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Article

Ligand-Less *in situ* Surfactant-Based Solid Phase Extraction for Preconcentration of Cobalt, Nickel and Zinc from Water Samples Prior to their FAAS Determination

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Uma nova e simples extração de fase sólida (LL-ISSPE), baseada em surfactante, sem ligantes e *in situ* foi desenvolvida para a pré-concentração de cobalto, níquel e zinco em amostras de água. Neste método, um surfactante catiônico contendo um grupo alquila (brometo de *n*-dodeciltrimetilamônio) é dissolvido na amostra aquosa e então um agente adequado de par iônico (ClO_4^-) é adicionado. Devido à interação entre o surfactante e o agente de par iônico, partículas sólidas são formadas e o precipitado do analito foi adsorvido na superfície do adsorvente. Após a centrifugação, o sedimento é dissolvido em 3,0 mL HNO_3 em etanol e então aspirado diretamente na chama do espectrômetro de absorção atômica em chama. Variáveis que afetam a eficiência da extração, como pH, concentrações de surfactante e par iônico, quantidade de CO_3^{2-}, tempo de extração, tempo e razão da centrífuga foram otimizados. Os limites de detecção para Co(II), Ni(II) e Zn(II) baseados em $3S_b/m$ foram 1,0, 1,5 e 0,3 ng mL^{-1}, respectivamente. O método proposto foi aplicado com sucesso na determinação dos íons de cobalto, níquel e zinco em amostras de água reais.

A new simple and rapid ligand-less *in situ* surfactant-based solid phase extraction (LL-ISSPE) was developed for preconcentration of cobalt, nickel and zinc in water samples. In this method, a cationic surfactant containing a proper alkyl group (*n*-dodecyltrimethylammonium bromide) is dissolved in the aqueous sample and then a proper ion-pairing agent (ClO_4^-) is added. Due to the interaction between surfactant and ion-pairing agent, solid particles are formed and precipitate of the analytes was adsorbed on surface of sorbent. After centrifugation, the sediment is dissolved in 3.0 mL HNO_3 in ethanol and then aspirated directly into the flame atomic absorption spectrometer. Variables affecting the extraction efficiencies such as pH, concentrations of surfactant and ion pair, CO_3^{2-} amount, extraction time, time and rate of centrifuge were optimized. Detection limits for Co(II), Ni(II) and Zn(II) based on $3S_b/m$ were 1.0, 1.5 and 0.3 ng mL^{-1}, respectively. The proposed method has been successfully applied for the determination of cobalt, nickel and zinc ions in real water samples.

Keywords: ligand-less *in situ* surfactant-based solid phase extraction, preconcentration, cobalt, nickel, zinc determination

Introduction

In general, potentially toxic metal ions are toxic, non-biodegradable, and tend to be accumulated in vital human organs. Therefore, the determination of trace potentially toxic metal species in environmental samples is nowadays made more demanding because of several metal species that have to be monitored the quality.[1]

Several atomic spectrometric techniques such as flame atomic absorption spectrometry (FAAS),[2-4] electrothermal atomic absorption spectrometry,[5,6] ultraviolet visible absorption spectrometry,[7,8] inductively coupled plasma mass spectrometry,[9] inductively coupled plasma optical emission spectrometry,[10] and voltammetric techniques[11] had been developed for the determination of potentially toxic metal species in different environmental samples.

FAAS with its relative low cost and good analytical performance is one of the main instruments in the research laboratories for determination of potentially toxic

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metal species such as zinc, nickel and cobalt. Accurate determination of trace potentially toxic metal species by FAAS is a challenge to analytical chemists because of their low concentrations. In addition, the influence of the matrix is also paramount. In order to solve these important problems, separation-enrichment techniques such as: liquid-liquid extraction,[12] solid phase extraction (SPE),[7,10,13] cloud point extraction,[11,14] coprecipitation,[15] liquid-liquid microextraction,[16] ultrasound-assisted extraction[17] and dispersive liquid-liquid microextraction[18,19] have been used by researchers around the world.

Recently Shemirani and Yousefi[20] demonstrated a surfactant-based SPE mode termed *in situ* surfactant-based solid phase extraction. In this method, a cationic surfactant containing a proper alkyl group was dissolved in the aqueous sample and then a proper ion-pairing agent was added. Due to the interaction between the surfactant and ion-pairing agent, very fine solid particles were formed.

In the present work, we have demonstrated a new *in situ* surfactant-based solid phase extraction that is simple, rapid, safe and efficient. In this method, termed ligand-less *in situ* surfactant-based solid phase extraction, due to interaction between surfactant and ion-pairing agent, very fine solid particles were formed. The adsorption mechanism in this method is similar to traditional coprecipitation. After formation of very fine solid particles, precipitate containing analyte was quickly adsorbed on surface of fine solid particles, because of the high surface area between fine solid particles and the aqueous phase. After centrifugation, the solid particles were sedimented at the bottom of the centrifuge tube. After this, the aqueous phase was removed by decantation of the centrifuge tube. Finally, the sedimented sorbent can be leached with acid in order to recover the analyte.

Experimental

Instrumentation

An atomic absorption spectrometer (SensAA GBC, Dandenong, Australia) equipped with deuterium background correction and air-acetylene burner was used for absorbance measurements. Cobalt, nickel and zinc hollow cathode lamps were used as light sources at wavelengths of 240.7, 232.0 and 213.9 nm, respectively. The operating parameters were set according to the manufacturer's recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain a maximum absorbance signal, while aspirating a sample. A pHmeter (Metrohm 692, Herisau, Switzerland) and a tabletop centrifuge (K240, Centurion West Sussex, United Kingdom) were used.

Reagents and solutions

All solutions were prepared from analytical grade reagents, and the water used in the process was from a Milli-Q purification system (Millipore, Bedford, MA, USA). Before use, all laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution, rinsed with deionized water and dried in an oven at 100 °C. Stock solutions of cobalt, nickel and zinc at concentration of 1000.0 mg L^{-1} were purchased from Merck (Darmstadt, Germany). A solution of 0.02 mol L^{-1} $KClO_4$ (JHD, Guangdong Guanghua Chemical Factory Co., Shantou, Guangdong, China) was prepared by dissolving appropriate amount of $KClO_4$ in deionized water. A solution of 0.2 mol L^{-1} *n*-dodecyltrimethylammonium bromide (DTAB) (Sigma-Aldrich, Munich, Germany) was prepared in deionized water and ethanol. Solutions of various metal salts (1000 mg L^{-1}) were used to study the interference of anions and cations.

Sample preparation

Wastewater, river water and well water samples were collected in acid leached polyethylene bottles. River water samples were collected from two local river (Kohpayeh and Shahdad, Kerman, Iran), and wastewater samples were from Bahonar copper factory (Kerman, Iran) and the copper factory in Sarcheshmeh (Rafsanjan, Iran). A well water sample was collected from the university ground water well (Kerman, Iran). Mineral water was purchased from a local supermarket. The only pretreatment was acidification to pH 2 with HNO_3, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered through a cellulose membrane of 0.45 µm pore size (Millipore) in order to prevent metals precipitation by colloidal sized particulate suspended in water.

Two certified reference materials (CRMs) furnished by the National Institute for Environment Studies (NIES) No. 1 pepperbush and NIES No. 7 tea leave have been analyzed. Approximately 0.5 g of NIES No. 1 and NIES No. 7 were weighted accurately into two Teflon cup and dissolved in concentrated nitric acid (ca. 10 mL) with heating on a water bath. The solutions were cooled, diluted and filtered. The filtrates were made to 250.0 mL with deionized water in two calibrated flask.

Ligand-less *in situ* surfactant-based solid phase extraction (LL-ISSPE) procedure

Forty milliliters of the sample solution were taken in a screw cap glass test tube and 2 mL phosphate buffer

0.2 mol L^{-1}, and 2.0 mL Na_2CO_3 0.5 mol L^{-1} was added to it and mixed. Then, 2 mL DTAB (0.2 mol L^{-1}) was added, the mixture was manually shook and 2 mL $KClO_4$ (0.02 mol L^{-1}) was added. A cloudy suspension of solid particles dispersed in the solution was formed. The cloudy solution was centrifuged at 3200 rpm for 5 min and the aqueous phase was decanted. The sediment was dissolved in 3.0 mL of 1.0 mol L^{-1} HNO_3, in ethanol, and the solution was aspirated directly into the flame of the atomic absorption spectrometer.

Results and Discussion

In this study, combination of *in situ* surfactant-based solid phase extraction with FAAS was developed for determination of trace amounts of cobalt, nickel and zinc ions. Due to interaction between DTAB and $KClO_4$, very fine solid particles were formed and a cloudy solution was formed. After formation of cloudy solution, nickel, cobalt and zinc hydroxides were adsorbed on surface of solid particles quickly. After centrifugation, the solid particles were sedimented at the bottom of the centrifuge tube, and the aqueous phase was decanted. After this, the solid particles were dissolved in 3.0 mL of 1.0 mol L^{-1} HNO_3 in ethanol, and the solution was aspirated directly into the flame of AAS. In order to obtain the best conditions, several parameters affecting the performance of the LL-ISSPE procedure such as volumes of DTAB, $KClO_4$ and Na_2CO_3, pH and potentially interfering ions were optimized. All experiments were performed using an aqueous solution containing 4.0 µg of cobalt, nickel and zinc.

Selection of appropriate anion

In LL-ISSPE procedure, the analyte ions should react with an appropriate anion. Therefore, selection of anion is very critical for LL-ISSPE procedure. Thus, several experiments were performed by adding 2 mL of various anions such as Cl^-, CrO_4^{2-}, CN^- and CO_3^{2-} (0.5 mol L^{-1}), while keeping the other variable constant. The results showed recoveries higher than 90% for all analyte ions obtained with CO_3^{2-}. Therefore, Na_2CO_3 (0.5 mol L^{-1}) was selected for the recovery of cobalt, nickel and zinc ions in all subsequent experiments.

Effect of pH on adsorption

In order to evaluate its effect, the pH of the sample solutions were adjusted in a range of 6-12 using dilute HCl and NaOH and the LL-ISSPE procedure was applied. As shown in Figure 1, the recovery of the analyte ions increased with increase in pH and the quantitative recoveries for Co(II), Ni(II) and Zn(II) ions obtained at the pH range 10-11. At higher pHs, Zn(II) ions may be changed to $Zn(OH)_4^{2-}$, therefore, the recovery of Zn(II) ions decreased. With respect to these results, pH 10.5 was selected as optimum pH in all subsequent works for preconcentration of the analyte ions. Therefore, in subsequent studies, the pH was maintained at approximately 10.5 using phosphate buffer 0.2 mol L^{-1}.

After the optimum pH was found (pH 10.5, phosphate buffer), the volume of buffer was also studied. The results showed that addition of 1-4 mL of buffer did not have any effect on the recovery of the analyte ions. Therefore, 2 mL phosphate buffer was used in all subsequent experiments.

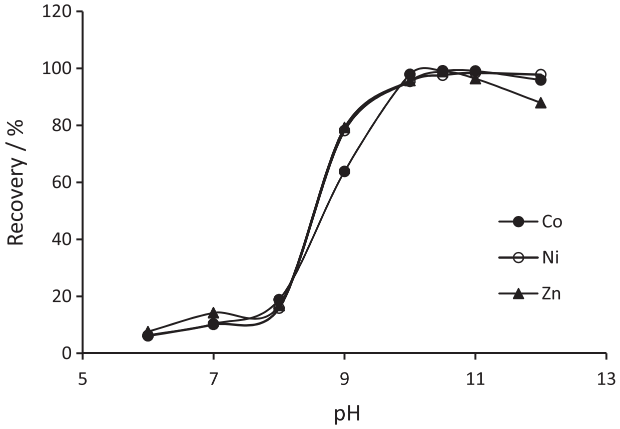

Figure 1. Effect of pH on the recovery of the analyte ions. Conditions: Co(II), Ni(II) and Zn(II), 4.0 µg; buffer 0.2 mol L^{-1}, 2 mL; Na_2CO_3 0.5 mol L^{-1}, 2 mL; DTAB 0.2 mol L^{-1}, 2 mL; $KClO_4$ 0.02 mol L^{-1}, 2 mL; centrifuge time, 5 min; centrifuge speed, 3200 rpm.

Effect of Na_2CO_3 volume

The effect of Na_2CO_3 volume on the recovery of the analyte ions was studied in a range of 0.5 to 4 mL, while keeping the other variable constant. The results showed that the recovery of the analyte ions increased from 0.5 to 1 mL and then remained constant. When a small volume of Na_2CO_3 was used, CO_3^{2-} was not enough for complete extraction and therefore, 2 mL Na_2CO_3 was chosen for the subsequent experiments.

Effect of surfactant concentration

In LL-ISSPE procedure, the amount of surfactant not only affected the extraction efficiency, but also the volume of surfactant-rich phase. Therefore, the effect of DTAB volume on the recovery of the analyte ions was studied in the range 0.5-3.0 mL (0.2 mol L^{-1}). The results showed that, the recovery of the analyte ions increased with the increase of surfactant volume from 0.5 to 1.5 mL and then remained constant. When a small volume of surfactant was used, sorbent was not enough for complete extraction. Therefore, 2 mL DTAB was chosen for the subsequent experiments.

Effect of ion-pairing agent volume

The volume of ion-pairing agent is one of the important factors in LL-ISSPE procedure. It predicted that by increasing the amount of $KClO_4$, more solid sorbent was formed and, therefore, recovery increased. For this purpose, the effect of $KClO_4$ volume was investigated in the range of 0.5-3.0 mL. The results showed that recovery of the analyte ions increased by increasing the $KClO_4$ volume up to 1.5 mL and then remained constant. So, 2 mL $KClO_4$ (0.02 mol L^{-1}) was selected for the subsequent experiments.

Effect of equilibrium time

The recovery of the analyte ions depended on the contact time of precipitate with the solid particles. On the other hand, fast sample preparation procedure is preferred in order to increase the sample throughput of the technique. Therefore, the effect of the equilibrium time from 1 to 10 min on the recovery percent was investigated. The results showed that quantitative recovery was obtained in the first minute. Therefore, the equilibrium time has no effect on the recovery percent of the analyte ions. The fast equilibrium is attributed to the high surface area of the sorbent particles.[20]

Effect of centrifuge time and rate

The effect of centrifuge rate on the recovery of the analyte ions was also studied in a range of 500-3500 rpm for 10 min. It was observed that, the recovery of the analyte ions increased with increase of centrifuge rate from 500 to 3000 rpm, and no significant difference was observed above 3000 rpm. Therefore, a centrifuge rate of 3200 rpm was selected in this study. The effect of centrifugation time on the recovery of the analyte ions was also studied in a range of 5-15 min at 3200 rpm. The results showed that a centrifuge time of 5 min was sufficient for complete separation of the sorbent particles. Therefore, a centrifuge time of 5 min at 3200 rpm was selected for the entire procedure.

Effect of foreign ions

The influence of matrix ions was also investigated. For this purpose, a fixed amount of Co(II), Ni(II) and Zn(II) ions was taken and different amounts of foreign ions were added to it, then, LL-ISSPE procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding ± 5% in the determination of the analyte ions. The results were given in Table 1 and showed that a large number of anions and cations used, have no considerable effect on the determination of the analyte ions.

Table 1. Tolerance limit of interference ions

Foreign ions	Interference/analyte ions ratio		
	Cobalt	Nickel	Zinc
$H_2PO_4^-$, HPO_4^{2-}	> 10000	> 10000	> 10000
Ca^{2+}, Mg^{2+}	> 2000	> 2000	> 2000
K^+, Na^+	> 2000	> 2000	> 2000
Al^{3+}	600	600	400
Ag^+	400	300	500
Cu^{2+}	200	250	250
Cr^{3+}	400	400	400
Fe^{3+}	300	400	300
Mn^{2+}	500	300	400
Cd^{2+}	400	400	300
Pb^{2+}	400	300	300

Conditions were the same as Figure 1.

Figures of merit

Under the optimized conditions, calibration curves were constructed for the determination of cobalt, nickel and zinc ions according to the LL-ISSPE procedure. For a sample volume of 40.0 mL, the calibration curves exhibited linearity over the range 3.0 to 300.0 ng mL^{-1} for cobalt, 5.0 to 250.0 ng mL^{-1} for nickel and 1.0 to 100.0 ng mL^{-1} for zinc. Detection limits based on three times the standard deviation of the blank divided by the slope of analytical curve ($3S_b/m$) for Co(II), Ni(II) and Zn(II) ions were 1.0, 1.5 and 0.3 ng mL^{-1}, respectively. Seven replicate determinations of a mixture of 50.0 ng mL^{-1} Co(II), Ni(II) and Zn(II) gave relative standard deviations ± 1.9%, ± 2.2% and ± 2.5%, respectively. The enrichment factors were calculated as the ratio of the analytical signal of analyte ions obtained after and before extraction. The enrichment factors (EF) for cobalt, nickel and zinc ions were 37.6, 35.4 and 39.6, respectively.

Accuracy of the method

The accuracy of the LL-ISSPE procedure has been studied by determination of Co(II), Ni(II) and Zn(II) ions in NIES No. 1 pepperbush and NIES No. 7 tea leaves.

Results were given in Table 2. It was found that there is no significant difference at the 95% confidence level between results obtained by the LL-ISSPE procedure and the certified values. These results are in agreement with certified values and demonstrated that the proposed method have good accuracy.

Table 2. Determination of the analyte ions in certified reference materials

Sample	Certified value / ($\mu g\ g^{-1}$)	Found[a] / ($\mu g\ g^{-1}$)
NIES, No. 1 Pepperbush	Co: 23.0 ± 3.0 Ni: 8.7 ± 0.6 Zn: 340 ± 20	Co: 22.7 ± 1.0 Ni: 8.9 ± 0.4 Zn: ALR[b]
NIES, No. 7 Tea leaves	Co: 0.12 Ni: 6.5 Zn: 33	Co: BLR[c] Ni: 6.4 ± 0.3 Zn: 32.4 ± 1.4

[a]Mean ± standard deviation (n = 3); [b]above linear range (concentration of Zn(II) is higher than linear range); [c]below linear range (concentration of Co(II) is lower than linear range).

Analysis of water sample

In order to test the possibility of applying the LL-ISSPE procedure to water samples with different matrices, further experiments were done on tap; river, well and mineral water. The recovery of the analyte ions from samples spiked with standard solutions was also studied. The results were given in Table 3 and showed that, the added ions can be quantitatively recovered from the samples by the LL-ISSPE procedure. As can be seen, a good agreement between added and detected concentration of the analyte ions was obtained.

In addition, for evaluating the accuracy of the LL-ISSPE procedure, a comparison between the obtained results by LL-ISSPE procedure and ICP-OES was performed. The performed *t*-test at 95% confidence level showed that there was no significant difference between the obtained results of the presented LL-ISSPE procedure and the ICP-OES method.

Comparison of LL-ISSPE procedure with other reported methods

A comparison of LL-ISSPE procedure with other reported methods for determination of Co(II), Ni(II) and Zn(II) ions was given in Table 4.[21-24] As shown in Table 4, the detection limits of the LL-ISSPE procedure, was better than some of the other reported methods.[22,24] The relative standard deviations of the LL-ISSPE procedure were lower than some of the other reported methods.[21,22,24]

Conclusions

In the present study, a new mode of *in situ* surfactant-based solid phase extraction was developed for preconcentration of Co(II), Ni(II) and Zn(II) ions prior to their FAAS determination without any chelating agent. This method was efficient, fast, simple, inexpensive and environment friendly. The accuracy of the method was assessed through recovery experiments and reference materials. In this method, low detection limits and good precisions were obtained. The LL-ISSPE procedure possesses advantages over existing SPE: (*i*) the sorbent was formed in sample

Table 3. Determination of the analyte ions in water samples

Sample	Found[a] by LL-ISSPE procedure / (ng mL^{-1})	Found by ICP-OES / (ng mL^{-1})	Added / (ng mL^{-1})	Found by LL-ISSPE procedure / (ng mL^{-1})	Found by ICP-OES / (ng mL^{-1})	Recovery / %
Kohpayeh river water (Kohpayeh, Kerman)	Co: 6.5 ± 0.3 Ni: 7.4 ± 0.3 Zn:18.3 ± 0.8	Co: 6.7 ± 0.3 Ni: 7.3 ± 0.4 Zn:18.0 ± 0.9	Co: 20.0 Ni: 20.0 Zn: 20.0	Co: 25.8 ± 1.1 Ni: 27.0 ± 1.2 Zn: 38.6 ± 0.8	Co: 26.4 ± 1.0 Ni: 26.7 ± 1.3 Zn: 37.7 ± 0.9	96.5 98.0 101.5
Shoor river (Shahdad, Kerman)	Co: 7.1 ± 0.4 Ni: 6.9 ± 0.2 Zn: 24.7 ± 1.0	Co: 6.9 ± 0.3 Ni: 7.2 ± 0.3 Zn: 25.0 ± 0.9	Co: 20.0 Ni: 20.0 Zn: 20.0	Co: 26.6 ± 1.2 Ni: 27.5 ± 1.3 Zn: 43.9 ± 1.9	Co: 27.0 ± 1.0 Ni: 26.7 ± 1.1 Zn: 44.7 ± 1.5	97.5 103.0 96.0
Tap water (drinking water of Kerman)	Co: 4.3 ± 0.2 Ni: BLR[b] Zn: 7.0 ± 0.3	Co: 4.5 ± 0.2 Ni: ND[c] Zn: 7.3 ± 0.4	Co: 20.0 Ni: 20.0 Zn: 20.0	Co: 24.7 ± 1.0 Ni: 20.7 ± 0.8 Zn: 26.3 ± 1.2	Co: 25.4 ± 0.9 Ni: 21.4 ± 0.8 Zn: 26.8 ± 1.0	102.0 103.5 96.5
Well water (Payame Noor University)	Co: 4.3 ± 0.2 Ni: 7.9 ± 0.4 Zn: 27.9 ± 1.2	Co: 4.0 ± 0.2 Ni: 7.5 ± 0.3 Zn: 27.4 ± 1.1	Co: 20.0 Ni: 20.0 Zn: 20.0	Co: 25.0 ± 1.1 Ni: 27.6 ± 1.2 Zn: 47.1 ± 1.0	Co: 24.3 ± 1.0 Ni: 26.8 ± 0.9 Zn: 48.5 ± 1.8	103.5 98.5 96.0
Mineral water	Co: BLR Ni: BLR Zn: 5.4 ± 0.2	Co: ND Ni: ND Zn: 5.7 ± 0.3	Co: 20.0 Ni: 20.0 Zn: 20.0	Co: 20.8 ± 0.7 Ni: 20.5 ± 0.8 Zn: 25.8 ± 0.4	Co: 21.3 ± 0.8 Ni: 20.9 ± 0.9 Zn: 26.4 ± 0.9	104.0 102.5 102.0

[a]Mean ± standard deviation (n = 4); [b]below linear range; [c]not detected.

Table 4. Comparison of the reported methods in the literature with the LL-ISSPE procedure

Detection method	Preconcentration factor	Linear range / (ng mL^{-1})	RSD / %	Detection limit / (ng mL^{-1})	Ref.
FAAS	20	Co: – Ni: – Zn: –	Co: 2.2 Ni: 2.1 Zn: 1.9	Co: – Ni: – Zn: –	21
EDXRFS[a]	–	Co: 2.0-400.0 Ni: 2.0-400.0 Zn: 2.0-200.0	Co: 6.4 Ni: 12.8 Zn: 7.1	Co: 1.9 Ni: 2.2 Zn: 2.5	22
UV-Vis	–	Co: 1000-20000 Ni: – Zn: 1000-10000	Co: – Ni: – Zn: –	Co: – Ni: – Zn: –	23
FAAS	4	Co: – Ni: – Zn: –	Co: 2.7 Ni: 3.5 Zn: 2.3	Co: 5.0 Ni: 7.5 Zn: 2.5	24
FAAS	13	Co: 3.0-300.0 Ni: 5.0-250.0 Zn: 1.0-100.0	Co: 1.9 Ni: 2.2 Zn: 2.5	Co: 1.0 Ni: 1.5 Zn: 0.3	This work

[a] Energy dispersive X-ray fluorescence spectrometry.

solution, (*ii*) the sorbent and support were the same, (*iii*) the cost of the method was low, (*iv*) the sorbent was a surfactant, which is safe, (*v*) small particle size and large surface area of the sorbent lead to short extraction time and high extraction recovery and (*vi*) LL-ISSPE method excludes the use of chelating agents.

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References

1. Duran, C.; Senturk, H. B.; Elci, L.; Soylak, M.; Tufekci, M.; *J. Hazard. Mater.* **2009**, *162*, 292.
2. Başbug, B.; Tokalioglu, S.; *J. Braz. Chem. Soc.* **2013**, *24*, 106.
3. Ebrahimi, B.; Bahar, S.; Moedi, S. E.; *J. Braz. Chem. Soc.* **2013**, *24*, 1932.
4. Başbug, B.; Tokalioglu, S.; *J. Braz. Chem. Soc.* **2013**, *24*, 523.
5. Burguera-Pascu, M.; Rodriguez-Archilla, A.; Luis Burguera, J.; Burguera, M.; Rondon, C.; Carrero, P.; *Anal. Chim. Acta* **2007**, *600*, 214.
6. Pekiner, O. Z.; Naeemullah, N.; Tuzen, M.; *J. Ind. Eng. Chem.* **2014**, *20*, 1825.
7. Janardhan Reddy, K.; Rajesh Kumar, J.; Ramachandraiah, C.; Thriveni, T.; Varada Reddy, A.; *Food Chem.* **2007**, *101*, 585.
8. Al-Kindy, S. M. Z.; Al-Bulushi, S. T.; Suliman, F. E. O.; *Spectrochim. Acta, Part A* **2008**, *71*, 676.
9. Mestek, O.; Kominkova, J.; Koplik, R.; Suchanek, M.; *Talanta* **2001**, *54*, 927.
10. Ribeiro, G. C.; Coelho, L. M.; Coelho, N. M. M.; *J. Braz. Chem. Soc.* **2013**, *24*, 1072.
11. Rahnama, R.; Eram, S.; Jamali, M. R.; *J. Braz. Chem. Soc.* **2014**, *25*, 658.
12. Aquino, E. V.; Rohwedder, J. J. R.; Facchin, I.; Pasquini, C.; *Talanta* **2002**, *56*, 643.
13. Mokhtari, B.; Pourabdollah, K.; *J. Braz. Chem. Soc.* **2013**, *24*, 1027.
14. Kolachi, N. F.; Kazi, T. G.; Khan, S.; Wadhwa, S. K.; Baig, J. A.; Afridi, H. I.; Shah, A. Q.; Shah, F.; Bavili Tabrizi, A.; *Food Chem.* **2007**, *100*, 1698.
15. Bahadır, Z.; Bulut, V. N.; Ozdes, D.; Duran, C.; Bektas, H.; Soylak, M.; *J. Ind. Eng. Chem.* **2014**, *20*, 1030.
16. Shamsipur, M.; Zahedi, M. M.; De Filippo, G.; Lippolis, V.; *Talanta* **2011**, *85*, 687.
17. Yebra-Biurrun, M. C.; Moreno-Cid, A.; Cancela-Pérez, S.; *Talanta* **2005**, *66*, 691.
18. Mohammadi, S. Z.; Shamspur, T.; Afzali, D.; Baghelani, Y. M.; Mansori, F.; *Quim. Nova* **2012**, *35*, 198.
19. Khani, R.; Shemirani, F.; Majidi, B.; *Desalination* **2011**, *266*, 238.
20. Yousefi, S. R.; Shemirani, F.; *Microchim. Acta* **2011**, *173*, 415.
21. Bag, H.; Rehber Turker, A.; Coskun, R.; Sacak, M.; Yigitoglu, M.; *Spectrochim. Acta, Part B* **2000**, *55*, 1101.
22. Kocot, K.; Zawisza, B.; Sitko, R.; *Spectrochim. Acta, Part B* **2012**, *73*, 79.
23. Staden, J. F. V.; Taljaard, R. E.; *Talanta* **2004**, *64*, 1203.
24. Kumar, M.; Rathore, D. P. S.; Singh, A. K.; *Talanta* **2000**, *51*, 1187.

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