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RAPID AND EFFICIENT DETERMINATION OF ZINC IN WATER SAMPLES BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AFTER HOMOGENEOUS LIQUID-LIQUID MICROEXTRACTION VIA FLOTATION ASSISTANCE

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ABSTRACT. A new application of homogeneous liquid–liquid microextraction via flotation assistance (HLLME-FA) has been developed for the determination of Zn(II) in the water samples by using graphite furnace atomic absorption spectrometry (GFAAS). 1-(2-Pyridylazo)-2-naphthol (PAN) was used as a chelating reagent. In this work, low density organic solvent was used as an extraction solvent and no centrifugation was required in this method. A special extraction cell was designed to facilitate collection of the low density extraction solvent. The predominant parameters influencing the HLLME-FA procedure, such as solution pH, concentration of PAN, extraction and homogeneous solvent types and volumes, ionic strength, and extraction time have been optimized. Applying all the optimum conditions in the process, the detection limit of 0.1 μg/L, linear range of 0.5–200 μg/L, and the precision (RSD%, n = 10) of 5.7% were obtained for zinc. The proposed procedure showed satisfactory results for the analysis of tap water, well water and sea water.

KEY WORDS: Homogeneous liquid-liquid microextraction, Flotation assistance, Zinc, Graphite furnace atomic absorption spectrometry, Water samples

INTRODUCTION

Monitoring trace metals like zinc in water samples is important for human health and the environment. Zinc is a metal with a brilliant shine bluish-gray color [1]. It is chemically active and is an essential trace element involved in antioxidant reactions. It can enhance the human immune system.

In literatures, many modern technologies such as atomic absorption spectrometry [2-4], inductively coupled plasma optical emission spectroscopy (ICP-OES) [5, 6], inductively coupled plasma mass spectrometry (ICP-MS) [7, 8] and electroanalytical techniques [9-11] have been reported to the determination of trace zinc, but direct determination of trace zinc at low concentration in complex matrices is often difficult because of insufficient sensitivity of this technique as well as the matrix interferences occurring in real samples. For this reason, a preliminary separation and preconcentration step is often required. Instrument detection limit of graphite furnace atomic absorption spectrometry (GFAAS) for zinc is around 1.0 μg L^{-1}. The instrument detection limit can only roughly characterize the performance of the system and is only a qualitative judgment basis, and it cannot usually be used for real analysis. Direct determination of trace amount of zinc in natural waters by using GFAAS is difficult due to various factors, particularly its low concentration and matrices effects. Pre-concentration and separation can solve these problems and can lead to a higher confidence level and easy determination of the trace amount of zinc in the real samples.

Several sample preparation methods such as liquid–liquid extraction (LLE) [12, 13], solid-phase extraction (SPE) [14], cloud point extraction (CPE) [15] and dispersive liquid–liquid microextraction (DLLME) [16] have been developed for the separation and preconcentration of

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*Corresponding author. E-mail: mrezaee@aeoi.org.ir zinc from complex matrices. Liquid–liquid extraction (LLE) suffers from being time-consuming and highly labor-intensive. Furthermore, it needs high-purity organic solvents and the subsequent disposal of the organic solvents brings about a great threat to the environment and human health. The main disadvantage of DLLME lies in its extractant solvent which is usually a halogenated solvent of highly toxic nature that is difficult to handle in the laboratory. Also, it needs centrifugation for phase separation. The significant drawback of CPE is of insufficient and low contact surface between the extraction phase and sample phase. In 2007, Soylak *et al.* have developed a microwave assisted digestion procedure for the determination of zinc, copper and nickel in tea samples by using flame atomic absorption spectrometry (FAAS) [17]. The relative standard deviations of the method were found below 8% for the three elements. The recoveries obtained for analytes are 96–98% and the performance of the method is very good for determination of these metals in tea samples. In 2009, cloud extraction was developed for preconcentration of trace copper, zinc, iron, and nickel in biological and environmental samples prior to their determination by flame atomic absorption spectrometry (FAAS) [18]. The metals react with 2-phenyl-1H-benzo[d] imidazole (PHBI) in a surfactant Triton X-114 medium. The detection limits of 1.8, 2.8, 1.4, and 2.1 ng mL^{-1} for copper, iron, zinc, and nickel, respectively, were obtained. In 1996, Amberlite-XAD-16-resin column procedure was used for the preconcentration and separation of zinc, copper, iron, cadmium, cobalt, and nickel from urine samples [19]. Flame atomic absorption spectrometry (FAAS) was used to determine Zn and Fe, while graphite furnace atomic absorption spectrometry (GFAAS) was used to determine Cd, Cu, Ni, and Co in the final solutions. Quantitative recoveries at 95% or above were found to be in the pH 4 to 8 range, with the optimum pH of 4 for quantitative recoveries of all working metal ions. In 2002, 1-(2-pyridylazo)-2-naphthol (PAN)-modified polymeric membranes for the effective batch pre-concentration and determination of zinc traces with flame atomic absorption spectrometry (FAAS) was developed [20]. The analytical curve was rectilinear up to 30 µg/L zinc with detection limit of 0.7 µg/L and a relative standard deviation lower than 2%. In 2011, cloud point extraction method was developed for preconcentration of trace quantities of zinc in aqueous extract of medicinal plants and blood samples of liver cancer patients using flame atomic absorption spectrometry [21]. The LOD by using complexing reagent (PAN) and surfactant (Triton X-114) was 1.52 µg/L and precision (%) was 4-5%. In 2003, polystyrene divinylbenzene resin (Amberlite XAD-16) functionalized by 1-(2-pyridylazo)-2-naphtol was synthesized and its sorption properties was investigated for preconcentration of Ni(II), Cd(II), Co(II), Cu(II), Pb(II) and Cr(III) in natural water samples [22]. The detection limits for Ni, Cd, Co, Cu, Pb, and Cr were 0.161, 0.056, 0.072, 0.079, 0.121, and 0.268 mg/L, respectively.

Dispersive liquid–liquid microextraction (DLLME) is one of the most effective liquid-phase microextraction techniques which primarily introduced by Rezaee *et al.* in 2006 [23]. This pretreatment technique is based on the rapid injection of two solvents: extraction and disperser solvents into the aqueous solution to make the analyte transfer to the extraction solvent easier and faster. DLLME reported for the determination of different compounds [24-27]. DLLME suffers from two limiting factors which are almost challengeable. First, the extraction solvents are mostly solvents with higher density than water to be easily sedimented. Second, the centrifugation step makes the general procedure longer and somehow tiring. In order to overcome this challenge, the novel microextraction technique, homogeneous liquid–liquid microextraction via flotation assistance (HLLME-FA), presented for the determination of various environmental pollution compounds [28-31]. In fact, HLLME-FA is a novel combination of dispersive liquid–liquid microextraction (DLLME) and homogeneous liquid–liquid extraction (HLLE) [32, 33]. HLLME-FA conquers the drawbacks of DLLME and HLLE by two main advantages. First, HLLME-FA is based on the utilization of low-density extraction solvents that makes this technique significant due to widespread range of low density solvents. Second, in HLLME-FA, a particular extraction cell is design to make the collection and extraction process easier and quicker. Therefore, the organic phase containing extracted analyte comes up and can be easily separated from the aqueous phase and no centrifugation is mandatory which shortens the extraction time. The extraction procedure of HLLME-FA is the injection of the mixture of extraction solvent and homogenous solvent into the sample solution in the designed cell. Then, the air or nitrogen floats in the solution; consequently, the extraction solvent collects on the top of the cell and can be taken easily.

In this research, HLLME-FA method as a rapid, primitive, easy, and efficient microextraction technique, coupled with graphite furnace atomic absorption spectrometry has been applied for the determination of zinc in the water samples. In order to obtain a high extraction efficiency, the effect of different parameters affecting the complex formation and extraction conditions (such as the type and volume of extraction and homogeneous solvents, pH, extraction time, the chelating agent amount, and ionic strength) have been investigated and optimized.

EXPERIMENTAL

Chemicals and reagents

All the chemicals used were of analytical reagent grade. Stock solutions of Zn(II) (1000 mg/L) were prepared by dissolving appropriate amounts of $Zn(NO_3)_2 \cdot 6H_2O$ in the double distilled water. Working standard solutions were obtained by appropriate dilution of the stock standard. The chelating agent, 0.01 mol/L 1-(2-pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) solution was prepared by dissolving the appropriate amount of PAN (Sigma-Aldrich, Louis, USA) in the absolute ethanol. 1-Undecanol, 2-octanol, toluene, methanol, acetone, ethanol, acetonitrile and sodium chloride were obtained from Merck (Frankfurter, Darmstadt, Germany). Youngling ultra-pure water purification system (Aqua Max^{TM}-ultra, Hogye-dong, Anyang, Korea) was used for the purification of the water. The pH of the solutions were adjusted by dissolving proper amount of ammonium acetate in the distilled water (2.5×10^{-3} M) and drop wise addition of nitric acid (0.5 M) and/or sodium hydroxide solutions (0.5 M). In this work, graphite furnace atomic absorption spectrometry (GFAAS) model PG-990 (PG Instruments Ltd, Alma Park, Wibtoft, Lutterworth, LE17 5BH. United Kingdom) was used for the all determinations. Instrument settings and furnace programs for the analysis of Zn by GFAAS was shown in the Table 1.

Table 1. Instrument settings and furnace programs for analysis of Zn by GFAAS.

Conditions	Zn
Wavelength (nm)	213.9
Lamp current (mA)	15
Injection volume (µL)	10
Heating program temperature ºC (ramp time (s), hold time (s))	
Drying 1	80 (5, 20)
Drying 2	200 (5, 20)
Pyrolysis	800 (5, 20)
Atomization	1800 (0, 4)
Cleaning	2100 (1, 2)

HLLME-FA procedure

A mixture of 1.0 mL of methanol (as a homogeneous solvent) and 100 µL of toluene (as an extraction solvent) was added to the home-designed microextraction cell. Twenty-two milliliters of the saline sample solution which pH was adjusted at 6 containing 100 µg/L of zinc was rapidly added into the microextraction cell by a syringe. Then, 200 µL PAN (0.01 M) as a ligand was added into 22 mL saline sample solution. A homogeneous solution was formed. After 1 min, using air flotation, the organic solvent was separated as a floating layer on the surface of the solution. Then, a few volumes of distilled water were added into the glass tube on the side of the cell to transfer the floated organic phase into the conical part of the extraction cell. Using a microsyringe, 10.0 µL of the collected organic solvent was injected into the GFAAS. The schematic of home-designed microextraction cell was shown in the Figure 1.

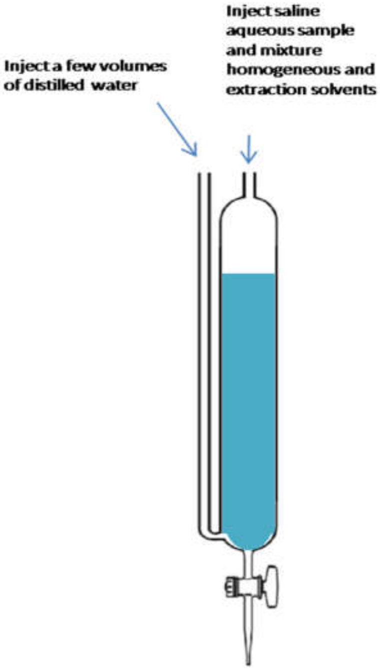

Figure 1. Schematic of home-designed microextraction cell.

RESULTS AND DISCUSSION

HLLME-FA combined with GFAAS has been developed for the determination of zinc in the water samples. In order to obtain high recovery, effects of different parameters such as solution pH, the concentration of PAN as a chelating agent, the type and volume of the extraction and homogeneous solvents, salt addition, and extraction time have been optimized. Optimization of the variables mentioned was performed using univariate method. All experiments were replicated three times.

Selection of extraction solvent

Extraction solvent is one of the most indicative and important factors in the HLLME-FA method. The extraction solvent must have low density and immiscibility with water and high extraction capability for the analyte. Some low-density solvents such as 1-undecanol, 2-octanol and toluene were tested. The obtained absorbance for 1-undecanol, 2-octanol and toluene were 0.612, 0.384 and 0.880, respectively. According to the obtained results, in toluene showed the highest absorbance. It seems that, because the structure of the PAN in the complex has benzene group and interaction with benzene group in toluene causes better extraction efficiency. Thus, toluene was selected as an extraction solvent.

Selection of homogeneous solvent

The main criterion for selecting the homogeneous solvent was its miscibility with the extraction solvent and aqueous sample. The effect of different homogeneous solvents including methanol, ethanol, acetone and acetonitrile were studied. The obtained absorbance for methanol, ethanol, acetone and acetonitrile were 0.860, 0.670, 0.380 and 0.320, respectively. The obtained results indicate that methanol exhibits the highest absorbance. Thus, methanol was selected as the homogeneous solvent for subsequent experiment.

Selection of extraction and homogeneous solvent volumes

The volume of the extraction solvent is an important factor for the extraction efficiency. It should be perfectly sufficient to extract metal complex with the highest efficiency. Consequently, the volume of the extraction solvent in the range of 50.0–150 µL was considered. It is mentioned that in less than 50.0 µL, the collected volume of toluene was not sufficient to inject into the GFAAS. Therefore, less than 50.0 µL was not considered. As can be seen (Figure 2), increasing the extraction solvent volume from 50.0 to 100 µL caused an increase in the absorbance. Higher than 100 µL, the absorbance decreased, because of dilution effect. Based on these results, the volume of 100 µL was selected for further studies.

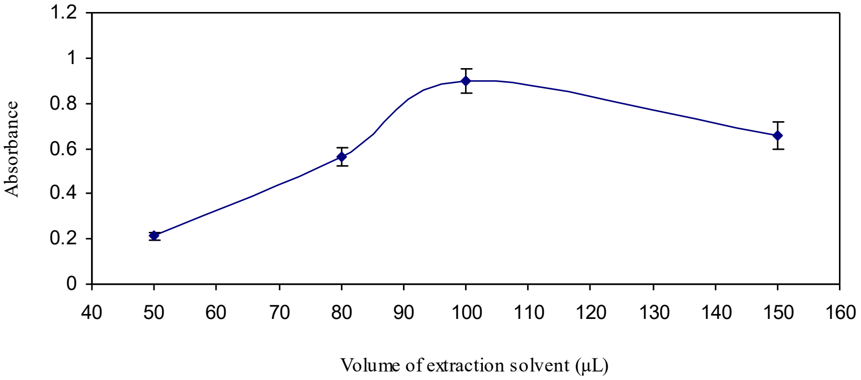

Figure 2. Effect of volume of extraction solvent on the absorbance.

In order to study the influence of the volume of homogeneous solvent on the extraction efficiency, different volumes of methanol (0.5, 1.0 and 1.5 mL) were used. The results (Figure 3) showed that increasing the volume of methanol led to a raise in absorbance up to 1.0 mL and then a decrease of analytical signal was observed. It seems that, at a low volume of methanol, cloudy solution was not properly formed resulting in a decrease in the absorbance. At a high volume of methanol, the solubility of the complex in the sample increased resulting in a decrease in absorbance. Thus, 1.0 mL was selected as the optimum volume of methanol.

Effect of pH

Extraction of metallic ions by HLLME-FA involves prior formation of a complex with sufficient hydrophobicity which is to be extracted into the small volume of the extraction solvent. Consequently, pH plays a prominent role for metal complex formation and extraction. The solution pH was studied in the range of 2–10. The results, illustrated in Figure 4, indicate that the absorbance is maximum in the pH 6. The progressive decreases in the extraction at pH < 6.0 might be due to the competition of the proton with the analyte for the reaction with PAN. On the other hand, reduction in the extraction efficiency at higher pH value could be due to the hydroxide formation of metal ion under alkaline conditions. Therefore, a pH of 6 was selected for subsequent studies.

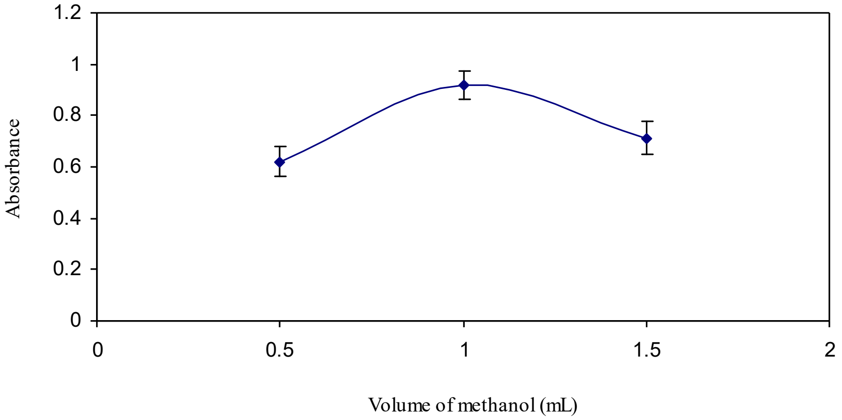

Figure 3. Effect of volume of homogeneous solvent on the absorbance.

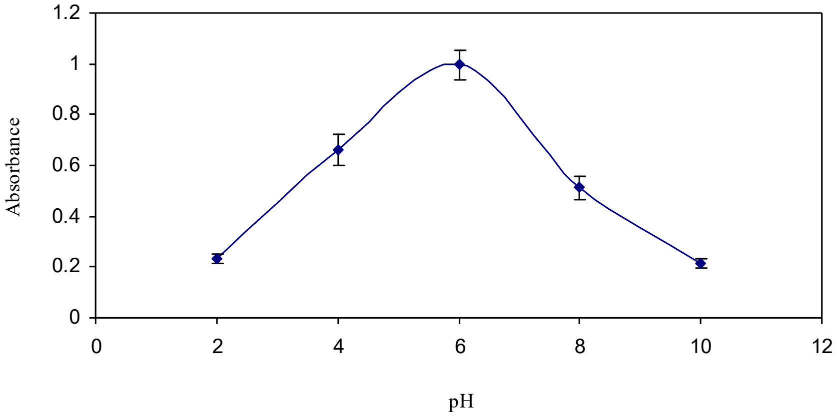

Figure 4. Effect of pH on the absorbance.

Effect of reagent concentration

The effect of the amount of PAN on the absorbance was investigated in the range of 100–600 µL (0.01 mol/L). According to the results shown in the Figure 5, the absorbance of zinc increases by increasing the concentration of PAN till 200 µL; after that, the absorbance decreases. This effect is probably caused by competition between complexing agent molecules, which are in excess in the solution, and Ni complex molecules for extraction solvent interaction. The optimum amount of 200 µL PAN was chosen for further study.

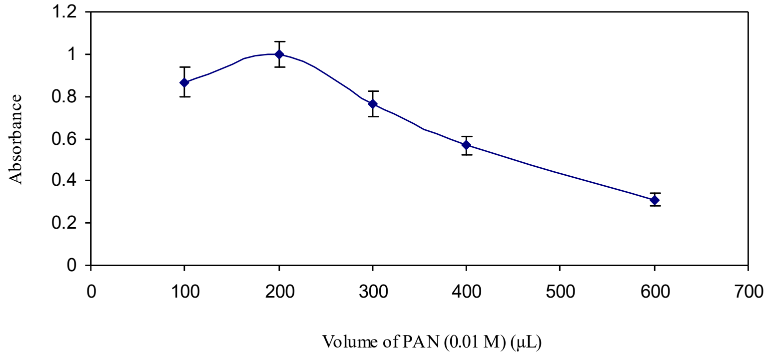

Figure 5. Effect of volume of ligand (0.01 M) on the absorbance.

Effect of salt addition

The influence of ionic strength was evaluated at 0.5–3 M NaCl. The HLLME-FA experimental conditions were the same as those described before. A plot of absorbance vs. ionic strength is shown in the Figure 6. Increasing the NaCl concentration up to 1.5 M increases the absorbance of the zinc, because of the salting-out effect. At salt concentrations higher than 1.5 M, the absorbance decreases, because the viscosity of the solution increases and dispersion was difficult. Therefore, 1.5 M of NaCl was selected as the optimum value for subsequent analysis.

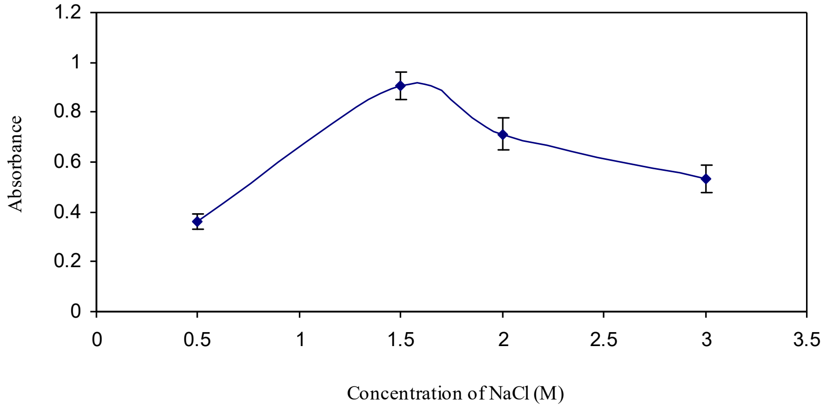

Figure 6. Effect of concentration of NaCl on the absorbance.

Effect of extraction time

In HLLME-FA method, the extraction time is considered the interval time between the beginning of the dispersion and the end of dispersion before the air flotation. Extraction time is a key factor which determines the speed and sensitivity of the analysis. The effect of the extraction time was investigated with the time varying from 1 to 20 min. The results showed that the time of 1 min is a good selection for the extraction time. More than 1 min, the absorbance are constant.

Interferences

Interferences were studied in the presence of different amounts of the foreign ions. An ion was considered as interfering, when it caused a variation in the extraction efficiency of the sample greater than 15%. The results obtained are given in Table 2. It can be seen that the presence of common coexisting ions has no significant influence on the extraction of Zn(II) ion under the selected conditions.

Quantitative analysis

Linearity for Zn was obtained in the concentration range of 0.5–200 µg/L, with a coefficient of determination of $r^2 = 0.978$. The limit of detection (LOD) obtained from $C_{LOD} = 3\ (S_d)_{blank} \cdot m^{-1}$ was 0.1 µg/L, where S_d is the standard deviation of 10 consecutive measurements of the blank and m the slope of the calibration curve. The relative standard deviation (RSD%) of the 10 replicate determinations was 5.7%, indicating that the method has good precision for the analysis of trace Zn in the samples.

Table 2. Effect of interference on preconcentration and determination of metal ion.

Interference	Interference to metal ion ratio	Recovery %
K^+	1000	98
Ca^{2+}	1000	96
Mg^{2+}	1000	94
Pb^{2+}	200	90
Cu^{2+}	100	88.4
Fe^{2+}	200	91.2
Co^{2+}	200	87.2
Ba^{2+}	1000	94

Table 3 compares the proposed method with the other extraction methods for the determination of zinc. Comparison of the proposed method with cloud-point extraction [35] for the extraction and determination of the analyte indicates that this novel method has a short extraction time for the determination of the zinc. Quantitative results of the proposed method such as detection limit and linear range are better than of homogeneous liquid-liquid extraction [34], cloud-point extraction [35], solid-phase extraction [36] and dispersive liquid-liquid microextraction [37] methods. In comparison with HLLE and DLLME methods [34, 37], the extraction solvent used in HLLME-FA method has a low density and low toxicity. In comparison with HLLE and DLLME methods, by using air flotation in HLLME-FA method, centrifugation step was omitted.

Table 3. Comparison of the proposed method with other extraction methods for the determination of zinc in water samples

Methods	RSD	Dynamic linear range (µg/L)	Limit of detection (µg/L)	Extraction time (min)	Ref.
HLLE[1]-FAAS	2.3	5-1000	5	2	[34]
CPE[2]-FAAS	2.5	10-100	6.5	15	[35]
SPE-FAAS	2.3	10-300	1.5	1	[36]
DLLME-spectrometer	1.4	30-220	11.2	A few seconds	[37]
HLLME-FA-GFAAS	5.7	0.5-200	0.1	1	This work

[1]Homogeneous liquid–liquid extraction. [2]Cloud-point extraction.

Real sample analysis

The proposed HLLME-FA-GFAAS procedure was applied to the determination of zinc concentration in the sea, tap, and well water samples. To determine the effect of matrixes on the extraction procedures, the relative recoveries of the samples spiked with the known amounts of analyte were investigated. The results obtained are summarized in Table 4. The relative recoveries vary from 89 to 95%, indicating the feasibility of the HLLME-FA method for the determination of zinc in the water samples.

Table 4. Determination of zinc in tap, sea and well water and relative recovery of spiked zinc in them.

Sample	Concentration of Zn (μg/L) ± SD[a], n = 3	Added Zn (μg/L)	Found Zn (μg/L) ± SD[a], n = 3	Relative recovery (%)
Tap water[b]	7.9 ± 0.4	10	17.2 ± 0.8	93
Sea water[c]	6.6 ± 0.4	10	15.5 ± 1.0	89
Well water[d]	3.5 ± 0.2	10	13.0 ± 0.6	95

[a]Standard deviation; [b]Was taken from our laboratory (Tehran. Iran); [c]Was taken from Caspian Sea (Sari, Iran); [d]Was taken from Tehran (Tehran, Iran).

CONCLUSION

The present study was successfully and effectively applied for the determination of trace zinc by HLLME-FA with perfect recovery and precision. In HLLME-FA procedure, toluene as an extraction solvent, methanol as a homogeneous solvent and PAN as a chelating reagent were used. This method showed good linearity (0.5–200 μg/L) and low LOD (0.1 μg/L) within a short time. The performance of the proposed method in extraction of zinc from tap, well, and sea water samples was satisfactory. Moreover, facile, easy, and rapid operation, short analysis time and low use of organic solvent with lower toxicity instead of solvent with high toxicity in DLLME (chlorinated solvents) are the highlight advantages of this method. The proposed technique utilized a homemade design extraction cell instead of a centrifugation step, thus, the operation of extraction became simple and fast. Finally, to the best of our knowledge, this is the first report dealing with HLLME-FA and GFAAS for the determination of zinc in the water samples.

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