-1	+1	+1	-1	+1	-1
9	-1	-1	-1	+1	+1	+1	-1	+1
10	-1	+1	+1	+1	-1	+1	+1	-1
11	+1	+1	+1	-1	+1	+1	-1	+1
12	-1	-1	-1	-1	-1	-1	-1	-1
13	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0

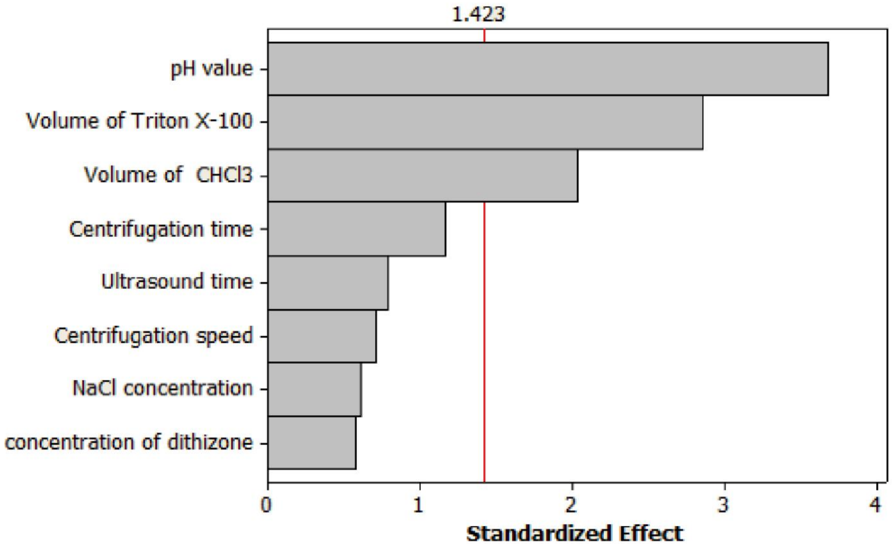

Figure 1 : Pareto chart of standardized effects for the plackett–burman design

traneous or nuisance variables[26].

An ANOVA test was used to evaluate the data and statistically significant effects were determined using a t-test with a 95% probability and visualized using main effects Pareto charts (Figure 1)[28]. The quantities of Volume of $CHCl_3$, Volume of Triton X-

100, pH value were statistically important and the quantity of pH value was the most significant factor having a positive effect on the extraction efficiency. In fact, increasing pH (from 2 to 6) increases complex formation and the transportation of the Cd-dithizone complex into the organic phase. Another significant variables were Volume of Triton X-100 and Volume of $CHCl_3$ respectively. Moreover, ionic strength, ultrasound time, centrifugation speed and concentration of dithizone revealed no significant effect on extraction efficiency (Figure 1).

Therefore, the factors considered in the next optimization step were pH value, Volume of Triton X-100, Volume of $CHCl_3$. Another factors were fixed at appropriate values (NaCl: 0.1%, centrifugation time: four min, centrifugation speed: 6000 rpm, ultrasound time: three min and concentration of dithizone: 5.0×10^{-6} $molL^{1-}$).

Optimization design

The next step in the present study was the optimization of the three factors chosen from the first screening design. A box-behnken design was used in order to obtain the best response. The examined levels of factors are given in TABLE 2.

The type of model applied to reflect a trend in the data. An important factor is the model order for describes the data and predicts a response accurately. A quadratic model can usually used in this design which a second order polynomial model and can be expressed as the following equation:

$$y = b_0 + \sum b_1 x_i + \sum b_{ii} x_i^2 + \sum b_{ij} x_i x_j$$

where Y is the response variable (relative area), Xi, Xj (i = 1,4; j = 1, 4 and i / = j) are the predictors (the independent variables), b_o is the intercept, and b_i, b_{ii}, and b_{ij} are constant regression coefficients of the model[29, 30]. This design shows that at least 15 run is needed for three variables. The experimental data showed good agreement with the second order polynominal equations. The coefficients of determination, R^2 and R^2 adjusted, were 96.40 and 89.91 respectively which were statistically acceptable at $p < 0.05$ levels. The large adjusted R^2 value indicates a good relationship between the experimental data and the fitted model[31]. The analysis of the obtained results by regression analysis of Box-Behnken design is shown in TABLE 3, and makes it possible to obtain the following equation:

$$y = 6.35433 + 5.8122\,X_1 + 5.23571\,X_2 + 9.5068\,X_3 - 0.0187\,X_1^2 - 0.03931\,X_2^2 - 4.65991\,X_3^2 - 0.00761\,X_1X_2 - 0.17861\,X_1X_3 + 0.09521\,X_2X_3$$

TABLE 2 : The experimental variables, levels and center points of the box-behnken design

Factors	level		
	Low(-1)	Center(0)	High(+1)
(X1) Volume of Triton X-100 (surfactant) (μL)	40	120	200
(X2) Volume of $CHCl_3$ (solvent extraction) (μL)	10	55	100
(X3) pH value	2	5.5	9

TABLE 3 : Results of regression analysis of box-behnken design

Term	Coefficient	Standard error Coefficient	T	P - value
Constant	6.35433	3.63195	0.833	0.443
X1	5.81220	0.71402	8.140	0.000
X2	5.23571	1.15143	4.547	0.006
X3	9.50680	1.67357	5.681	0.002
X1X1	-0.01870	0.00250	-7.583	0.001
X2X2	-0.03931	0.00781	-5.046	0.004
X3X3	-4.65991	1.28174	-3.620	0.015
X1X2	-0.00761	0.00412	1.815	0.129
X1X3	-0.17861	0.05410	-3.300	0.021
X2X3	0.09521	0.09621		

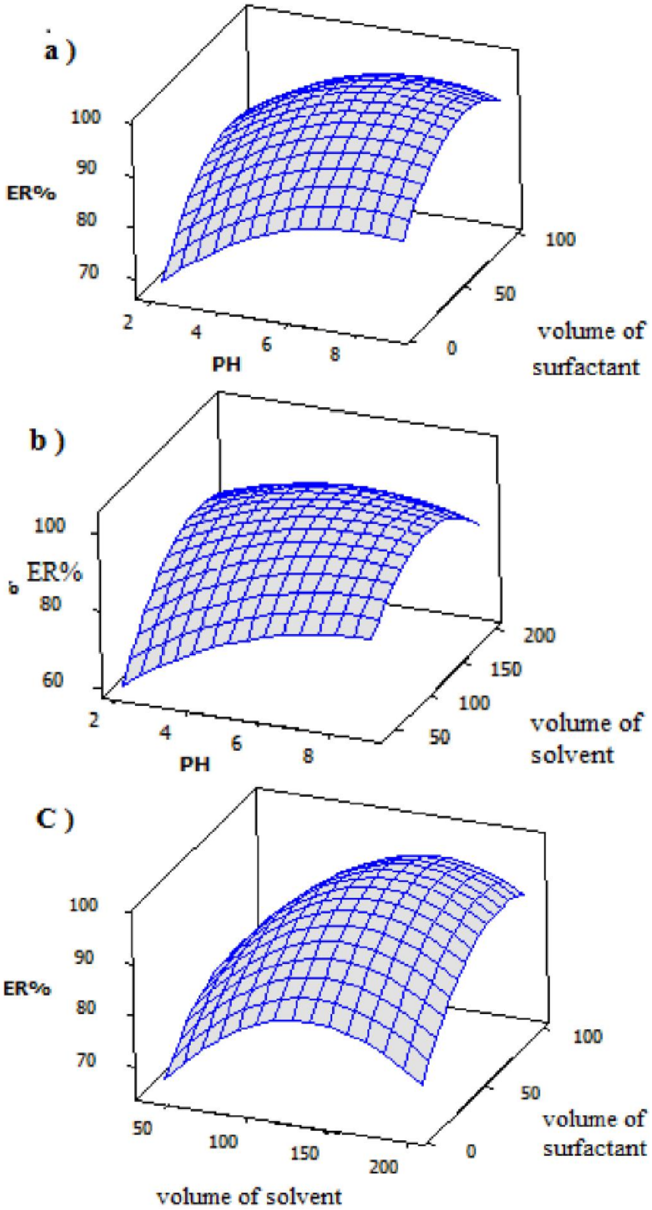

Figure 2 : Response surfaces for the box-behnken design(a) Volume of surfactant – PH, Volume of solvent 120 µl(b) Volume of solvent - PH, Volume of surfactant 55 µl (c) Volume of solvent - Volume of surfactant, PH 5.5

Figure 2 shows the response (extraction recovery, ER%) to variables and it depicts the response surface plots of ER versus significant variables. The surface plot (Figure 2a and 2b) showed existence of a significant positive interaction between the volume of solvent extraction, volume of surfactant and pH (with increasing pH, volume of solvent extraction and volume of surfactant, the ER% slightly increases). This may be attributed to the fact that when pH increases, the formation of Cd –dithizon complex and transition of complex into extraction solvent increase. Figure 2c showed that the ER % highly increases when Volume of solvent and surfactant increase. According to the overall results and optimization plot (Figure 3), the following experimental conditions were chosen: Volume of $CHCl_3$, 137 µl; Volume of Triton X-100, 72 µl and pH value, 6.8.

Effect of coexisting ions

Dithizone can be reacted with many metal ion within a wide pH range and a nonionic complex formed. However, the metal-dithizone complexes may be co–extracted into acceptor phase with analyte. To study the interferences of metal ion on extraction procedures, 10 ml solution contain 50 µg l^{-1} of Cd^{2+} and 5000 µg l^{-1} of each ion metal were extracted under the optimized conditions. Some of the species tested, such as Hg^{2+}, Pb^{2+}, Cu^{2+} and Ni^{2+} did interfere (TABLE 4).

Evaluation of performance of the method

Under optimal conditions, the limits of detection (LOD), linear calibration ranges, the relative standard deviation (RSD) and other characteristics of the method were calculated to evaluate the analytical performance of the proposed method. Three replicate extractions were performed for each concentration level. The calibration line showed a good linearity over the ranges of 0.5 – 94 µgL^{-1} with correlation coefficients (r^2) 0.9923 and the regression equation after the extraction procedure was A= 0.0093 $C_{Cd^{2+}}$ -0.005. The limit of detection (LOD), was calculated as the ratio between three times the standard deviation of blank signal and the slope of calibration curve after preconcentration, was 0.4µg L^{-1}. The relative standard deviation (RSD) for the analysis of five replicate solution containing 50 µg$L^{-1}$$Cd^{2+}$ was 6.5%. Enrichment factor, calculated as the slope ratio of two calibration curves for Cd^{2+} with and without preconcentration, calibration curve before the preconcentration procedure was A = 0.0001 $C_{Cd^{2+}}$ + 0.033 within a dynamic range from 100 to 2000µg L^{-1}, was 93 times.

Analysis of real samples

In order to test the applicability of the proposed

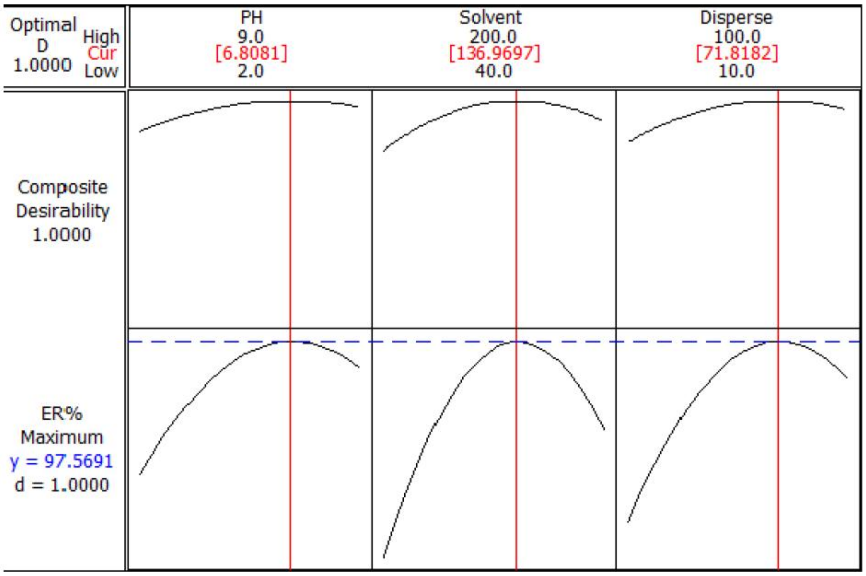

Figure 3 : Optimization plate for response(ER%). Dashed line and red line indicated the maximum of ER% and the factor values after optimization, respectively

TABLE 4 : Effect of diverse ions on the determination of 50 µg L^{-1}of cadmium

Coexisting ions	Recovery (%)
Ag^{+}	96.3
Hg^{2+}	92
Co^{3+}	97
Pb^{2+}	85.8
Fe^{3+}	103
Cu^{2+}	93
Ni^{2+}	92
As^{3+}	105.1
Zn^{2+}	96
Cr^{3+}	99

TABLE 5 : Results (mean ±standard deviation based on three replicate analysis) of determination of cadmium in real sample

Sample	Spike (µg.l^{-1})	Found (µg.l^{-1})	Recovery (%)
Tap water [a]	0	ND[b]	-
	10	9.62 ± 0.5	96.2
	50	49.15 ±0.6	98.3
River water[c]	0	7.2 ± 0.4	-
	10	16.3 ± 0.7	94.77
	50	58.59 ± 0.4	102.4

a Obtained from mashhad; b Not detected; c Obtained from torghabeh.

UASEME method for the analysis of real samples, tap and river water (obtained of Mashhad and Torghabeh) were analyzed. The water samples were pretreated as describedin Section 2.3 extracted using UASEME method and determined by FAAS. The recoveries for the spiked samples were in acceptable range of 94.6–103.1% and the RSDs were from 2.18% to 5.06%. (TABLE 5).

CONCLUSION

Ultrasound-assisted surfactant-enhanced

emulsification microextraction (UASEME) procedure combined with FAAS was successfully used for preconcentration and determination of cadmium at trace levels. Using of multivariate chemometric techniques is a powerful aid to obtain the optimum condition for the extraction by UASEME procedure. Thus, a multivariate strategy based on an experimental design using a Plackett–Barman design for screening and a Box–Behnken design is applied for optimization of significant factors. This method showed a good repeatability, high enrichment factor and extraction recovery for the analysis of real samples.

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