

# Ultrasound-assisted emulsification solidified floating organic drop microextraction-GFAAS for determination of ultratrace aluminum: Response surface methodology and Box-Behnken Design

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## Abstract

A simple, inexpensive and easy-to-use method of ultrasound-assisted emulsification of solidified floating organic drops microextraction (UAE-SFODME) coupled to GFAAS was developed for the extraction and preconcentration of aluminum. The factors affect the UAE-SFODME of aluminum, using alizarin red S (ARS) as complexing agent, were determined using one-factor-at-a time and further optimization was carried out by Box-Behnken design and response surface methodology (RSM). Under the optimized conditions: extraction solvent 180  $\mu\text{L}$ , pH 4.07, volume of dispersive solvent 60.0  $\mu\text{L}$ , ARS 2.0 mg, and sample volume of 25 mL, an enrichment factor of 80, a detection limit of 0.16  $\mu\text{g L}^{-1}$  and a relative standard deviation of 3.5-5.0 % were obtained. The method was effectively applied for analyzing different water samples and milk powder.

**Keywords:** Ultrasound-assisted emulsification; Microextraction; Response surface methodology.

## 1. Introduction

Aluminum is the most abundant metal in the Earth's crust [1]. It distributes throughout nature such as water and plants, so the main route of aluminum input to human is through foods, intravenous infusion and by environment, drinking water, beverages, medicines, cosmetics and the use of aluminum cooking

utensils [2]. It was suggested that exposure to aluminum might present a hazard to health. It degenerates brain cells and causes Parkinson and Alzheimer diseases [3]. Serious toxic effect of aluminum was observed on patients with renal failure subjected to dialysis, such as anemia, encephalopathy, and dialysis dementia [4].

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Accumulation of aluminum in the human body also results in lung cancer, breast cancer, and bladder cancer [5]. Aluminum has an effect on red blood cells, parathyroid glands and chromosomes, too. The WHO guideline for the permissible level of aluminum in drinking water is only  $0.2 \text{ mg L}^{-1}$  [6]. Therefore, the determination of very low levels of aluminum has become increasingly very important in environmental chemistry since its negative role in the human life. It is generally impossible to determine trace aluminum in environmental samples directly because of interfering species in the surrounding matrix, yet many real samples have aluminum concentration lower than of the detection limits of common techniques such as flame or electrothermal atomic absorption spectroscopy (FAAS and ETAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES). Hence, an initial sample pretreatment for aluminum preconcentration and matrices separation is often necessary. Several methods have been reported for the separation and preconcentration of aluminum, such as liquid-liquid extraction [7], ion exchange [8], solid-phase extraction (SPE) [9], single drop microextraction [10], and cloud point extraction [11]. Recently, dispersive liquid-liquid microextraction (DLLME) is much interested. In this method, an appropriate mixture of solvent and dispersant extractor is injected rapidly into an aqueous sample and a cloudy solution comprising droplets dispersed in the solvent is formed. After that, the sample is centrifuged to achieve phase separation [12]. Despite the main advantages of DLLME, the major drawback of DLLME is the use of chlorinated solvents such as chlorobenzene, chloroform, and carbon tetrachloride, which are toxic and environmentally unfriendly [13]. In order to overcome these problem, a novel modality of DLLME termed as solidified floating organic drop microextraction (SFODME) was proposed. It is based on DLLME and solidification of floating organic drop. This technique is easily carried out, a mixture of the dispersing and extraction solvent is injected into the aqueous sample and after centrifuging, the sample is

placed in an ice bath. The organic solvent is solidified and transferred to a tube to allow the organic solvent to return to the liquid state [14]. Extracting solvent that has less density than water, low water solubility, low volatility, low toxicity and a melting point close to room temperature (in the range of  $10\text{--}30 \text{ }^\circ\text{C}$ ) is used [15]. This technique has the advantages of the speed, simplicity, short extraction time, low cost, and high efficiency while consuming very small volumes of organic solvent [16]. SFODME has been successfully applied to determine the organic analytes [17], and trace elements [18-20]. Newly, a new mode of SFODME based on ultrasound assisted emulsification (UAE-SFODME) has been developed [21]. This approach facilitates the emulsification phenomenon and provides the large contact surface between the sample and the droplets of extractants which speeds up mass transfer, as fast as DLLME and shorter extraction time than SFODME [22].

There are many factors affecting the extraction efficiency. Generally, both empirical and statistical methods can be used to optimize of an extraction process. In comparison to empirical methods, statistical approaches are able to verify interaction effects with reduced test runs. Response surface methodology (RSM) is a famous and beneficial statistical method used for investigating the main and interactive effects of numerous variables to obtain a favorable response [23-25]. The main step of RSM is established a quantitative relationship between the interested response and the explanatory variables. Indeed, the response surface plots can be obtained where the response is quantitatively related to one or more explanatory variables. The resulted model may be employed to predict future values or used in the optimization process to determine experimental conditions on which minimal or maximal response could be achieved. To model the relationship between response and the significant variables usually multiple linear regression (MLR) is used [26-30].

According to the literature search, there has been no reference about earlier reports on the UAE of

aluminum. Thereby, we consider, for the first time, the possibility of implementation of UAE-SFODME in combination with optimization method (e.g., Box-Behnken design) in trace aluminum analysis. Alizarin red S (1,2-Dihydroxy-9,10-Anthracenedione) was used as the complexing agent. The possible factors affecting the extraction efficiency such as, the pH of the sample, sonication and centrifugation time, ligand concentration, ionic strength, and dispersing solvent volume were studied and optimized. The optimized procedure was applied to determine the amount of aluminum in powdered milk and different water samples.

## 2. Materials and methods

### 2.1. Chemicals and solutions

All chemical reagents were of analytical grade and obtained from Merck (Merck, Germany). Deionized water was used throughout the whole work. Stock standard solution of aluminum of  $1000 \text{ mg L}^{-1}$  was also obtained from Merck. Working solutions of different concentrations of aluminum were prepared daily by diluting the stock solution. The interfering solutions containing  $1000 \text{ g mL}^{-1}$  of interfering ion were prepared by dissolving appropriate amounts of respective pure nitrate salts in deionized water.  $0.357 \text{ g}$  of alizarin red S, as chelating agent, was dissolved in  $10.0 \text{ mL}$  acetone (dispersive solvent). 1-Undecanol was used as the extracting solvent. An acetate buffer solution ( $\text{pH}=4.0$ ,  $0.05 \text{ mol L}^{-1}$ ) was used to control the pH of the solutions. Pipettes and vessels were kept in  $10 \%$  nitric acid for at least  $24 \text{ h}$  and then washed with deionized water.

### 2.2. Apparatus

The analysis was performed by ContrAA 300 a high resolution-continuum source atomic absorption spectrometer (Analytik Jena, Jena, Germany), equipped with a heated graphite tube atomizer and a flame atomizer in two separate sample compartments. A  $300\text{-W}$  xenon short-arc lamp is used as continuous radiation source. Usage of a high-resolution double monochromator including of a prism pre-disperser and an Echelle grating monochromator in this instrument

provides a spectral bandwidth as narrow as  $1.5 \text{ pm}$  per pixel. A linear charge coupled device (CCD) array is employed as detector. It was shown previously that atomic absorption spectrometer equipped with a high-resolution continuum source could be applied in the elemental analysis with high precision [31]. The peak height was used as analytical signal for all quantifications.

The pH of the solutions was measured using a pH meter model Sension3 (Hach, USA) with a combined glass-calomel electrode. A centrifuge model RotixA50 S (Hettich Zentrifugen, Germany) was used to accelerate the phase separation process. A  $37\text{-kHz}$  ultrasonic water bath (Elmasonic E 30 H,  $240 \text{ W}$ , Elma, Singen, Germany) was used for assisting the emulsification of the organic solvent. Sonication was done at ambient temperature. During sonication, the rise in temperature of the ultrasonic bath was controlled by addition of ice-water ( $2 \text{ }^\circ\text{C}$ ) to the bath.

### 2.3. UAE-SFODME procedure

$0.5 \text{ mL}$  of aqueous solutions typically containing  $2 \text{ } \mu\text{g L}^{-1}$  of Al (III) was transferred into test tubes, and  $0.5 \text{ mL}$  of buffer solution was added. With the aid of a  $250 \text{ } \mu\text{L}$  syringe, a mixture of  $180.0 \text{ } \mu\text{L}$  1-undecanol and  $60.0 \text{ } \mu\text{L}$  of acetone containing  $0.0020 \text{ g}$  ARS was rapidly injected into the tube. It should be noted that preliminary studies showed that if the complexing agent (ARS) is to be present in the organic phase, the extraction process proceeds more quickly compared to the situation in which ARS is added to the aqueous phase. The tube was sonicated for  $3 \text{ min}$ . In this step, aluminum ions were reacted with ARS and extracted into 1-undecanol. Then, the mixture was subjected to the centrifugation for  $10 \text{ min}$  at  $3000 \text{ rpm}$  to accelerate phase separation. As a result, the dispersed fine droplets of the extraction phase were collected on the top of the vial. The vial was transferred into an ice bath and cooled for  $2 \text{ min}$ . The solidified solvent was removed with a spatula and transferred into a vial where it melted quickly at room temperature. Then, it was injected into the graphite furnace atomic

absorption spectrometer for the determination of aluminum.

#### 2.4. Experimental design and model development

Box-Behnken design (BBD) is a spherical, rotatable, or nearly rotatable quadratic design. It is based on three-level incomplete factorial design including the central point and middle points of the edges [32]. The number of experimental runs ( $N$ ) is defined by the expression  $N = 2k(k - 1) + C_p$ , where  $k$  is the number of variables and  $C_p$  is the number of center points [33]. The center point was repeated three times to assess the repeatability of the method. The Minitab 17 software (Minitab, Inc., State College PA, USA) was employed to design the experimental matrix.

The main step in RSM is to find an empirical equation which relates response to the experimental conditions. Using BBD, one can use a multiple quadratic equation, also called MLR, such as shown in eq. (1).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_i X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where  $Y$  is dependent variable, and  $X_1, X_2, \dots, X_k$  are the independent variables.

Accuracy of the resulted models were checked and stated with various descriptive statistical analysis such as  $F$  value, squared correlation coefficient ( $R^2$ ), adjusted determination of coefficient ( $R^2_{\text{adjusted}}$ ), and predicted  $R^2$ . A predictive model is considered good if  $R^2$  and  $R^2_{\text{adjusted}}$  are close to 1. 3D response surface plots were generated and used to investigate the interactions between variables.

#### 2.5. Preparation of real samples

The proposed procedure was applied for the determination of aluminum in river waters, inlet and outlet dialysis fluids, and milk powder.

River water samples were collected from Arvand and Bahmanshir River (Khorramshahr, Abadan, Iran). All water samples were only filtered through a 0.44- $\mu\text{m}$  filter paper and, then, the described procedure was applied. In the case of milk powder, 50.0 mg of the sample was digested using 30.0 mL of concentrated  $\text{H}_2\text{SO}_4$  and 12.0 mL concentrated  $\text{HNO}_3$ . The mixture was heated to dryness and the residue was dissolved

with 10.0 mL of  $\text{HNO}_3$  (0.1 mol  $\text{L}^{-1}$ ) and heated to concentrate. After cooling and diluting with water, the solution was adjusted to pH 4-5. The final volume was made up to 50.0 mL with deionized water. The procedure was also employed to Inlet and outlet of dialysis fluids without any pretreatment.

#### 3. Results and discussion

In this work, solidified floating organic drop microextraction was applied to the extraction and preconcentration of aluminum prior to analyzing by GF-AAS. Ultrasound irradiation was carried out to accelerate mass transfer process in this procedure. Ultrasound radiation disperses a microvolume of water immiscible extraction solvent in an aqueous sample solution and facilitates the emulsification phenomenon. After a period of time, the floated extractant was frozen and easily collected for analysis.

Box-Behnken surface design was employed to optimize experimental parameters which influence the aluminum extraction. It was found that a wide variety of factors such as pH, type of dispersive solvent and its volume, amount of complexing agent, ionic strength, sonication time, and centrifugation time could influence on the extraction process. To determine effective factors and their proper levels for BBD-RSM, effects of the above mentioned experimental factors were firstly examined by the one-factor-at-a time (OFAT) procedure. OFAT is the most popular screening tools that used to find effective factors from a pool of potentially important factors. After recognizing effective factors, BBD-RSM was used to further study the interaction between factors by response surface methodology and to find optimum conditions for aluminum recovery. Note that the percent of extraction recovery ( $ER\%$ ) and enhancement factor were calculated according to equations. 2 and 3, respectively.

$$ER\% = \left( \frac{C_o V_o}{C_{aq} V_{aq}} \right) \times 100 \quad (2)$$

$$\text{Enrichment factor} = \frac{C_o}{C_{aq}} \quad (3)$$

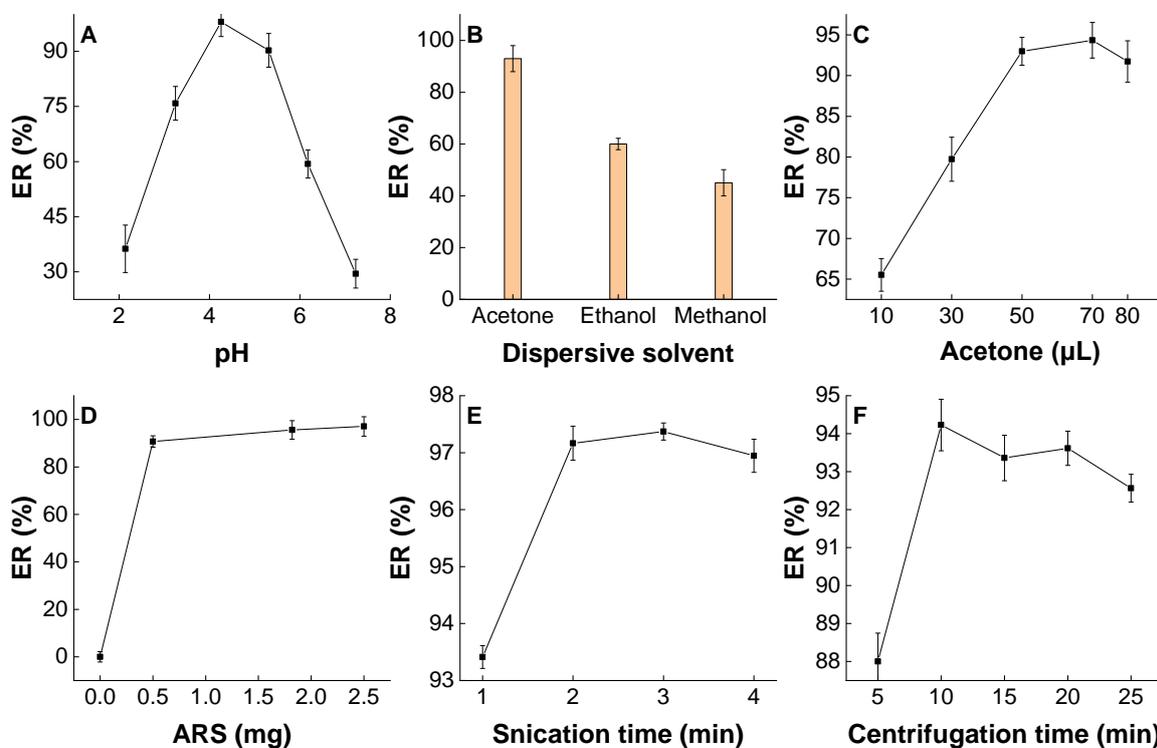
### 3.1. OFAT experiments

The pH has an important role on the complex formation and consequent extraction. So, the effect of pH on the UAE-SFODME extraction of aluminum was evaluated in the range of 2-7. As shown in Fig. 1a, the recovery increased by increasing pH and reached maximum at pH 4.3 and then decreased at higher pHs. At higher pHs, recovery diminished due to the reaction of aluminum ions with hydroxyl. At lower pHs,  $H^+$  ions compete with aluminum ions for ARS. Consequently, the sample solution was adjusted at 4.3 for subsequent works.

Dispersive solvent should be miscible in both the aqueous and organic phases. In this study, preliminary studies showed that utilization of the complexing agent in the organic phase brings about the extraction process proceeds more quickly. Different dispersive solvent including acetone, ethanol, and methanol were tested. Volume of dispersive solvent was kept constant at 50  $\mu$ L. Among these solvents, the best extraction efficiency was obtained when acetone was employed

(Fig. 1b). This is probably due to higher solubility of ARS in acetone compared to the others. Moreover, several experiments were also carried out using different volumes of acetone in the range of 10-80  $\mu$ L to get more insight into the effect of the dispersive solvent volume. As highlighted in Fig. 1c, the recovery increases with increasing volume of acetone up to 70.0  $\mu$ L. In the presence of large amount of acetone, large contacting area provides by the better dispersion. However, excessive amount of acetone reduce volume of extraction phase. Thereby, 70.0  $\mu$ L acetone was chosen as the optimal value in the later experiments.

The influence of alizarin red S on the aluminum extraction was evaluated in the range of 0-2.5 mg. As seen in Fig. 1d, no extraction was identified in the absence of the complexing agent. Extraction could be observed in the presence of ARS and recovery increases smoothly by increasing amount of ARS. More amounts of ARS was not practiced owing to limited dissolving of ARS in acetone. As a result, all



**Fig. 1** Effect of different experimental factors on the extraction recovery of Al: a) pH; b) type of dispersive solvent; c) volume of dispersive solvent (acetone); d) ARS; e) sonication time; f) centrifuge time.

further experiments were performed using 2.5 mg of ARS.

Sonication time is an important part in the proposed extraction process. Sonication produces fine droplets of organic solvent into the aqueous solution and causes high contact area between the aqueous phase and the extraction solvent. The effect of sonication time on the extraction efficiency was examined in the range 1-4 min while other experimental conditions were kept constant. As seen in Fig. 1e, maximum recovery was achieved at time 3 min and then decreased slightly. Therefore, duration time 3 min was chosen as the optimum for the next studies.

Centrifugation speeds up the separation of extractant with aqueous phase. Hence, the effect of centrifugation time upon the extraction efficiency was assayed in the range of 5-25 min at the rate of 3000 rpm. As shown in Fig. 1f, complete separation occurred at time of 10 min and much longer extraction efficiency was not acquired at longer times. So, a centrifugation time of 10 min was selected.

To investigate the influence of ionic strength on the performance of the proposed UAE-SFODME, different experiments were performed by adding different amounts of NaNO<sub>3</sub> (0-5% (w/v)). Other experimental conditions were kept constant. To better understand the effect of ionic strength on the extraction of aluminum ions, no buffer was added and pH adjusting was carried out using minimal amounts of dilute solution of nitric acid and/or sodium hydroxide. By increasing the NaNO<sub>3</sub> from 0 to 2%, the recovery increased sharply due to the salting-out effect. The same experiments were conducted in the presence of 0.025 mol L<sup>-1</sup> buffer solution. The results showed that salt addition has no significant effect on the recovery in the later situation because buffer solution maintained ionic strength at constant level. Thus, no salt addition was commended.

### 3.2. BBD-RSM data analysis

Based on the OFAT studies, the most effective factors on the extraction of aluminum ions were recognized to be pH, amount of complexing agent (ARS), volume of dispersive solvent (acetone), and sonication time. To

ensure that all experiments are carried out at the equilibrium, sonication time was kept at the optimum value found in the previous study, e.g., 3 min. The remaining factors were more investigated by employing BBD and the response surface methodology (RSM). A set of 15 experiments was design with the aid of Minitab software. For each factor, three levels were assigned and coded by (-1, 0,+1). The independent factors, their notations and levels are listed in Table 1. Each experiment was done in triplicate and the average extraction recoveries was considered as the response. The design matrix is also shown in Table 1. Using BBD experimental design it is possible to consider a quadratic polynomial regression model to evaluate and quantify the influence of variables on the responses (see Eq. 1). Eq. 4 shows the resulted MLR model and its analysis of variance is given in Table 2.

$$ER\% = 92.0 + 1.7X_1 + 4.6X_2 + 1.8X_3 - 2.8X_1^2 - 2.2X_2^2 + 2.9X_3^2 - 0.3X_1X_2 - 0.6X_1X_3 - 0.9X_2X_3 \quad (4)$$

$$N = 15; R^2 = 0.96; R_{adj}^2 = 0.90; F = 14.96$$

where *ER*, *X*<sub>1</sub>, *X*<sub>2</sub>, and *X*<sub>3</sub> refer to extraction recovery, pH, volume of acetone, and amount of ARS, respectively.

The regression sums of squares as a percentage of total sums of squares was 96.4%, indicating that most portion of variance in the response was explained by the regression equation. More details about Eq. 4 including normal probability curve, residual plot, and histogram of residuals was given in supporting information (Fig. S1). However as can be seen in Table 2, there are some not-significant variables that have to be removed. The best fitted regression model equation after removing not-significant variables was as follows:

$$ER\% = 92.0 + 1.7X_1 + 4.6X_2 + 1.8X_3 - 2.8X_1^2 - 2.2X_2^2 + 2.9X_3^2$$

$$N = 15; R^2 = 0.95; R_{adj}^2 = 0.91; F = 24.57 \quad (5)$$

Statistical parameters of this model were given in the Eq. 5 and presented in detailed in Table 3 (see also Fig S2 and Table S2). The obtained  $R^2$  and  $R^2_{adj}$  values of the model were 0.95 and 0.91, respectively.

The main and interaction effects of parameters can be evaluated from the outputs of experimental design; that is the main task of experimental design. Response surface curves facilitate investigating the main and interaction effects and finding the optimal level for each variable, as well. The response surface plots are shown in Fig. 2. The plots were obtained by changing two variables while keeping the other constant. Response surface plots show that extraction recovery of aluminum increases with increasing pH as well as rising the volume of dispersive solvent (Fig. 2a), which may be related to increasing the number of droplets at this situation that supply best conditions for efficient extraction.

**Table 1.** Variables, their notations, and levels in Box-Behnken design together with the result for each run.

Factors	Notation	Levels		
		Low	Center	High
		-1	0	+1
pH	$X_1$	3	4	5
Acetone ( $\mu\text{L}$ )	$X_2$	30	50	70
ARS (mg)	$X_3$	0.5	1.5	2.5

Run	$X_1$	$X_2$	$X_3$	ER %
1	+1	+1	0	93.8
2	-1	0	+1	92.4
3	0	-1	+1	91.9
4	-1	+1	0	90.1
5	-1	-1	0	79.7
6	0	-1	-1	84.6
7	0	+1	+1	99.0
8	0	0	0	93.1
9	+1	-1	0	84.71
10	+1	0	+1	93.5
11	-1	-	-1	89.5
12	0	0	0	91.4
13	0	0	0	91.6
14	+1	0	-1	93.1
15	0	+1	-1	95.3

**Table 2.** ANOVA analysis of the full quadratic polynomial model.

Source *	Sum of squares	Degree of freedom	Mean Squares	F value	P-value	
Model	308.07	9	34.23	14.96	0.0041	Significant
$X_1$	22.87	1	22.87	10.00	0.0250	Significant
$X_2$	172.96	1	172.96	75.61	0.0003	Significant
$X_3$	25.80	1	25.80	11.28	0.0201	Significant
$X_1X_2$	0.37	1	0.37	0.1628	0.7033	Not significant
$X_1X_3$	1.53	1	1.53	0.6690	0.4506	Not significant
$X_2X_3$	3.11	1	3.11	1.36	0.2964	Not significant
$X_1^2$	28.75	1	28.75	12.57	0.0165	Significant
$X_2^2$	17.42	1	17.42	7.62	0.0399	Significant
$X_3^2$	30.08	1	30.08	13.15	0.0151	Significant
Residual	11.44	5	2.29			
Lack of Fit	9.76	3	3.25	3.89	0.2112	Not significant
Pure Error	1.67	2	0.84			

Model Summary Statistics					
Response	Std Dev	$R^2$	Adjust- $R^2$	F	Predicted- $R^2$
ER%	1.51	0.96	0.90	14.96	0.50

\*  $X_1$ ,  $X_2$ , and  $X_3$  refer to pH, volume of acetone, and ARS, respectively.

**Table 3.** ANOVA analysis of the RSM model after removing not significant terms.

Source	Sum of squares	Degree of freedom	Mean Squares	F value	P-value	
Model	303.06	6	50.51	24.57	< 0.0001	Significant
$X_1$	22.87	1	22.87	11.12	0.0103	Significant
$X_2$	172.96	1	172.96	84.13	< 0.0001	Significant
$X_3$	25.80	1	25.80	12.55	0.0076	Significant
$X_1^2$	28.75	1	28.75	13.99	0.0057	Significant
$X_2^2$	17.42	1	17.42	8.47	0.0196	Significant
$X_3^2$	30.08	1	30.08	14.63	0.0051	Significant
Residual	16.45	8	2.06			
Lack of Fit	14.77	6	2.46	2.94	0.2752	Not significant
Pure Error	1.67	2	0.84			
Model Summary						
Statistics						
Response	Std Dev	R <sup>2</sup>	Adjust-R <sup>2</sup>	F	Predicted- R <sup>2</sup>	
ER%	1.43	0.95	0.91	24.57	0.80	

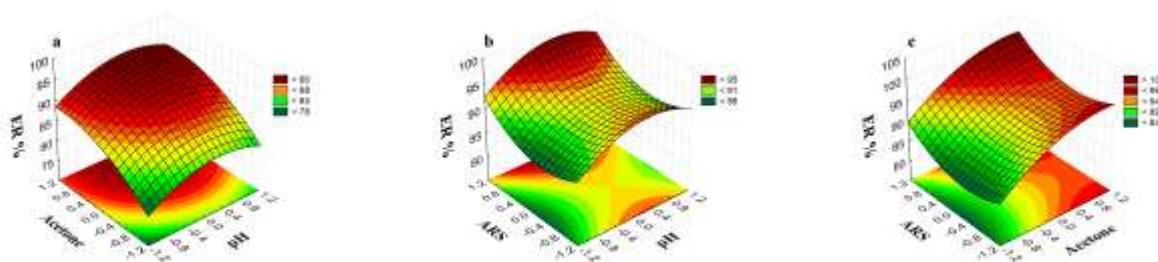
It is clear from Fig. 2b that the extraction increased with the increase in the ARS amount. As a conclusion, all studied factors had positive influences on the extraction of aluminum. The curvature of the plots in Fig. 2 has only one source; that is nonlinearity relationships between factors and the response.

Numerical optimization based on the desirability function was done to find optimum conditions for pH and amounts of ARS and acetone. The optimum values for pH, volume of acetone, and amount of ARS were found to be 4.07, 60  $\mu$ L, and 2.0 mg, respectively. Under the optimized conditions, the attained ER % value was 99.03.

### 3.3. Figures of merit of the proposed model

The figures of merit of this method including dynamic linear range (DLR), limit of detection (LOD), enrichment factor, and relative standard deviation (RSD) were explored to estimate performance characteristics of the proposed procedure. Under the optimized conditions, the calibration curve was linear in the range of 1-19  $\mu$ g L<sup>-1</sup> (Fig. 3). The equation of the

calibration graph was  $y = 0.0145x + 0.0592$  (where  $y$  is absorbance signal and  $x$  is the concentration of aluminum ( $\mu$ g L<sup>-1</sup>) in aqueous phase) with the correlation coefficient of 0.997. Concentration of aluminum ion in the real samples such as natural waters is usually very low. In order to explore the possibility of obtaining high enrichment factor, the effect of sample volume on the extraction was studied. For this purpose, different volume (1–100 mL) of sample solution containing 0.01  $\mu$ g of aluminum was extracted at optimum condition in the proper size vial. The extract was then separated and quantized by GF–AAS. The results showed that the quantitative recovery (>95%) was obtained for sample volume up to 20 mL. Thus, an enrichment factor of 80 could be calculated for the proposed method based on the Eq. 5. Limit of detection was acquired equal to 0.16  $\mu$ g L<sup>-1</sup>. It calculated based on  $3S/m$  (where  $S$  and  $m$  are standard deviation of the blank and slope of calibration graph, respectively). The repeatability of this method was



**Fig. 2** The response surface plots for aluminum extraction: a) acetone-pH; b) ARS-pH; c) ARS-acetone.

measured by analyzing various standard solutions of aluminum. The relative standard deviation (R.S.D.) was between 3.5-5.0 % for five replicate extractions.

### 3.4. Interference study

In order to investigate the effect of interfering ions, 1.0 mL of the solution containing  $2 \mu\text{g L}^{-1}$  aluminum and some potentially interfering ions were treated in accordance to the proposed extraction procedure. Tolerance limits of some interfering ions are given in Table 4. Tolerance limit was considered as the maximum concentration of the foreign ion produced an analytical signal which has no more than 5% difference with the analyte solution alone. As can be seen from Table 4, the extraction and analysis of aluminum in the presence of the investigated ions is selective and, therefore, analysis of aluminum in the real samples is possible.

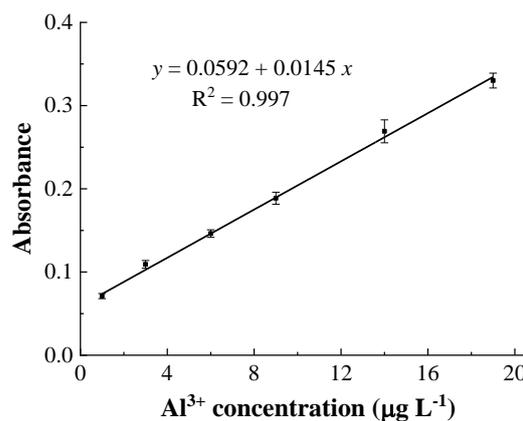
### 3.5. Real sample analysis

To test the suitability of the proposed procedure, it was employed to determine aluminum in different real samples including river water, dialysis water, and milk powder. The results given in Table 5 indicate that the matrices of the considered real samples have little effect on the extraction and determination of

aluminum. This emphasizes good accuracy of the method and to be free of systematic error.

**Table 4.** Tolerance limit of foreign ions on the recovery of aluminum ( $2 \mu\text{g/L}$ ).

Species assayed	Tolerance limit ( $\mu\text{g L}^{-1}$ )
$\text{K}^+$ , $\text{Na}^+$ , $\text{CO}_3^{2-}$	200
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	100
$\text{Ni}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Co}^{2+}$	50
$\text{Fe}^{2+}$ , $\text{Cu}^{2+}$	20



**Fig. 3** Calibration graph for Al after extraction with the proposed method under the optimized conditions

**Table 5.** Analysis of aluminum in various real samples.

Sample	Added Al	Found Al	Recovery (%)
Bahmanshir river water	–	17.5 ± 2.3 (µg L <sup>-1</sup> )	–
	5 (µg L <sup>-1</sup> )	22.3 ± 1.8 (µg L <sup>-1</sup> )	96
Arvand river water	–	23.4 ± 3.4 (µg L <sup>-1</sup> )	–
	5 (µg L <sup>-1</sup> )	28.7 ± 2.7 (µg L <sup>-1</sup> )	106
Inlet dialysis water	–	ND	–
	5 (µg L <sup>-1</sup> )	4.9 ± 2.5 (µg L <sup>-1</sup> )	98
Outlet dialysis water	–	ND	–
	5 (µg L <sup>-1</sup> )	5.1 ± 3.3 (µg L <sup>-1</sup> )	102
Milk powder	–	14.1 ± 1.6 (µg g <sup>-1</sup> )	–
	5 (µg g <sup>-1</sup> )	19.0 ± 3.1 (µg g <sup>-1</sup> )	98

**Table 6.** Comparison of the proposed method with the other methods reported in the literature for the determination of aluminum.

Method	Separation method	Reagent	Detection limit (µg L <sup>-1</sup> )	RSD%	Real sample(s)	Ref
Spectrophotometry	SPE	Chrome azurol S	4.9	1.5	Drinking water	38
Spectrofluorimetry	SPE	8-Hydroxyquinoline	3.4	<10	Hair and dialysis samples	39
Spectrofluorimetry	Solvent extraction	8-Hydroxyquinoline	2.2	8.7	biological fluids and dialysis	40
GF-AAS	UAEME	8-Hydroxyquinoline	0.19	5.9	Dialysis samples	41
GF-AAS	DLLME	8-Hydroxyquinoline	0.3	4.9	Dialysis samples	41
<b>GF-AAS</b>	<b>UAE-SFODME</b>	<b>Alizarin red S</b>	<b>0.16</b>	<b>3.5-5.0</b>	<b>Dialysis samples, River waters, and Milk powder</b>	<b>This work</b>

### 3.6. Comparison to the previous reports

The analytical figures of merit of the proposed UAE-SFODME method are compared in Table 6 against several fluorometric, spectrophotometric and atomic absorption spectrometric methods reported in the literature for determination of trace levels aluminum. These comparisons show superior of the proposed method in term of simple operation and lower in LOD.

### 4. Conclusion

Here, 1-Undecanol as a low density organic solvent and alizarin red S, as complexing reagent, was used in the UAE-SFODME method for the extraction and determination of ultratrace amounts of aluminum. The optimization of process was carried out using BBD

under response surface methodology and the results showed that the pH, volume of dispersive solvent, and amount of complexing agent have significant effect on the extraction recovery of aluminum. The interaction between variables was also investigated by plotting response surface plots. Under the optimal conditions (extraction solvent 180 µL, pH 4.07, volume of dispersive solvent 60.0 µL, and ARS 2.0 mg) extraction recovery of 99.6 % and preconcentration factor up to 80 was obtained, allowing to reach the LOD in the order of 0.16 µg L<sup>-1</sup> with an acceptable precision. The obtained results in this work emphasize the ability of the presented method for extracting and measuring aluminum in various real samples.

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