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Fe_3O_4 nanoparticles and ultrasound assisted dispersive liquid-liquid microextraction of lead(II) for its microsampling flame atomic absorption spectrometric determination in food and environmental samples

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ABSTRACT

A method for isolation of lead from aqueous samples as Chicago sky blue 6B chelate based on the combination of Fe_3O_4 nanoparticles and ultrasound assisted dispersive liquid-liquid microextraction (NPU-DLLME) prior to flame atomic absorption spectrometry was developed. The amount of Fe_3O_4 nanoparticles added and the length of ultrasound exposure were optimized. Quantitative recovery was achieved at pH 6. The limit of quantification for solid samples was calculated 8.5 mg kg^{-1}. The relative standard deviation (RSD) determined for a standard solution containing 4.5 µg Pb(II) was 2.7%. The evaluation of accuracy was performed with wastewater and corn bran certified reference materials. The method was applied to the determination of lead in water and some spices.

Key words: Fe_3O_4 nanoparticles and ultrasonication-assisted dispersive liquid-liquid microextraction, Chicago sky blue 6B, lead, preconcentration, water, spice.

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1. Introduction

Lead, which is considered a carcinogenic element for humans, is harmful even at very low concentrations.[1] Therefore, its sensitive determination in food and water is important.[2-4] For flame atomic absorption spectrometry or graphite furnace atomic absorption spectrometry, sample pretreatment is necessary because of matrix interferences when concentrations of lead are low.[5-8] Methods employed for that purpose are solid phase extraction (SPE)[4,9], cloud point extraction (CPE) [10] and dispersive liquid–liquid microextraction (DLLME).[11]

Among these methods, DLLME has many advantages, such as a short extraction time and less solvent use low solvent use.[12-14] DLLME involves the formation of a cloudy emulsion of an organic solvent in an aqueous sample. This allows lead to partition into the organic phase when complexed with a suitable chelating agent. [15-17] Many recent studies have been performed to improve DLLME efficiency, further reduce the extraction time and decrease the amount of solvent used.

Song and co-workers [17] have developed ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME) with low solvent consumption for determination of polycyclic aromatic hydrocarbons in seawater.

Fe_3O_4 [18] and ultrasonication [17] were used to improve extraction efficiency of analytes in the microextraction studies. According to our literature review, the usage of Fe_3O_4 nanoparticles and ultrasonification in the microextraction studies without using dispersing solvent is new. This combination is firstly used in the literature in the presented work. It is an important advantage due to reduced amount of organic solvents in the microextraction studies.

In this work, ultrasound assisted DLLME in combination with the use Fe_3O_4 nanoparticles is employed for extraction of lead(II) as Chicago Sky Blue 6B complex for the determination of lead contents of food and environmental samples.

2. Experimental

2.1. Chemicals and Reagents

All reagents and chemicals were of analytical grade. The distilled and deionized water was prepared (Millipore Milli-Q, Bedford, USA) with 18 MΩ cm^{-1} resistivity. Standard solution of Pb(II) (1.00 g L^{-1}) were prepared by dissolving the nitrate salt (E. Merck, Darmstadt, Germany) in water. The working standard solutions were prepared by serial dilutions of the stock standard solution. A solution of 0.025% (w/v) of Chicago Sky Blue 6B (Sigma-Aldrich, St. Louis, MO, USA) was prepared using deionized water.

The phosphate buffer solutions (0.1 mol L^{-1}) for pH 2.0-4.0, acetate buffer solution (0.1 mol L^{-1}) for pH 5.0, phosphate buffers (0.1 mol L^{-1}) for pH 6.0-7.0 and ammonium/ammonia buffer solution (0.1 mol L^{-1}) for pH 8 were prepared and used to adjust of pH of sample solutions. Certified reference materials were used (SPS-WW2 Waste water Level 2, Spectrapure Standards AS, Oslo, Norway and NIST RM 8433 corn bran, National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA). Fe_3O_4 nanoparticles were synthesized using a procedure reported earlier.[19] They were characterized in the same literature.[19]

2.2. Instrumentation

A flame atomic absorption spectrometer (Model 3110 Perkin-Elmer, Norwalk, CT, USA) including an air–acetylene flame and a hollow cathode lamp was used. The instrumental parameters were adjusted as recommended by the manufacturer. The extractant phase was injected into the AAS with a Teflon funnel using a home-made microsample introduction system.[20] The absorbance signal was measured according to the peak height in the continuous aspiration mode.[21]

A Nel pH-900 (Ankara, Turkey) and a Metrohm pH meter (model 691, Switzerland) with a combined glass electrode were used for pH measurement. An ALC PK 120 Model centrifuge (Buckinghamshire, England) was used during the centrifugation processes. VWR international model vortex mixer (Darmstadt, Germany) and Sonorex Ultrasonic Bath (Model No. DT-255, Bandelin Co, Germany) were used in the experiments.

2.3. Fe_3O_4 nanoparticles and ultrasound-assisted DLLME procedure

Fifteen mL of model solution containing 4.5 µg lead(II) was placed in a 50-mL centrifuge tube, then 2 mL of phosphate buffer was added and the pH of the sample was adjusted to 6.0 using 0.01 mol L^{-1} NaOH and/or 0.01 mol L^{-1} HCl solutions. The water suspension of Fe_3O_4 nanoparticles (100 µL, 0.1%) and Chicago sky blue 6B (25 µg) were added to the sample. Then, 200 µL carbon tetrachloride as the extractor solvent was injected rapidly into the sample using a 5.0-mL syringe, and the mixture was exposed to ultrasonic waves for 1 minute. In this step, a cloudy solution was formed. The mixture was next centrifuged for 10 min at 4000 rpm, and the aqueous supernatant was removed with a syringe. The sediment pellet was mineralized by addition of 200 µL concentrated HNO_3 (65% w/w, E. Merck, Darmstadt, Germany) at 25 ◦C for 5 minutes at vortex and the final volume was adjusted to 400 µL. An aliquot of 50 µL of the final solution was introduced to the FAAS nebulizer using a microinjection system to measure the lead concentration.

2.4. Application to real samples

Water samples including tap water, river water, dam water, wastewater and lake water were collected from various regions of Turkey. The samples were filtered through membrane filters with 0.45 µm pores. The procedure given above (Section 2.3) was then used for each of the samples. The same procedure was also applied to the SPS-WW2 wastewater certified reference material.

Spice samples (Cumin (*Cuminum cyminum*), cinnamon (*Cinnamomum verum*) and lesser galangal (*Alpinia officinarum*)) were purchased from a local market at Riyadh City, KSA. Spice samples were first washed with deionized water and dried at 60 °C. Then, 0.5 g of the spiece samples and/or NIST RM 8433 corn bran certified reference material was separately weighed into beakers. Concentrated nitric acid (15 mL) was added to the beakers, and the beakers were heated on a hot plate at 100 °C to dryness. The residues in the beakers were cooled, 10 mL of concentrated HNO_3 and 5 mL of H_2O_2 were added, and the beakers were heated to dryness. After cooling to room temperature, the mixture was dissolved in water and filtered from blue band filter paper and its volume was completed to 15 mL with water. The procedure given Section 2.3 was applied to each sample.

3. Results and Discussion

3.1. Optimization

Extraction procedures have been reported to be significantly dependent on the pH of the solution because of the effect of the concentration of the hydrogen ion in the sample solution on the complex formation between the analyte and the chelating agent.[12, 22, 23] The pH of the lead solution was tested in the range of 2 to 8 for the micro extraction procedure. The results are given in Figure 1. A pH of 6 was found to be suitable for quantitative recovery. Therefore, pH 6 was chosen for further experiments.

DLLME depends on the formation of a complex between the analytes and the chelating agent.[15] Therefore, the amount of the chelating agent should be sufficient to react with all analytes; otherwise, the recovery will be reduced. The amount of chelating agent must not be in excess because of economic and safety concerns. In the present work, the amount of Chicago sky blue 6B as chelating agent was optimized. The results in Figure 2 reveal that 25 µg of chelating agent solution was sufficient to obtain quantitative recoveries of lead(II). Therefore, 25 µg of Chicago sky blue 6B was chosen for further experiments.

Due to importance amount of Fe_3O_4 nanoparticles on the adsorption of lead(II)-chicago sky blue 6B metal chelates on Fe_3O_4 nanoparticles, the amount of water suspension of Fe_3O_4 nanoparticles (0.1 %) was optimized (Figure 3). A volume of 100 µL of the nanoparticle solution is sufficient for quantitative recovery of lead(II). Excess Fe_3O_4 nanoparticles decrease the recovery % of lead(II), due to prevention of ligand and analyte interactions with excess Fe_3O_4 nanoparticles. Therefore, 100 µL of the suspension of Fe_3O_4 nanoparticles was chosen for further experiments.

The effect of addition of Fe_3O_4 nanoparticles on the amount of ethanol as the dispersing solvent was also studied. The results in Figure 4 show that quantitative recovery values for lead(II) were obtained in the absence of dispersing solvent when 100 µL Fe_3O_4 nanoparticles was added. In the absence of the Fe_3O_4 nanoparticles, 2000 µL of ethanol was required to obtain quantitative recovery of lead(II).

These results demonstrate that DLLME can be operated without using dispersing solvent. This finding is very promising for the extraction techniques because reducing the amount of solvent is the ways for green chemistry.

Ultrasonic waves were combined with the microextraction procedure to improve the recovery.[17] The time of exposure to ultrasound was studied showing that 1 minute is sufficient for quantitative recovery. For longer periods, the recovery is decreased, possibly due destruction of the complex by ultrasound.

The suitable extraction solvent must have low water solubility to allow the formation of a cloudy solution including small droplets during the microextraction procedure and to give higher recoveries.[24-29] In the present work, different extraction solvents were tested with extraction solvent-nanoparticles mixture, including carbon tetrachloride, chloroform and dichloromethane, giving recoveries of 100%, 47% and 64 %, respectively. The recovery with carbon tetrachloride without nanoparticles was 75%. Carbon tetrachloride was selected for further experiments with nanoparticles mixture. Additionally, the amount of carbon tetrachloride was examined by testing volumes of 50, 100, 150, 200 and 300 μL. Two hundred μL of carbon tetrachloride was sufficient to give a quantitative recovery (101.0 %).

The volume of the lead sample solution is an important parameter that influences the preconcentration factor and the limit of detection of the extraction method. In the present work, different sample volumes were tested over the range of 10-50 mL. Quantitative recovery was obtained using volumes of up to 15 mL. The preconcentration factor was 37.5 when the sample volume and the final volumes were 15 mL and 400 μL, respectively.

3.2. Effect of coexisting ions

Evaluation of the matrix or coexisting ions is important for the optimization of the extraction method.[30-35] The influence of Na^+, K^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Fe^{3+}, Zn^{2+}, SO_4^{2-}, F^-, CO_3^{2-}, NO_3^- and Cl^- was tested under optimal conditions. The results are presented in Table 1. The recoveries of lead(II) were all quantitative in the range from 95% to 100%.

3.3. Analytical figures

The analytical performance of the NPU-DLLME procedure was evaluated using 15 mL of a model solution. The detection limits of lead(II) based on three times the standard deviations of the blank (N=7) divided to preconcentration factor was found 5.7 µg L^{-1}.The limit of quantification (LOQ), calculated as three times the LOD, was 17.0 µg L^{-1}.

The LOD and LOQ values for solid samples were calculated as 2.9 mg kg^{-1} and 8.5 mg kg^{-1}, respectively. The relative standard deviation (RSD) determined from seven analyses of the standard solution of Pb(II) (4.5 µg) was 2.7%.

The accuracy of the proposed NPU-DLLME procedure was evaluated by performing the addition/recovery tests on water samples as shown in Table 2. The proposed NPU-DLLME procedure demonstrates high efficiency in the addition/recovery tests for lead in tap water samples. Recovery was not less than 100 %.

The validation of the presented method was checked by the analyzing SPS-WW2 Waste water Level 2 and NIST RM 8433 corn bran certified reference materials. The results are given in Table 3. This efficiency is confirmed which show quantitative recoveries (100 %) from the certified reference materials. It was found that there was no significant difference between the result obtained and the certified results.

3.4. Application to real samples

NPU-DLLME was applied to lead determination in water and food samples (Table 4) confirming the high reproducibility of the method.

4. Conclusions

A preconcentration method without the use of a dispersing solvent was developed based on DLLME combined with Fe_3O_4 nanoparticles and ultrasonic waves. Chicago sky blue 6B was used as the chelating agent for the extraction and preconcentration of Pb(II) from water and food samples before determination by AAS. The findings in the present work are important for the extraction techniques because reducing the amount of solvent is the way to green chemistry. The developed NPU-DLLME procedure is environmental friendly from economic and safety views. Other advantages of the proposed method were: minimum amount of reagents, simplicity and enhancement of sensitivity. Table 5 compares the proposed NPU-DLLME procedure to previously reported methods from the literature for lead determination. The detection limit and preconcentration factor of DLLME method are superior from literature values with some exceptions.

5. Acknowledgments

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Figure Captions

Figure 1. Effect of the pH on recovery of Pb(II) (N=3, Amount of Chicago sky blue 6B: 25 µg, volume of Fe_3O_4 nanoparticles: 100 µL of 0.1 % solution, Volume of CCl_4: 200 µL, sample volume: 15 mL).

Figure 2. Effect of amount of Chicago sky blue 6B on the recovery of Pb(II) (N=3, pH: 6, volume of Fe_3O_4 nanoparticles: 100 µL of 0.1 % solution, Volume of CCl_4: 200 µL, sample volume: 15 mL).

Figure 3. Effect of volume of Fe_3O_4 nanoparticles on the recovery of Pb(II) (N=3, pH: 6, Amount of Chicago sky blue 6B: 25 µg,, Volume of CCl_4: 200 µL, sample volume: 15 mL).

Figure 4. Effect of the presence of Fe_3O_4 nanoparticles on the amount of ethanol as the dispersing solvent (N=3, pH: 6, Amount of Chicago sky blue 6B: 25 µg, amounts of Fe_3O_4 nanoparticles: 100 µL of 0.1 % solution, Volume of CCl_4: 200 µL, sample volume: 15 mL).

Table 1. Effect of the presence of coexisting ions on the recovery of Pb(II) (N=3, Concentration of lead(II) in the model solutions: 0.3 mg L^{-1})

Ions	**Concentration (mg L^{-1})**	**Added as**	**Recovery, %**
K^+	2000	KCl	100±0.5 [a]
Na^+	8000	NaCl	99±0.5
Cl^-	2000	KCl	100±0.5
CO_3^{2-}	2000	$Na_2 CO_3$	95±0.5
NO_3^-	2000	KNO_3	96±0.6
Mg^{2+}	1000	$Mg(NO_3)_2$. $6H_2O$	96±0.4
Ca^{2+}	1000	$CaCl_2$	96±0.5
SO_4^{2-}	500	Na_2SO_4	98±0.6
F^-	500	NaF	100±0.4
Co^{2+}	10	$Co(NO_3)_2.6H_2O$	95±0.3
Ni^{2+}	10	$Ni (NO_3)_2.6H_2O$	100±0.5
Cu^{2+}	10	$Cu(NO_3)_2.3H_2O$	95±0.5
Cd^{2+}	10	$Cd(NO_3)_2.4H_2O$	96±0.7
Fe^{3+}	5	$Fe(NO_3)_3.9H_2O$	100±0.4

Zn^{2+}	5	$Zn(NO_3)_2$	96±0.1

[a] Mean ± standard deviation

Table 2. Addition/recovery study of lead(II) from tap water samples (sample volume: 15 mL, N=3.)

Added, µg L^{-1}	Found, µg L^{-1}	Recovery, %
0	0	-
83	84 ± 12 [a]	101
165	167 ± 19	101

[a] Mean ± standard deviation

Table 3. Evaluation of the proposed NPU-DLLME procedure using certified reference materials

Certified reference materials	Certified value	Found value	Recovery, %
SPS-WW2 wastewater	500 ± 3 μg L^{-1}	502 ± 22 μg L^{-1}	100
NIST RM 8433 corn bran	140 ± 34 μg Kg^{-1}	141±0.29 μg Kg^{-1}	101

Table 4. Application of NPU-DLLME for water and food samples (N=3)

Real Samples	**Concentration**
Ground Water	0.16 ± 0.01 [a] μg L^{-1}
Dam Water	0.14 ± 0.01 μg L^{-1}
Wastewater	0.63 ±0.11 μg L^{-1}
Cumin (*Cuminum cyminum*)	3.19 ± 0.19 mg kg^{-1}
Cinnamon (*Cinnamomum verum*)	1.31 ± 0.012 mg kg^{-1}
Lesser galangal (*Alpinia officinarum*)	6.00 ± 0.01 mg kg^{-1}

[a] Mean ± standard deviation

Table 5. Comparison of NPU-DLLME with other methods for lead isolation/analysis

Preconcentration Method	**Detection Method**	**LOD (μg L^{-1})**	**Ref.**
Temperature controlled ionic liquid microextracion	FAAS	5.8	12
Ionic liquid DLLME	FAAS	1.5	20
DLLME	ICP-AES	12	15
Nanoparticles ultrasound assisted DLLME	FAAS	5.7	This study

LOD: Limit of detection

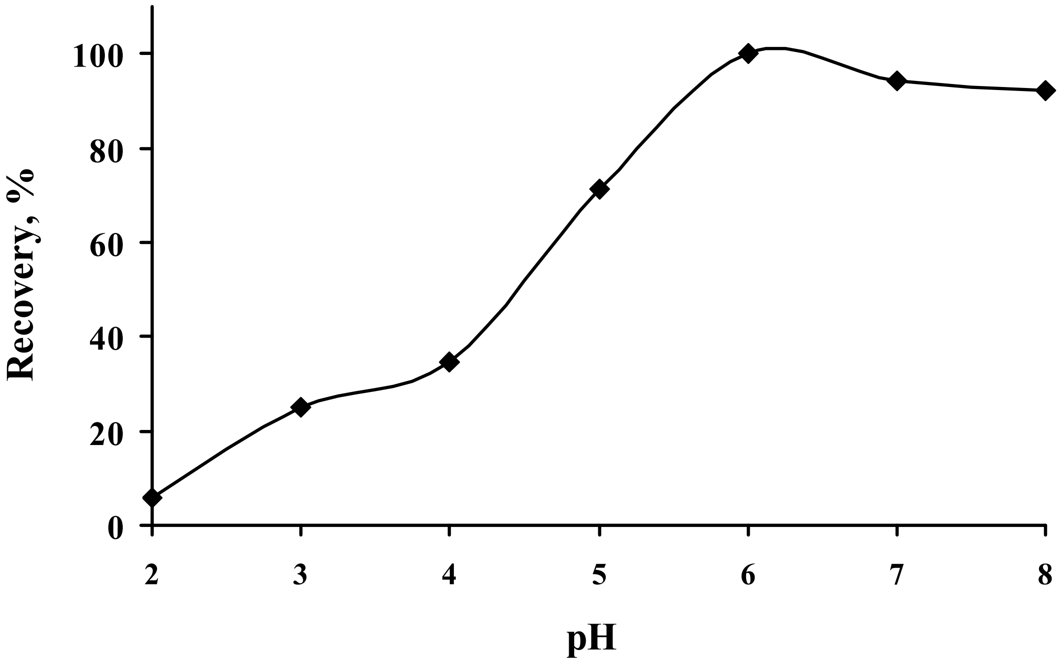

Figure 1

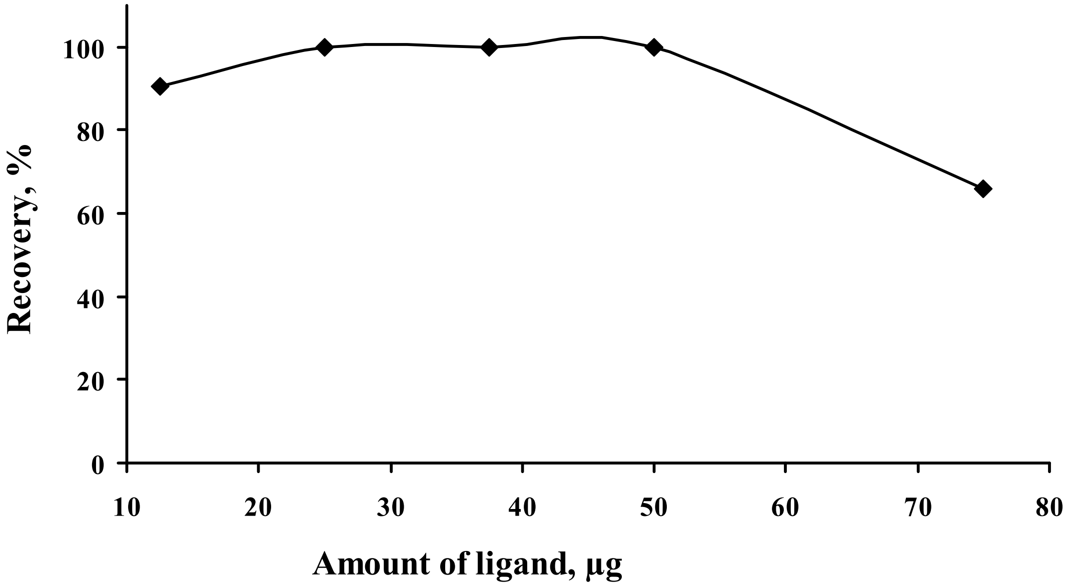
Recovery, %
0
20
40
60
80
100
10
20
30
40
50
60
70
80
Amount of ligand, µg

Figure 2

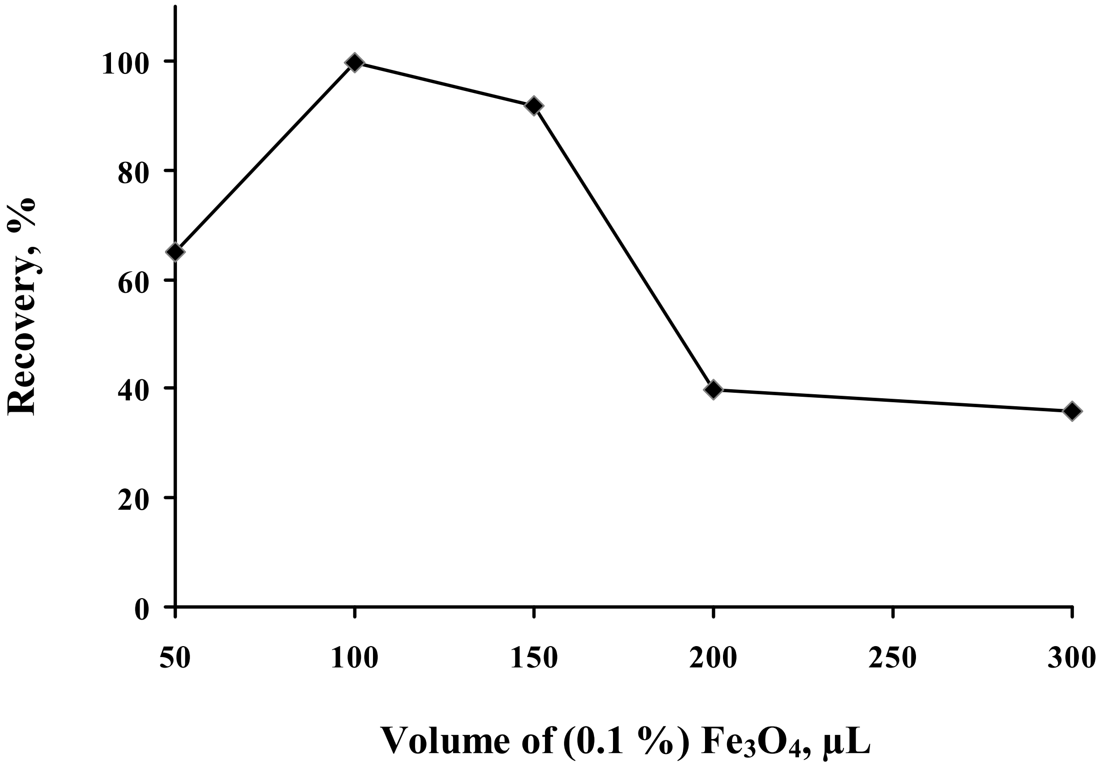
Recovery, %
0
20
40
60
80
100
50
100
150
200
250
300
Volume of (0.1 %) Fe3O4, µL

Figure 3

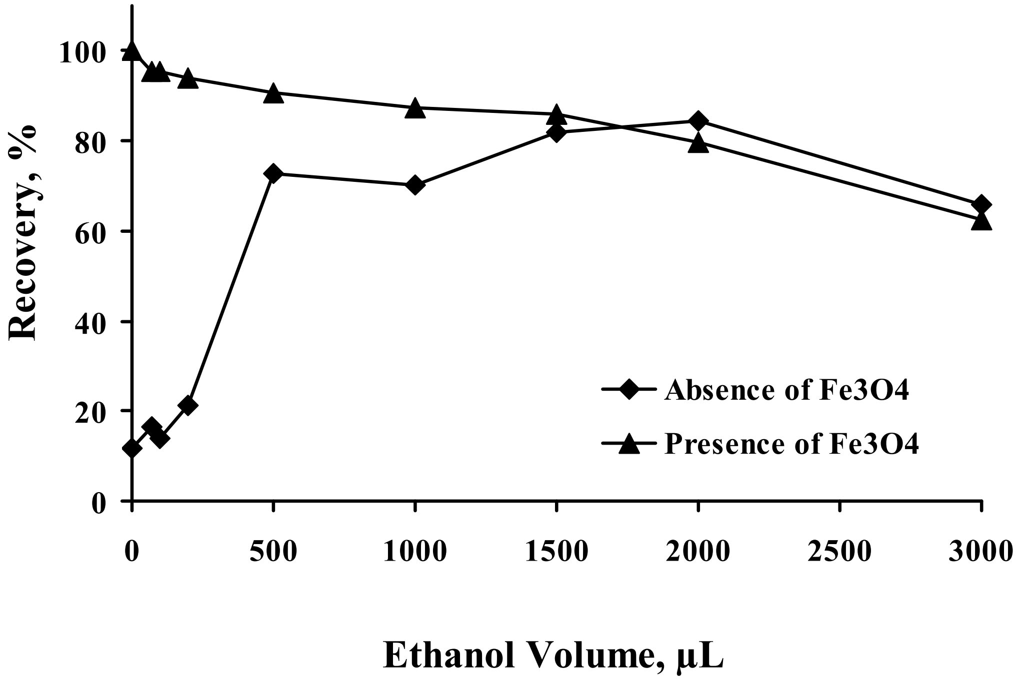
Recovery, %
100
80
60
40
20
0
0
500
1000
1500
2000
2500
3000
Ethanol Volume, µL
Absence of Fe3O4
Presence of Fe3O4

Figure 4