



**Supramolecular based-Ligandless ultrasonic assisted-  
dispersion solidification liquid liquid microextraction of  
uranyl ion prior to spectrophotometric determination with  
dibenzoylmethane**

Journal:	<i>RSC Advances</i>
Manuscript ID	RA-ART-11-2015-023355.R1
Article Type:	Paper
Date Submitted by the Author:	13-Dec-2015
Complete List of Authors:	Shokrollahi, Ardeshir; Yasouj University, Chemistry Behrooj Pili, Hadi; Yaouj University
Subject area & keyword:	Separation science < Analytical

# Supramolecular based-Ligandless ultrasonic assisted-dispersion solidification liquid liquid microextraction of uranyl ion prior to spectrophotometric determination with dibenzoylmethane

Ardeshir Shokrollahi\*, Hadi Behrooj Pili

Department of Chemistry, Yasouj University, Yasouj, Iran

Tel: +9874-32223048 Fax: +98743-2242147

E-mail addresses: [ashokrollahi@mail.yu.ac.ir](mailto:ashokrollahi@mail.yu.ac.ir)

## Abstract

A simple, efficient, rapid and environmentally friendly method has been developed for preconcentration and determination of ultratrace amounts of uranyl ion in water sample by supramolecular based-ligandless ultrasonic assisted-dispersion solidification liquid liquid microextraction procedure before spectrophotometric detection. The methodology is based on the dispersion-solidification liquid liquid microextraction of uranyl ion with decanoic acid/THF supramolecular solvent in the absence of chelating agent. Several factors affecting the microextraction efficiency, such as pH, type and volume of supramolecular solvent, sonication time, ionic strength were investigated and optimized. Under the optimized conditions, the enhancement factor and preconcentration factor were obtained 54.43 and 33.33 respectively. The calibration curve was linear in the range of 4.00 to 311.85 ng mL<sup>-1</sup> of uranyl ion with R<sup>2</sup>= 0.9967 and detection limit based on three times the standard deviation of the blank (3S<sub>b</sub>) was 2.00 ng mL<sup>-1</sup> in original solution. The relative standard deviation for seven replicate determination of 125.00 ng mL<sup>-1</sup> uranyl ion was ±2.87%. The developed method was successfully applied to the extraction and determination of uranyl ion in natural water samples.

Keywords: Uranyl ion, supramolecular solvent, decanoic acid, spectrophotometry

## Introduction

It is well known that uranium is toxic as well as being radioactive; the safety profiles for uranium compounds are well established<sup>1</sup>. Uranium has both chemical and radiological toxicity but, for natural uranium, the main concern is due to its chemical toxicity. In the human body, uranium tends to be concentrated in specific locations and, because of its radioactivity, can increase the risk of bone cancer, liver cancer, and blood disease<sup>2, 3</sup>. The greatest risk to health caused by the uranium toxicity is the likelihood of damage to the structure of the kidneys, which can cause acute renal failure<sup>4</sup>. Therefore, it is necessary from an analytical point of view to develop sensitive and economical methods for the determination of trace amount of uranium.

Numerous techniques have been used for the determination of uranium including inductively coupled plasma mass spectrometry<sup>5</sup>, adsorptive stripping voltammetry<sup>6, 7</sup>, α-spectrometry<sup>8</sup>, neutron activation<sup>9</sup>, molecular fluorescence spectrometry<sup>10</sup>, gas chromatography<sup>11</sup>, complexometric titration<sup>12</sup>, fluorescence sensor<sup>13</sup>, Photo acoustic spectroscopy<sup>14</sup> and luminescence<sup>15</sup>. Although some of these methods have good sensitivity, they involve expensive instruments, well controlled experimental conditions, and profound sample-making. Spectrophotometry has been used for determination of uranium separately and simultaneously<sup>16-20</sup>. The common availability of the instrumentation, the simplicity of procedures, speed, precision and accuracy of the technique make spectrophotometric methods attractive<sup>21</sup>. In spite of mentioned advantages, direct determination of trace uranium by spectrophotometric methods is not sufficiently sensitive so that a preconcentration step is necessary. Several techniques for the separation and preconcentration of trace amounts of uranium have been established, including cloud point extraction<sup>1, 22</sup>, solid sorbents such as polymer-XAD resin series<sup>23</sup>, polyurethane foam<sup>24</sup>, ion

imprinting polymers<sup>25, 26</sup>. However, these techniques suffer some disadvantages including high cost, long processing time and the use of large volume of toxic chemicals.

In the last decade, modern trends in analytical chemistry are toward miniaturization and minimization of organic solvent used in sample preparation. The dispersive liquid–liquid microextraction (DLLME) method was proposed by Assadi et al. in 2006<sup>27</sup>, and immediately attracted extensive attention among researchers. The advantages of DLLME are simple, rapid, low consumption of organic solvent, high preconcentration factor and fast extraction without requiring the use of any apparatus<sup>28-30</sup>. However, the extraction solvents adopted in this technique is required greater density than in water, such as chlorobenzene, carbon tetrachloride and chloroform. Clearly the solvents are toxic and environment-unfriendly. In order to overcome the disadvantages of DLLME, a simple and efficient liquid phase microextraction technique based on the solidification of a floating organic microdrop (LPME-SFO) was reported<sup>31</sup>, in which, a less-toxic and low-density extraction solvent with a proper melting point was used. However, the extraction time was somewhat longer in LPME–SFO than that in DLLME, thus it cannot satisfy the demand of fast analysis. To overcome these problems, a floating organic droplets technique combined with DLLME, which is called DLLME based on solidification of floating organic droplets (DLLME-SFO), was established<sup>32-35</sup>. For DLLME-SFO, novel organic solvents with low density, proper melting point and minimization of toxicity were selected. In this method, a trace volume of organic droplets can be easily collected by solidifying it in the ice bath.

In recent years, supramolecular solvent-based microextraction has been developed as an environment friendly alternative method to other microextraction technique for determination of organic and inorganic species<sup>36-42</sup>. The term supramolecular has been used for two recent alkyl carboxylic acid aggregate-based solvents (water-induced reverse micelle-rich phase and tetrabutylammonium (TBA)-induced vesicle-rich phase)<sup>43, 44</sup>. Supramolecular solvents are water-immiscible liquids made up of supramolecular assemblies dispersed in a continuous phase. They are produced from amphiphile solutions by a sequential self-assembly process occurring on two scales, molecular and nano, and constitute a valuable strategy to replace organic solvents in analytical extraction procedures. First, amphiphilic molecules spontaneously form three-dimensional aggregates (e.g. aqueous and reversed micelles or vesicles) above a critical aggregation concentration. Then, the produced nanostructures self-assemble in larger aggregates with a extensive size distribution in the nano and microscale regimes by the action of an external stimulus (e.g. temperature, electrolyte, pH, solvent) and separate from the bulk solution by a mechanism that remains inexpressible<sup>44</sup>. The main properties of the SUPRASs are the high concentration of amphiphiles, 0.1-1 mg  $\mu\text{L}^{-1}$ , and different types of the interactions offered by them for analyte extraction (i.e. ionic, hydrogen bonding,  $\pi$ -cation and hydrophobic) allows achieving high enrichment factors using low solvent volumes<sup>45</sup>. Ruiz and coworkers have developed a new preconcentration strategy based on the coacervation of decanoic acid reverse micelles for extraction of organic compounds of wide polarity range<sup>44</sup>, but this technique is tedious, labor intensive and time consuming procedure; because of stirring mixture of sample and extraction solvent for several minutes to rise the extraction rate. Until to present, the greater part of microextraction applications to preconcentrate the metals are based on the formation of hydrophobic chelates or ion pairs in the extracting solvent choosing a specific chelating agent. It may be useful to emphasize that using less number of reagent increases the ease of the procedure. In the literature, there are a few studies on ligandless liquid–liquid microextraction for the preconcentration and determination of metal ions<sup>46-48</sup>.

This article deals with the evaluation of Supramolecular based-Ligandless ultrasonic assisted-dispersion solidification liquid liquid microextraction (SM-LLUA-DSLLME) for the simple, effective, rapid, sensitive and inexpensive ligandless ultrasonic assisted dispersion-solidification liquid liquid microextraction of uranyl ion from aqueous sample and its spectrophotometric determination with dibenzoylmethane (DBM) (Fig.1) as chromogenic reagent.

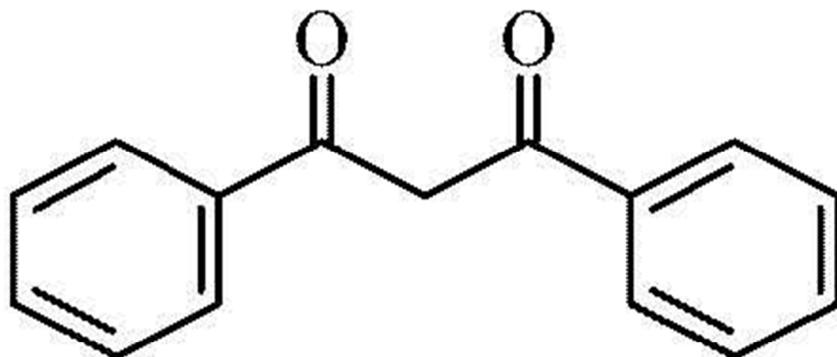


Figure 1. Molecular structure of Dibenzoylmethane (DBM)

## Experimental

### Apparatus

A Perkin-Elmer Lambda 25 (Waltham, MA, USA) UV/vis spectrometer was used for recording absorbance spectra and 350  $\mu\text{L}$  quartz suprasil cylindrical micro-cell with 10-mm light path was prepared from Dabitech (, Germany). A Metrohm pH meter (model 713) with a combined glass electrode was used for pH measurements. An ultrasonic bath with heating system (Tecno-GAZ SPA UltraSonic System, Italy) at 40 kHz of frequency and 130 W of power was used for the ultrasound-assisted extraction procedure. Centrifuge, RHB model (Germany) was used for the accelerate separation phases. A Biohit prolinepipettor 100-1000 $\mu\text{L}$  was used for injecting samples into the cells.

### chemicals

Analytical grade uranyl ion nitrate and other salts Merck (E. Merck, Darmstadt, Germany ) were of the highest purity available. Decanoic acid, THF and methanol were purchased from merck and DBM was purchased from fluka. A stock solution of uranyl ion ion was prepared by dissolving an appropriate amount of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 0.5  $\text{mol L}^{-1}$  nitric acid. Working solution of decanoic acid was prepared by dissolving 55 mg of this reagent in 0.50 mL of THF for each microextraction. All solutions were prepared with doubly distilled water. Working solution of DBM was prepared by dissolving an appropriate amount of this reagent in methanol. Nitrate salts of cadmium, cobalt, nickel, copper, thorium, magnesium, cerium, calcium and other salts from Merck were of the highest purity available and used without any further purification.

### Spectrophotometric titration and Stoichiometry of complex

Standard stock solutions of DBM ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) and the uranyl ion ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) were prepared by dissolving exactly weighted amount of pure solid compounds in precalibrated 25.0 mL volumetric flasks and diluted to the mark with methanol. Working solutions were prepared by dilution of the stock solutions. Titration of the 2.6 mL ( $3.84 \times 10^{-5} \text{ mol L}^{-1}$ ) of DBM was carried out by the addition of uranyl ion using a pre-calibrated microsyringe at 25.0  $^\circ\text{C}$  in 0.05  $\text{mol L}^{-1}$  TEAP. The spectrum was recorded after each addition.

### SM-LLUA-DSELLME Procedure

In order to obtain optimized SM-LLUA-DSELLME conditions, 10.00 mL of aqueous solution containing 125  $\text{ng mL}^{-1}$  uranyl ion was poured into a screw bottom glass centrifuge tube the solution pH was adjusted to 3.5 by the addition of nitric acid or sodium hydroxide. Then the sample solution was placed in ultrasonic bath and simultaneously 0.5 mL of THF containing 55 mg of

decanoic acid was injected rapidly into the cited solution using a 1.00-mL syringe. The mixture was kept in an ultrasonic bath for 2 minutes. The supramolecular solvent spontaneously formed into the bulk solution. Then, the sample was centrifuged for 5 min at 3000 rpm and a two-phase solution was obtained. After centrifugation, due to difference in the density between the aqueous phase and supramolecular solvent, the fine droplets of supramolecular solvent float at the top of the test tube. The test tube was then transferred into a beaker containing crushed ice for cooling. After 5 min, the extraction solvent solidified and was then transferred into a conical vial using simple spatula, where it melts quickly at room temperature. Subsequently, 100  $\mu\text{L}$  of chromogenic solution ( $10^{-2}$  mol  $\text{L}^{-1}$  DBM in methanol) was added to the separated phase, and then diluted to 300 microliters with methanol. The palm yellow complex of uranyl ion and DBM was formed immediately, 280 microliters of this solution transferred to UV-cuvette by micropipette. Absorbance of the uranyl ion-DBM complex was measured at 400 nm against reagent blank.

### Preparation of real samples

Analysis of water samples (tap water, river water and waterfall water) for the determination of uranyl ion contents was performed in the following way: About 100 mL of sample was passed through a sintered glass funnel and enough amount of concentrated  $\text{HNO}_3$  was added to achieve a concentration of 0.5 M. Also 0.0186 g of  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$  was added to reach a concentration of  $5.0\times 10^{-4}$  M. The water samples were stored in polyethylene bottles. Then the procedure given in 2.4 section was applied for analysis.

## Results and discussion

### Optimization of SM-LLUA-DSSLME

The extraction efficiency SM-LLUA-DSSLME procedure depends on some important experimental parameters which should be investigated in detail. The effects of, type and amount of extraction and disperser solvent solvents, effect of the salt, sample pH, sonication and extraction time were investigated and optimized. A comparison between the corresponding signal of uranyl ion solution after microextraction and it's of a reference uranyl ion solution in diluent solvent, confirm that the proposed method has a good efficiency for extraction of uranyl ion from water samples.

### Study of complexation between chromogenic reagent and analyte

The complexation between the DBM (L) and the uranyl ion (M) was investigated via spectrophotometric method. The solutions were titrated according to spectrophotometric titration procedures, and the spectra were recorded. As shown in Fig. 2a, significant changes in the ligand spectrum occurred after adding of M ion, upon which a new peak appeared at about 400 nm. These results indicate relatively strong interaction between L and the M ion. Analyzing the spectral data over the ranges of 386-464 nm yielded the stoichiometry, stability constants and molar absorbance spectra of the ligand- M complexes. These were calculated by using the HypSpec program, a new version of the PHab program<sup>49,50</sup>. The best fit to the spectrophotometric data show that two complexes for M ion, were obtained, these being  $\text{ML}$  ( $\epsilon = 3.87\times 10^4$  mol  $\text{L}^{-1}\text{cm}^{-1}$ ) and  $\text{ML}_2$  ( $\epsilon = 1.93\times 10^4$  mol  $\text{L}^{-1}\text{cm}^{-1}$ ) whose stability constants are  $5.71\pm 0.01$  and  $5.05\pm 0.02$ , respectively. The mole ratio plot at  $\lambda_{\text{max}} = 400$  nm and molar absorbance spectra of the respective titration spectra are depicted on Fig. 2b and 2c respectively. The corresponding distribution diagrams were obtained by the Hyss 2009 program, a new version of a software program that had previously been used in other reports<sup>50</sup> (Fig.2d).

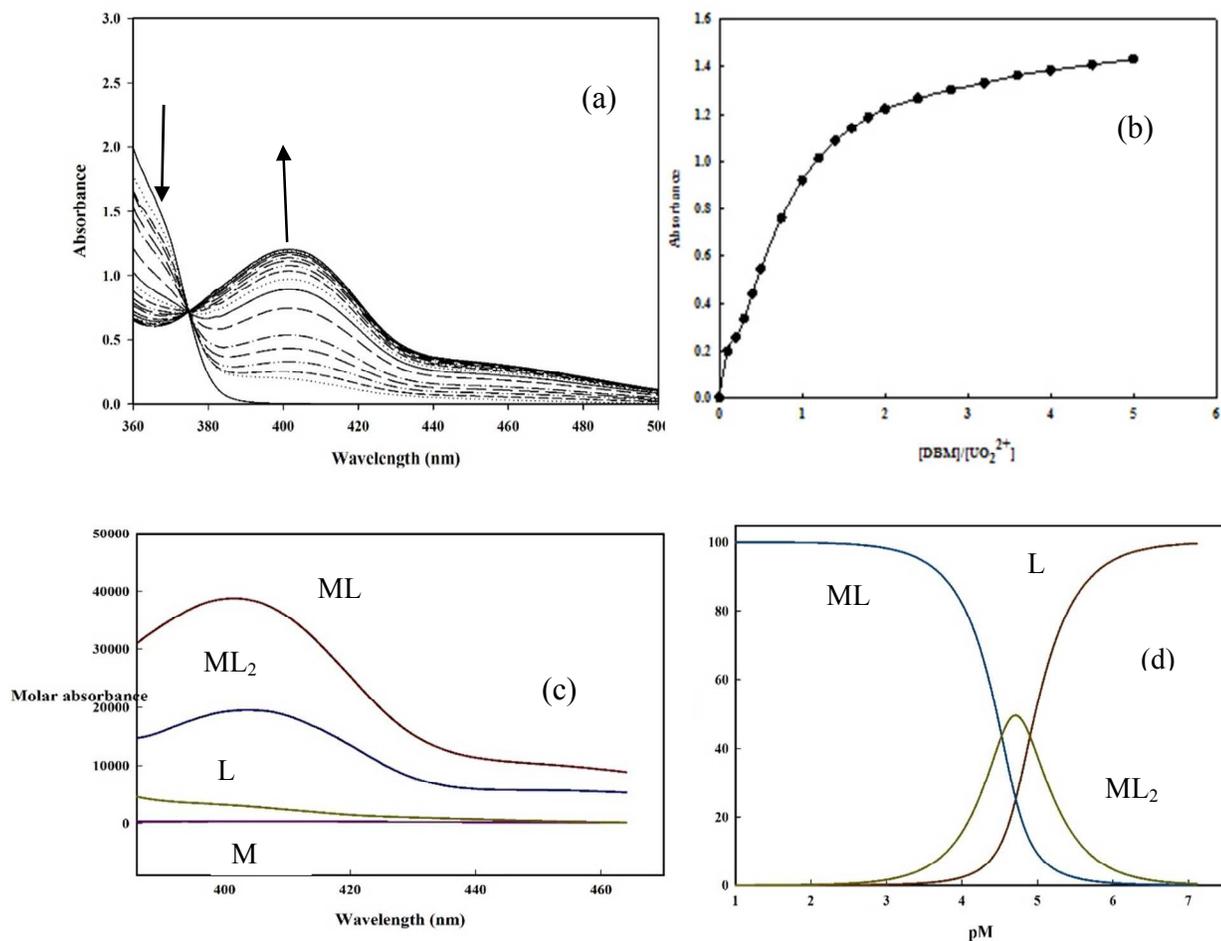


Figure 2. UV-Vis spectra for titration of 2.6 mL DBM ( $3.8 \times 10^{-5} \text{ mol L}^{-1}$ ) with  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of uranyl ion ( $T = 25 \text{ }^\circ\text{C}$ ,  $I = 0.05 \text{ M}$  TEAP) (a), the corresponding absorption mole ratio plot at 400 nm (b), molar absorptance spectra of different species (c) and the corresponding distribution diagram (d).

#### Effect of types of extraction and disperser solvents

The selected extraction solvent must meet several requirements. It must have low volatility, low toxicity, low melting point close room temperature (in the range of  $10\text{--}30 \text{ }^\circ\text{C}$ ), lower density than water and low solubility in water. Moreover, it must be able to extract the desired analytes well. Before selecting the disperser solvent, it is necessary to consider its miscibility with the extraction solvent and aqueous sample and could form a cloudy state when injected with the extractant into water, toxicity and cost. The choices of extraction and disperser solvents types are very important in the SM-LLUA-DLLME. Decanoic acid (extraction solvent) in THF (self-assembly agent and disperser solvent) are the most appropriate system for analytical applications that can made up reversed micelles according to literature<sup>44</sup>. THF plays double role, not only acts as disperser solvent but also causes self-assembly of decanoic acid. Consequently, decanoic acid and THF were selected as extraction and disperser solvent, respectively.

#### Effect of pH

The pH of the sample solution is one of the most important factors in supramolecular solvent microextraction for the formation of the supramolecular solvent and for extraction of target analytes. Therefore, the effect of pH in the range of  $1.5\text{--}4$  on uranyl

ion microextraction was studied. The results depicted in Fig. 3 showed that the absorbance of uranyl ion is highest in pH about 3.5; therefore, pH 3.5 was chosen to achieve high-extraction efficiency.

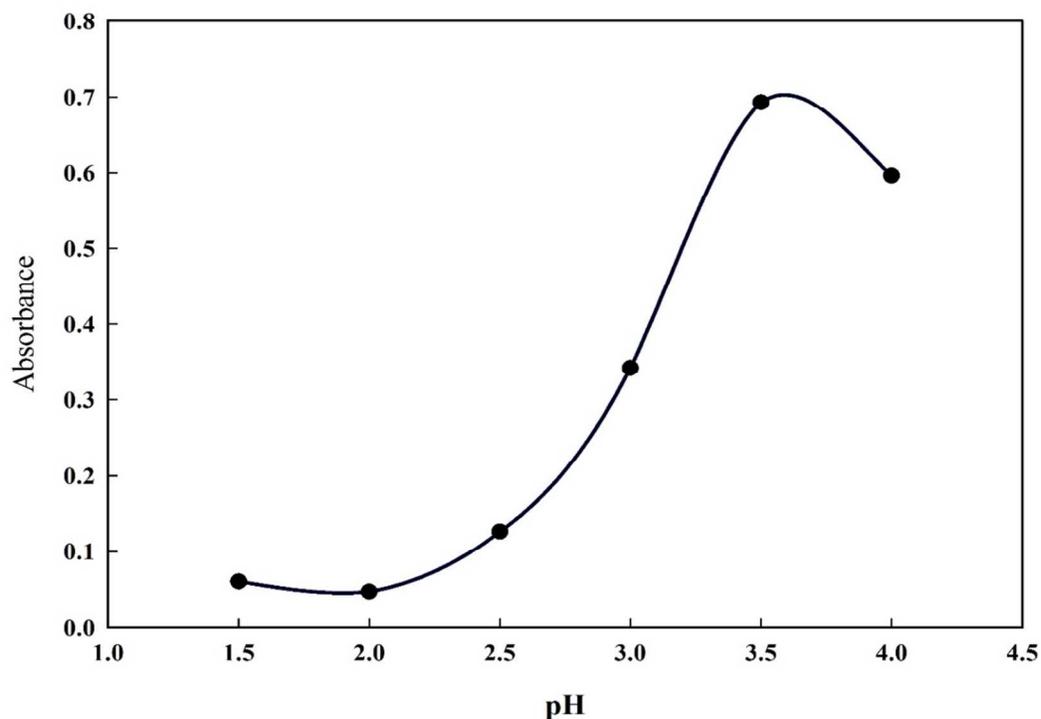


Figure 3. Effect of pH of the solution on the obtained signal by SM-LLUA-DSLLME - spectrophotometry (conditions: Uranyl ion , 125 ng mL<sup>-1</sup>; amount of decanoic acid , 55 mg, salt concentration, 0.15 mol L<sup>-1</sup>, sonication time, 2 min).

#### ***Effect of the weight to volume ratio of Decanoic acid and THF***

The composition and volume of the supramolecular solvent have key role greatly affecting its extraction capability<sup>51</sup>. The supramolecular solvent used was prepared decanoic acid reverse micelles dispersed in a THF/water continuous phase. The effect of changing the decanoic acid /THF ratio on the extraction efficiency of uranyl ion was studied in the range 0.04 to 0.22 mg/ $\mu$ L-1. For this purpose, a set of experiments was done using different amounts of decanoic acid (20–110 mg) and while the volume of THF was fixed as 500  $\mu$ L. The results were shown in Fig. 4. 0.55 mg of decanoic acid was sufficient for quantitative extraction of uranyl ion. After selection of the finest value of decanoic acid, the volume of THF was examined by varying from 250 to 1000  $\mu$ L. 500  $\mu$ L of THF was selected as optimum value. The results shown in Fig. 4 and Fig. 5 point to that higher extraction efficiency for uranyl ion can be attained when the decanoic acid /THF ratio was set at 55/500 mg/ $\mu$ L<sup>-1</sup>.

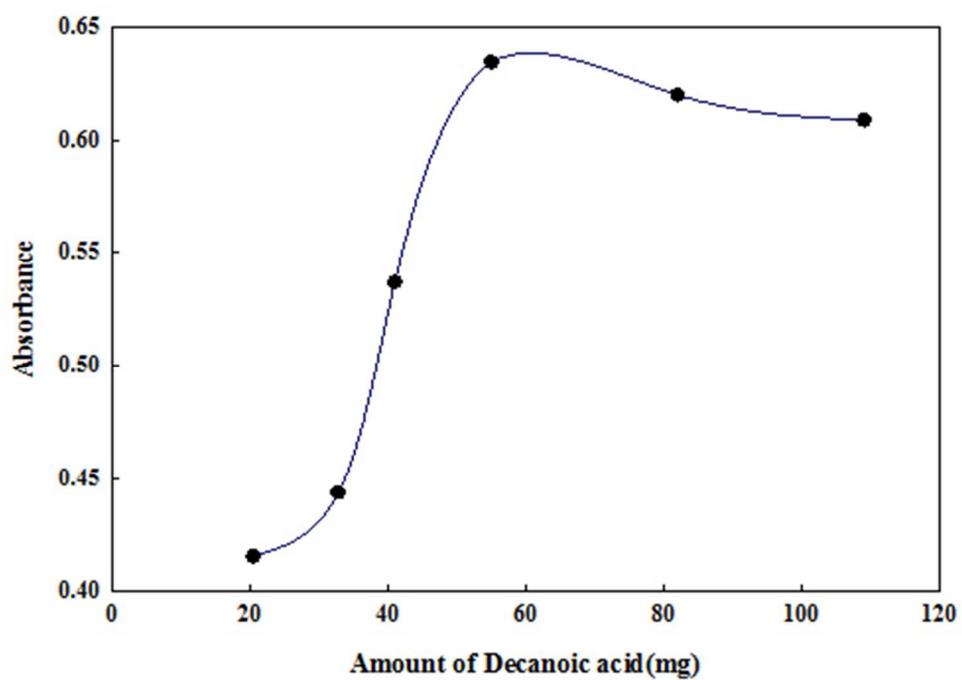


Figure 4. Effect of the amount of decanoic acid (microextraction solvent) on the obtained signal by SM-LLUA-DSSLME - spectrophotometry (conditions: Uranyl ion , 125 ng mL<sup>-1</sup>; volume of THF, 500  $\mu$ L.; pH, 3.5, salt concentration, 0.15 mol L<sup>-1</sup>,sonication time, 2 min.).

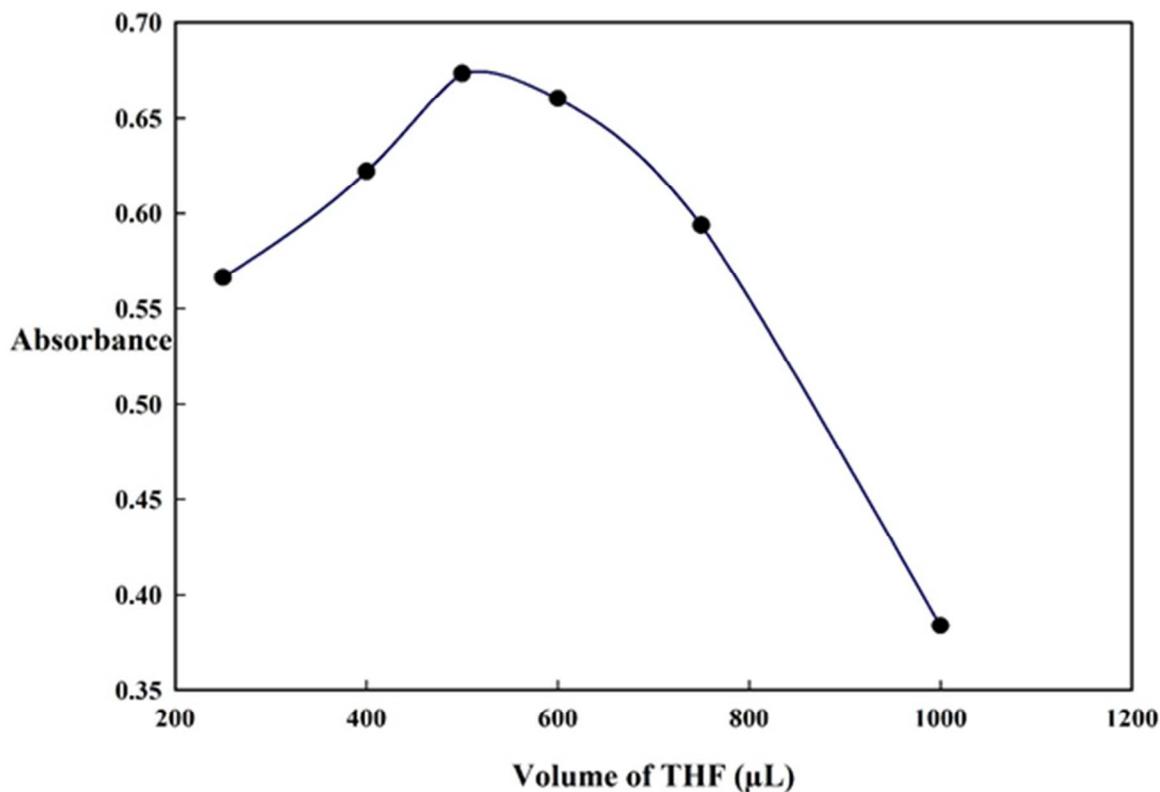


Figure 5. Effect of the volume of THF (disperser solvent) on the obtained signal by SM-LLUA-DSSLME -spectrophotometry (conditions: Uranyl ion, 125 ng mL<sup>-1</sup>; amount of decanoic acid, 55 mg.; pH, 3.5, salt concentration, 0.15 mol L<sup>-1</sup>, sonication time, 2 min).

#### Salt effect

The additions of salt to the aqueous sample can significantly improve the extraction of several analytes in LLE. This is possibly due to the salting out effect. Hence, the series of experiments were performed with addition of salt (KCl) in the range of 0–0.3 mol L<sup>-1</sup> to the spiked aqueous solution (125.00 μg L<sup>-1</sup>, uranyl ion). The extraction efficiency of uranyl ion was increased with increasing the salt concentration from 0 to 0.15 mol L<sup>-1</sup> and thereafter gradually decrease in the trend was observed, shown in Fig. 6. The higher concentration of salt (>0.15 mol L<sup>-1</sup>) can reduce the diffusion rates of the analyte into the organic phase that caused the decrease in extraction efficiency of uranyl ion from aqueous phase to organic phase. Therefore, 0.15 mol L<sup>-1</sup> of salt was added in order to obtain the better extraction of uranyl ion from the sample solution.

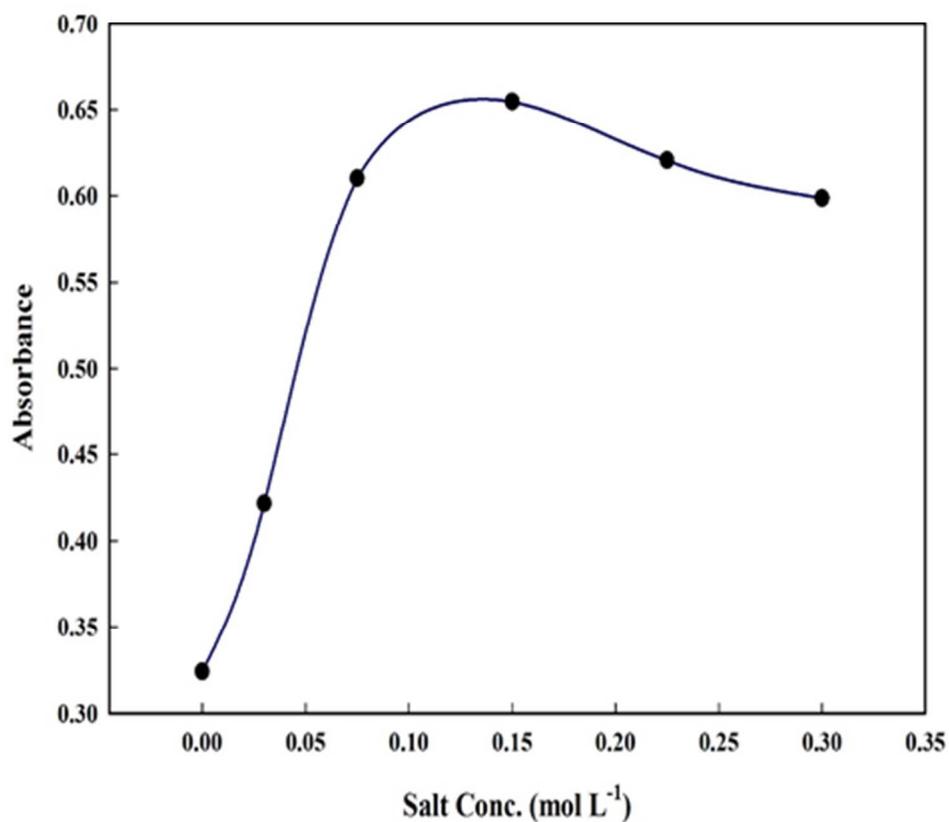


Figure 6. Effect of salt concentration on the obtained signal by SM-LLUA-DSSLME -spectrophotometry (conditions: Uranyl ion , 125 ng mL<sup>-1</sup>; amount of decanoic acid, 55 mg.; amount of decanoic acid, 55 mg.; volume of THF, 0.5mL, pH, 3.5, sonication time, 2 min.).

#### Effect of the extraction time

An optimum extraction time is the minimum time necessary to achieve equilibrium between the aqueous and the organic phase so that the extraction of the analyte, the sensitivity, and the speed of extraction is maximized. The extraction time is defined as interval time between the injection of the THF and decanoic acid and the starting of centrifuge. The effect of extraction time was examined in the range of 0.5 to 10 min with the constant experimental conditions. The obtained results

showed that the extraction time was no significant influence on the signal. Therefore, the method was time-independent, which was the most important advantage of this technique. In this method, the most time-consuming step was the centrifuging of sample solution in the extraction procedure that took about 10 min.

#### Effect of the ultrasonic time

The aim of ultrasound was to achieve the complete contact and mixing between the extraction solvent and the sample solution. Adequate ultrasonic time would improve the extraction efficiency. So an ultrasonic process was applied to accelerate the formation of a fine cloudy dispersive mixture and investigated its influence on extraction performances in various time ranging from 0.0 to 10.0 min. The results (Fig. 7) indicated that the absorbance were obviously increased from 0 to 2.0 min and then only slightly changed when the ultrasonic time was more than 2.0 min. This is due to the finer extractant droplets were formed by ultrasonic vibration in the first 2.0 min and then the fine droplets keep constant even prolonging the ultrasonic time. Moreover, if the ultrasonic time was more than 2.0 min, the volume of organic phase decreases which presumably due to the dispersion of droplets of the extractant in aqueous phase and the volatile loss of the analytes. Therefore, to enable a rapid procedure and stability cloudy solution, a 2.0-min sonication time was used in all subsequent experiments.

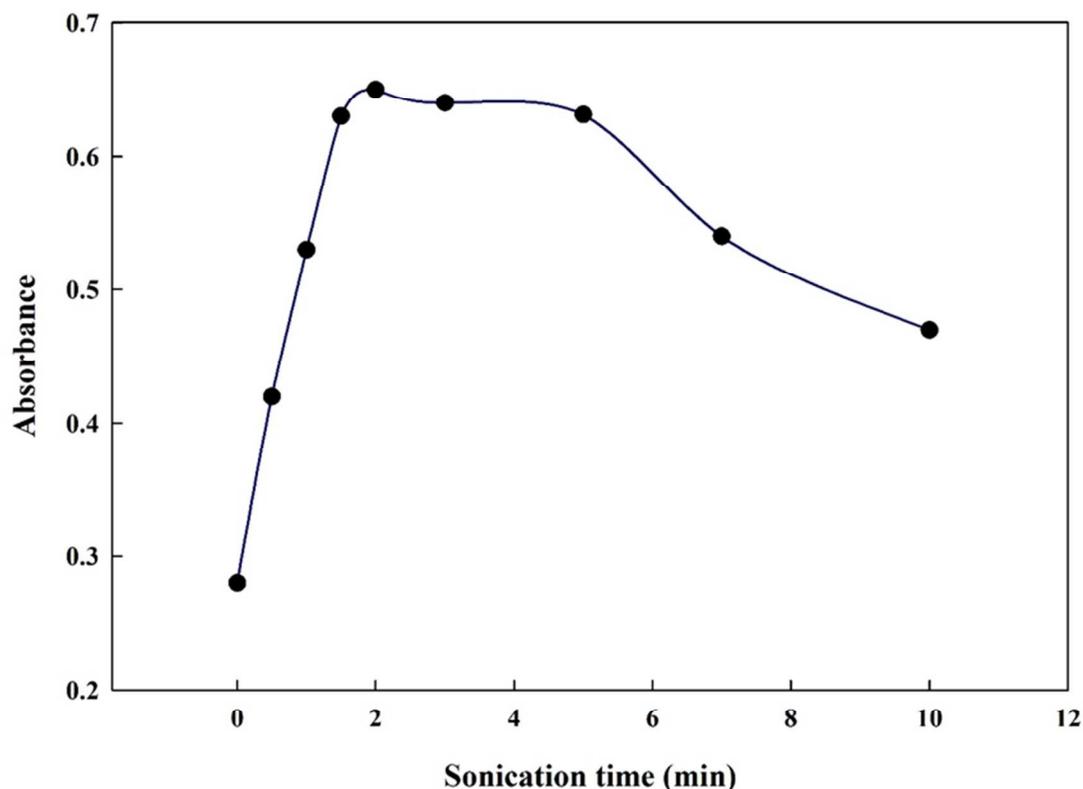


Figure 7. Effect of the sonication time on the obtained signal by SM-LLUA-DSSLME -spectrophotometry (conditions: Uranyl ion , 125 ng mL<sup>-1</sup>; amount of decanoic acid, 55 mg.; volume of THF, 0.5mL, pH, 3.5, salt concentration, 0.15 mol L<sup>-1</sup>).

#### Analytical figures of merits

Under the optimal conditions obtained above, the analytical performance of the proposed method was investigated. The results are listed in Table 1. A calibration curve was obtained under the optimized conditions with a linear dynamic range of 4.00–311.85×10<sup>-6</sup> ng mL<sup>-1</sup> and a correlation coefficient ( $R^2$ ) of 0.9967. The detection limits (defined as the concentration that

produces a signal equivalent to three times the standard deviation of the blank signal) were  $2.00 \text{ ng mL}^{-1}$  (3dB/slope). The relative standard deviation (R.S.D.) for seven replicate measurements of  $125 \text{ ng L}^{-1}$  of uranyl ion was 2.87%. The preconcentration factor that define as ratio of the initial aqueous volume (10 mL) to the final volume ( $300\mu\text{L}$ ) was obtained 33.33. Finally, the calculated enhancement factor was up to 54 on the basis of division of sensitivity after and before extraction (line equations for calibration curves are shown in Table 1).

Table 1. Analytical characteristics of SM-LLUA-DSLLME for determination of uranyl ion

Parameters	Analytical feature
Dynamic range ( $\text{ng mL}^{-1}$ )	4.00-311.85
Calibration equation before microextraction	$y = 0.0817x + 0.0928$ ( $R^2 = 0.9924$ )
Calibration equation after microextraction	$y = 4.4557x + 0.0578$ ( $R^2 = 0.9967$ )
Repeatability (R.S.D.%) (n= 7)	2.87
Limit of detection ( $\text{ng mL}^{-1}$ )	2.00
Enhancement factor	54.53
Preconcentration factor	33.33

#### Interference study

The effect of different cations and anions on the determination of  $125.00 \text{ ng mL}^{-1}$  uranyl ion ion by the proposed method was studied. An ion was considered to be an interfere when it caused a variation greater than  $\pm 5\%$  in the absorbance of the sample. For the determination of  $125.00 \text{ ng mL}^{-1}$  uranyl ion by this method, the foreign ions can be tolerated at the levels given in Table 2. Most of the cations and anions examined do not interfere with the extraction and determination of uranyl ion, and many of them are tolerated at very high levels. However, some of the species interfered on the determination of uranyl ion ion. The interfering effect of these ions was removed in the presence  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  of EDTA as a proper masking agent.

Table 2. Tolerance limit of diverse ions on the determination of 125 ng mL<sup>-1</sup> uranyl ion.

Foreign ion/dye	Tolerable limits of interferences (ng mL <sup>-1</sup> )
Br <sup>-</sup> , I <sup>-</sup> , Na <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup>	100000
Ca <sup>2+</sup> , Mg <sup>2+</sup>	50000
Ba <sup>2+</sup>	12500
Co <sup>2+</sup> , Cd <sup>2+</sup>	10000
Ni <sup>2+</sup> , Cu <sup>2+</sup>	5000
Al <sup>3+</sup> , Fe <sup>3+</sup>	1250 <sup>a</sup>
Th <sup>4+</sup> , Ce <sup>3+</sup>	500 <sup>a</sup>

<sup>a</sup> After addition of 1.0×10<sup>-4</sup> molL<sup>-1</sup> EDTA

### Comparison with other methods

Table 3 compares the characteristic data of the proposed method with other methods for determination of uranyl ion which have been reported in the literature. As shown in Table 3, the analytical characterizes of the proposed method is better or comparable to those in reported methods.

Table 3. Comparison of the proposed method with some preconcentration methods

Method	LOD <sup>(a)</sup> (ng mL <sup>-1</sup> )	R.S.D. <sup>(b)</sup> (%)	Enhancement factor	Linear range (ng mL <sup>-1</sup> )	References
CPE	0.06	3.0	286	0.2–10.0	52
SPE	2.0	2.3	-	5.0–100.0	53
SFODME	0.1	3.7	125	0.8–75.0	54
MA-DLLME	6.7	1.64	135	20.0–350.0	55
SPE	20	1.6	100	-	56
LL-UA-DSSMLLME	2.0	2.87	54	4.0–311.8	This work

(a) Limit of detection

(b) Relative standard deviation

### Analytical application

In order to establish the validity of the procedure, the proposed method was applied to extraction of uranyl ion by standard addition technique in three water samples including tap water, river water and waterfall water. No target analyte was found in these samples. To examine the relative recoveries, water samples spiked at concentrations of 10.0 and 100.0 ng mL<sup>-1</sup> were extracted under the optimized conditions. The results illustrated in Table 4 reveal that recovery of spiked sample at 95% confidence level is satisfactory.

Table 4. Determination of uranyl ion ( $\text{ng mL}^{-1}$ ) in natural water samples by SM-LLUA-DSSLME and calculated recovery in spiked samples.

Sample	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1(a)}$ )	Recovery (%)
	0.00	Nd <sup>(b)</sup>	-
Tap water (Yasouj city)	10.00	10.04±0.04	104.42
	100.00	96.60±0.03	96.60
	0.00	Nd	-
River water (Yasouj city)	10.00	9.80±0.05	98.00
	100.00	102.20±0.03	102.20
	0.00	Nd	-
Waterfall water (Yasouj city)	10.00	10.15±0.02	101.52
	100.00	97.46±0.4	97.46

(a) Mean±standard deviation (n= 3).

(b) Not detected.

## Conclusion

This work has been demonstrated combination of supramolecular based-igandless ultrasonic assisted-dispersion solidification liquid liquid microextraction (SM-LLUA-DSLME) with spectrophotometry provides a method for trace determination of uranyl ion in water samples. The main benefits of this methodology were: minimum use of toxic organic solvent, simplicity, low cost, enhancement of sensitivity, and rapid analysis time. Under the optimized conditions, high enhancement and preconcentration factor were obtained. An ultrasound-assisted process was applied to accelerate the formation of a fine cloudy dispersive solution, which was markedly increased the extraction efficiency and reduced the equilibrium time. The developed method was successfully applied to the preconcentration and determination of uranyl ion in spiked natural water samples and calculated recoveries were satisfactory. Although the obtained results in this work are related to determination of uranyl ion, the method could be easily applied for the determination of other metal ion, using different analytical instruments.

## References

1. L. Domingo, in: M.W. Corn (Ed.), *Handbook of Hazardous Materials*, Academic Press, London, 1993, pp. 705–711.
2. R. Mehra, S. Singh and K. Singh, *Radiat. meas.*, 2007, 42, 441-445.
3. M. R. Jamali, Y. Assadi, F. Shemirani, M. R. M. Hosseini, R. R. Kozani, M. Masteri-Farahani and M. Salavati-Niasari, *Anal. Chim. Acta*, 2006, 579, 68-73.
4. L. Zikovskiy, *J. Radioanal. Nucl. Ch.*, 2006, 267, 695-697.
5. M. Demidova and A. Saprykin, *J. Anal. Chem.*, 2004, 59, 45-49.
6. J. Wang and R. Setiadji, *Anal. Chim. Acta*, 1992, 264, 205-211.
7. R. Djogić and M. Branica, *Anal. Chim. Acta*, 1995, 305, 159-164.
8. T.-L. Ku, K. G. Knauss and G. G. Mathieu, *Deep Sea Res.*, 1977, 24, 1005-1017.
9. J. Holzbecher and D. E. Ryan, *Anal. Chim. Acta*, 1980, 119, 405-408.
10. T. Florence and Y. Farrar, *Anal. Chem.*, 1963, 35, 1613-1616.
11. R. Sieck, J. Richard, K. Iversen and C. Banks, *Anal. Chem.*, 1971, 43, 913-917.
12. S. Marsh, M. Betts and J. Rein, *Anal. Chim. Acta*, 1980, 119, 401-404.
13. X. Shu, Y. Wang, S. Zhang, L. Huang, S. Wang and D. Hua, *Talanta*, 2015, **131**, 198-204.
14. S. K. Gupta, A. Dhobale, M. Kumar, S. Godbole and V. Natarajan, *J. Molec. Struc.*, 2015, **1084**, 89-94.
15. S. Kumar, S. Maji, M. Joseph and K. Sankaran, *Spectrochim. Acta Part A*, 2015, **138**, 509-516.
16. M. N. Alam, N. Rahman and S. N. H. Azmi, *J. Hazard. Mater.*, 2008, **155**, 261-268.
17. A. Niazi, N. Ghasemi, M. Goodarzi and A. Ebadi, *JCCS*, 2007, **54**, 411-418.
18. J. B. Ghasemi and E. Zolfonoun, *Environ. Monit. Assess.*, 2012, **184**, 3971-3981.
19. J. B. Ghasemi and E. Zolfonoun, *Talanta*, 2010, **80**, 1191-1197.
20. J. H. Yoe, F. Will III and R. A. Black, *Anal. Chem.*, 1953, **25**, 1200-1204.
21. A. Safavi, H. Abdollahi, M. Hormozi Nezhad and R. Kamali, *Spectrochim. Acta Part A*, 2004, **60**, 2897-2901.
22. H. S. Ferreira, M. de Almeida Bezerra and S. L. C. Ferreira, *Microchim. Acta*, 2006, **154**, 163-167.
23. S. Seyhan, M. Merdivan and N. Demirel, *J. Hazard. Mater.*, 2008, **152**, 79-84.
24. S. Katragadda, H. Gesser and A. Chow, *Talanta*, 1997, **44**, 1865-1871.
25. G. D. Saunders, S. P. Foxon, P. H. Walton, M. J. Joyce and S. N. Port, *Chem. Commun.*, 2000, 273-274.
26. R. Say, A. Ersöz and A. Denizli, *Sep. Sci. Technol.*, 2003, **38**, 3431-3447.
27. M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr. A*, 2006, **1116**, 1-9.
28. S. Berijani, Y. Assadi, M. Anbia, M.-R. Milani Hosseini and E. Aghaee, *J. Chromatogr. A*, 2006, **1123**, 1-9.
29. L. M. Ravelo-Pérez, J. Hernández-Borges, M. Asensio-Ramos and M. Á. Rodríguez-Delgado, *J. Chromatogr. A*, 2009, **1216**, 7336-7345.

30. C. Cortada, L. Vidal, R. Pastor, N. Santiago and A. Canals, *Anal. Chim. Acta*, 2009, **649**, 218-221.
31. M. R. Khalili Zanjani, Y. Yamini, S. Shariati and J. Å. Jönsson, *Anal. Chim. Acta*, 2007, **585**, 286-293.
32. H. Xu, Z. Ding, L. Lv, D. Song and Y.-Q. Feng, *Anal. Chim. Acta*, 2009, **636**, 28-33.
33. M.-I. Leong and S.-D. Huang, *J. Chromatogr. A*, 2008, **1211**, 8-12.
34. L. Lili, H. Xu, D. Song, Y. Cui, S. Hu and G. Zhang, *J. Chromatogr. A*, 2010, **1217**, 2365-2370.
35. F. Kamarei, H. Ebrahimzadeh and A. A. Asgharinezhad, *J. Sep. Sci.*, 2011, **34**, 2719-2725.
36. A. Ballesteros-Gómez, S. Rubio and D. Pérez-Bendito, *J. Chromatogr. A*, 2009, **1216**, 530-539.
37. S. García-Fonseca, A. Ballesteros-Gómez, S. Rubio and D. Pérez-Bendito, *J. Chromatogr. A*, 2010, **1217**, 2376-2382.
38. S. Jafarvand and F. Shemirani, *Anal. Methods*, 2011, **3**, 1552-1559.
39. M. Moradi, Y. Yamini, F. Rezaei, E. Tahmasebi and A. Esrafil, *Analyst*, 2012, **137**, 3549-3557.
40. M. Moradi, Y. Yamini, M. Tayyebi and H. Asiabi, *Anal. Bioanal. Chem.*, 2013, **405**, 4235-4243.
41. F. Rezaei, Y. Yamini, M. Moradi and B. Daraei, *Anal. Chim. Acta*, 2013, **804**, 135-142.
42. F. Rezaei, Y. Yamini, M. Moradi and B. Ebrahimpour, *Talanta*, 2013, **105**, 173-178.
43. F.-J. Ruiz, S. Rubio and D. Pérez-Bendito, *Anal. chem.*, 2006, **78**, 7229-7239.
44. F.-J. Ruiz, S. Rubio and D. Pérez-Bendito, *Anal. chem.*, 2007, **79**, 7473-7484.
45. E. M. Costi, M. D. Sicilia and S. Rubio, *J. Chromatogr. A*, 2010, **1217**, 1447-1454.
46. S. Z. Mohammadi, D. Afzali, M. A. Taher and Y. M. Baghelani, *Talanta*, 2009, **80**, 875-879.
47. Ç. A. Şahin and I. Durukan, *Talanta*, 2011, **85**, 657-661.
48. S. Z. Mohammadi, D. Afzali and Y. M. Baghelani, *Anal. Chim. Acta*, 2009, **653**, 173-177.
49. P. Gans, A. Sabatini and A. Vacca, *Talanta*, 1996, **43**, 1739-1753.
50. A. Shokrollahi, A. Abbaspour, M. Ghaedi, A. N. Haghighi, A. Kianfar and M. Ranjbar, *Talanta*, 2011, **84**, 34-41.
51. A. Ballesteros-Gómez, M. D. Sicilia and S. Rubio, *Anal. Chim. Acta*, 2010, **677**, 108-130.
52. T. Madrakian, A. Afkhami, A. Mousavi, *Talanta*, 2007, **71**, 610-614.
53. Y. Liu, X. Cao, Z. Le, M. Luo, W. Xu, G. Huang, *J. Braz. Chem. Soc.* 2010, **21**, 533-540.
54. A. Ghiasvand, N. Heidari, P. Hashemi, *Anal. Methods*, 2014, **6**, 5992-5998.
55. A. Niazi, N. Khorshidi, P. Ghaemmaghami, *Spectrochim. Acta Part A*, 2015, **135**, 69-75.
56. D. Dojozan, M. H. Pournaghi-Azar and J. Toutounchi-Asr, *Talanta*, 1998, **46**, 123-128.

