

Determination of trace amount of Zn²⁺ ion in soil, blood and vegetable and water samples by flame atomic absorption spectrometry after cloud point extraction using selective synthesis ligand 2-(3- indolyl) – 4,5 di phynyl imidazole

Gholamhossein Vatankhah^{1*}, Mahboube Ebrahimi² and Masoud Saberi¹

¹ Department of Chemical Engineering, Bushehr Branch, Islamic Azad University, Bushehr, Iran

² Department of Agriculture Science, Payame Noor University, Tehran, Iran

Received May 2018; Accepted June 2018

ABSTRACT

A simple, sensitive and feasible cloud-point extraction (CPE) methodology has been developed for the separation and preconcentration of cadmium and lead ions in real samples. The metals in the aqueous solution were complexes with 2-(3- indolyl) - 4,5 di phynyl imidazole (IDPI), at pH = 7.0 and Triton X-114 was added as surfactant. The variables effecting like concentration of Triton X-114 and HNO₃, bath temperature, centrifuge rate and time on the cloud-point extraction were optimized. Under optimum conditions, the response are linear over concentration range of 0.077-1.29 (μg mL⁻¹) for Zn²⁺ and RSD % (n =5) 1.6 for Zn²⁺, Detection limits (3SDb/m, n = 10, m = slope of calibration) of 0.14 (μg.mL⁻¹) Zn²⁺ respectively. The enrichment factors was 33, the preconcentration factors was 27 for Zn²⁺ respectively. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated. The proposed method was successfully applied to the ultra-trace determination of cadmium in real samples.

Keywords: cloud-point extraction; 2-(3- indolyl) - 4,5 di phynyl imidazole (IDPI); separation, preconcentration

1. INTRODUCTION

Zinc is one of the least common elements and has been estimated to make up 0.0005-0.02% of the earth's crust. It is an essential element in the growth of many kinds of organisms, both plants and animals. Zinc is present in all body tissues and fluids [1] and is an essential component of a large number (>300) of enzymes participating in the synthesis and degradation of carbohydrates, lipids, proteins, and nucleic acids, as well as in the metabolism of other micronutrients. This metal is a cofactor of several enzyme systems and constitutes the active center of carbonic anhydrase. The

insulin compound is a zinc-containing protein while zinc is also present in most foods, particularly those high in protein [2]. Zinc stabilizes the molecular structure of cellular components and membranes and in this way contributes to the maintenance of cell and organ integrity. Furthermore, zinc plays an essential role in polynucleotide transcription and thus in the process of genetic expression. Its involvement in such fundamental activities probably accounts for the essential nature of zinc for all life forms. Moreover, zinc plays a central role in the immune system,

*Corresponding author: gh.vatankhah@gmail.com

affecting a number of cellular and humeral immunity aspects [3,4]. Zinc deficiency in the human diet has been found to retard growth and maturity and also to cause anemia. On the other hand, zinc is a man-made environmental pollutant. The concentration of zinc in unpolluted natural water is low.

Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available to determine of trace metals with enough sensitivity for most of applications. However, the determination of trace metal ions in some real samples is difficult because of various factors, their low concentrations and matrix effects [4]. Preconcentration and separation can solve these problems and lead to a higher confidence level and easy determination of the trace elements by less sensitive, but more accessible instrumentation such as flame atomic absorption spectrometry (FAAS)[5,6]. There are many methods of preconcentration and separation such as liquid-liquid extraction (LLE) [7,8], ion-exchange techniques [9,10], co-precipitation [11]. The determination of very low concentrations of trace elements usually requires separation and preconcentration step [12-14]. The use of micellar solutions in different areas of analytical chemistry has attracted much attention in recent years and separations based on cloud point extraction are becoming an important and practical application in the use of surfactants in analytical chemistry [15-18].

Cloud point extraction (CPE), employed in analytical chemistry to separate and preconcentrate organic compounds and metal ions, has been well reviewed [19-21]. As a green liquid-liquid extraction method, compared with the traditional

organic liquid-liquid extraction, cloud-point method needs a small amount of non-flammable and non-volatile surfactants that are benign to the environment. Aqueous solutions of non-ionic surfactants may separate in two phases in a narrow temperature range, called the cloud-point temperature. By using appropriate conditions, such as the temperature and pH, the solution containing the surfactant becomes turbid and separates into surfactant-rich phases (in a small volume) and the remaining larger volume (bulk solution) into the diluted aqueous solution with the surfactant concentration, which is about equal to its critical micelle concentration (CMC). The hydrophobic analytes of the solution are extracted into the surfactant-rich phase. Since the volume of the surfactant in the rich phase is very small compared to the initial volume, a high enrichment factor can be obtained [22, 23].

However, despite the critical importance of Zn^{2+} monitoring in many industrial, environmental, clinical and pharmaceutical samples, only a few cases of the use of CPE for the separation and preconcentration of Zn^{2+} has been reported in the literature [24-27].

In this work, a cloud-point preconcentration procedure was introduced for determination of Zn^{2+} ion, after the formation of complex with 2-(3-indolyl) - 4,5 di phenyl imidazole (IDPI)[28]. The lipophilic IDPI- Zn^{2+} complexes, completely extracted from aqueous solution to the concentrated micellar medium, and the analytes were ultimately analyzed by flame atomic absorption spectrometry [29].

2. EXPERIMENTAL

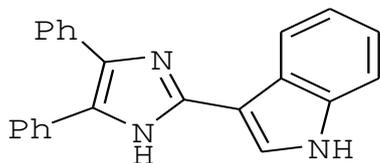
2.1. Reagents

All solutions were prepared with deionized water. Analytical-grade methanol, acids, and other chemicals used in this study

were obtained from Merck. A 1.0% (w/v) Triton X-114 from E. Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in a 100 mL volumetric flask with stirring. All chemicals such as nitrate of Zn (II) and other cations were of analytical grade purchased from Merck. The 2-(3-indolyl) – 4,5 di phynyl imidazole.(IDPI) was synthesized, purified and characterized according to the literature[28].

2.2. Synthesis of Ligand 2-(3-indolyl) – 4,5 di phynyl imidazole.(IDPI)

A mixture of benzil (1mmol), ammonium acetate (3mmol) and substituted benzaldehydes (1mmol), was added silica-bonded N-propylsulfamic acid (0.1 g) in solvent free condition at 80 °C for the appropriate time. and heated at 80 °C in an oil bath. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and remaining washed with warm ethanol (2-5 mL). After cooling, the corresponding 2,3-dihydroquinazolinone products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:3)] to give pure 2-(3-indolyl) – 4,5 di phynyl imidazole.(IDPI) in 90% yield. (Scheme1) was synthesized according to literature [28].



Scheme 1. 2-(3-indolyl) – 4,5 di phynyl imidazole.(IDPI)

Mp: 302-305 °C

¹H-NMR (DMSO-*d*₆, 400 Hz) δ: 7.05-7.16 (m, 3H), 7.23-7.28 (m, 3H), 7.37 (d,

3H, J=7.8 Hz), 7.44 (d, 2H, J=7.3 Hz), 7.56 (d, 2H, J=7.1 Hz), 7.93 (d, 1H, J=2.5 Hz), 8.40 (d, 1H, J=8.6 Hz), 11.29 (s, 1h), 12.20 (brs, 1H).

¹³C-NMR (DMSO-*d*₆, 100 MHz) δ: 106.8, 111.6, 119.7, 121.5, 121.8, 123.7, 125.1, 126.8, 128.1, 128.7, 136.2, 143.7, 145.3, 171.7.

IR(KBr) (cm⁻¹): 3412, 3055, 1621, 1598, 1491, 1451, 1336, 1208, 1182, 1049, 940, 854, 761, 749, 696.

Elemental analysis: C, 82.36; H, 5.11; N, 12.53.

Found: C, 82.17; H, 5.17; N, 12.29.

2.3. Instrumentation

ASHIMADZU AA-680 atomic absorption spectrometer equipped with deuterium background correction, Zn hollow-cathode lamps as the radiation source, was used for absorbance measurements at wavelengths of 213.9 nm respectively. The instrumental parameters were adjusted according to the manufacturer's recommendations. A UV-Vis spectrophotometer Jasco model V-570 (Japan) was used for spectrophotometric titrations. An A30 E 148 centrifuge was used to accelerate the phase separation process. A Metrohm 692 pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

2.4. General procedure

For CPE, an aliquot of 15 ml of a solution containing zinc ion, 0.1 % Triton X-114 and 0.26mM of IDPI was adjusted to pH 7.0 with HCl. The mixture was kept for 20 min in the thermostatic bath maintained at 50 °C. The phase separation is accelerated by centrifuging at 4000 rpm for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this

way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 500 μl of 2.0 M HNO_3 in methanol and then the zinc ion content was readily evaluated by FAAS.

2.5. Application of real samples

2.5.1. Water samples

Tap, well, natural mineral and sea water samples were collected in acid-leached polyethylene bottles. Bushehr tap water sample was collected from our Lab (Bushehr, Iran). The natural mineral water, well water samples and sea water sample was prepared from Persian Gulf (Iran). were selected from Bushehr and Persian Gulf, respectively in Iran. All water samples were collected (if needed), filtered through 0.45 μm Millipore cellulose acetate membrane filters to remove particles and diluted with distilled water to the ratio of 1:1. The samples were then adjusted to pH 7.0 and immediately analyzed [30].

2.5.2. Soil samples

Accurately weighed 1.0 g of soil samples from near Bushehr petrochemical center (less than 200 meshes), dried at 110 $^\circ\text{C}$ were poured into a 250-mL beaker and 10 ml concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete dry and the mixture was cooled to room temperature, A second 10-mL portion of concentrated nitric acid was added and the procedure. Then 10 mL concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 mL of 1 M HCl and the solution was then filtered into a 100-mL calibrated flask, using a syringe filter (0.45 μm pore sized). The sample was neutralized by proper amounts of a 1 M NaOH solution and finally diluted to the mark with water [31].

2.5.3. Blood samples

Homogenized blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO_3 and 2 mL 70 % HClO_4 was added and heated for 1 hour. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to 7.0 and diluted to mark with deionized water [32].

2.5.4. Vegetable sample

Spinach sample was bought from Bushehr, Iran. Afterwards, they were taken in small mesh. A 40 g sample was heated in silica crucible for 3 hours on a hot plate and the charred material was transferred to furnace for overnight heating at 650 $^\circ\text{C}$. The residue was cooled, treated with 10. mL concentrated nitric acid and 3 mL 30% H_2O_2 and again kept in furnace for 2 hours at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 7.0 made up to 15 mL by addition of KOH [33].

3. RESULTS AND DISCUSSION

The aim of this work was to develop a simple, sensitive and available method for the preconcentration and determination of trace amounts of Zn^{2+} ion in various real samples using flame atomic absorption spectrometry coupled with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and IDPI concentrations, heating time and temperature, centrifuge time and rate, as well as the effect of electrolyte on absorbance, were optimized. The

complexation study yields important information about the interaction between the ligand and metal ions. Recently, we have used the spectrophotometric method for this purpose, before using IDPI for the CPE of the metal ions.

3.1. Spectrophotometric investigation

The spectra of IDPI with the addition of Zn^{2+} ion, corresponding mole ratio plot and curve fitting at wavelength of 545 nm, are depicted in Fig 1, respectively. The resulting complexes have attracted increasing attention, generally due to their reactivity mainly in the area of binding small molecules. Consequently, we study the complexat ion of Zn^{2+} ion in methanol. Typical spectra and mole ratio plot were depicted in Fig. 1 for Zn^{2+} ion. As it were observed, significant apparent changes in the spectrum of ligand, on addition of metal ions indicate that, the ligand has strong interaction with metal ions and is an efficient sorbent for trace metal

enrichment. Further analyzing the absorbance at maximum wavelength using Kinfite program the stoichiometry and stability constant of IDPI complexes with understudy metal ions[34,35]. The stability constant for complexat ion of this ligand with these metal ions is as following. For ML the stability constant is 5.85 ± 0.01 for Zn^{2+} ion, He cumulative stability constant for ML_2 is 9.97 ± 0.04 for Zn^{2+} ion, This nature seems to be not originated from their backbone structure of ligands but mainly from the use of ligand-N-donors on the complexat ion. The extraction mechanism corresponds to a cation exchange, in which a complex of stoichiometric formula (ML or/and ML_2) is formed and liberating at the same time 2 mol H^+ ions into solution. The results of the present investigation show that the reagent H_2L can be successfully used for the quantitative extraction of heavy metals ions.

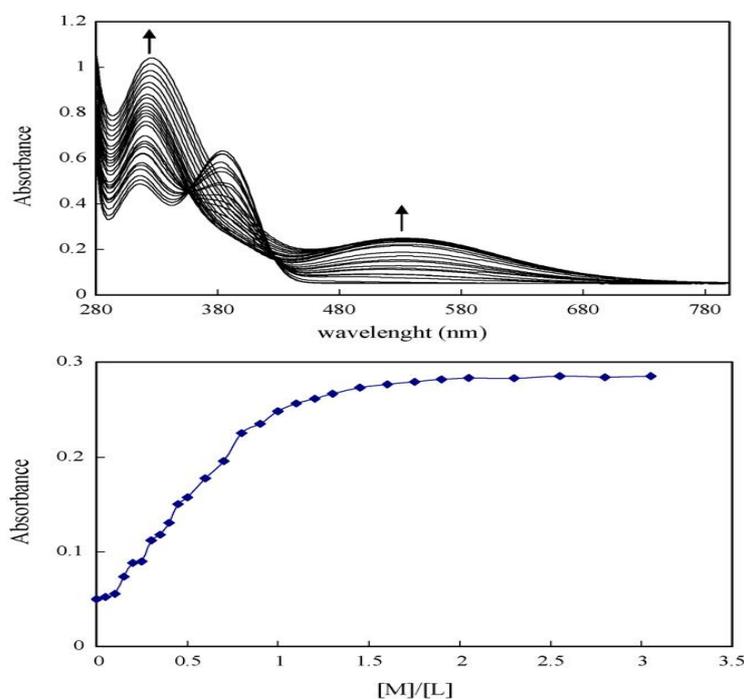


Fig. 1. UV-visible spectra for titration of L ($7.41 \times 10^{-5} \text{ mol L}^{-1}$) with Zn^{2+} ($1.00 \times 10^{-3} \text{ mol L}^{-1}$) in MeOH ($T=25^{\circ}\text{C}$ and $I = 0.05 \text{ mol L}^{-1}$). (a) The molar ratio plot in max = 545 nm. (b) The corresponding computer-fitted curve of absorbance vs. $[Zn^{2+}/L]$.

3.2. Effect of pH

A complex with sufficient hydrophobicity is required for separation of metal ions. The mentioned complex can be extracted in a small volume of surfactant-rich phase. The extraction efficiency is dependent on the pH at which complex formation occurs. Therefore, pH is the most important parameter affecting the extraction efficiency and it is necessary to choose the optimum pH at first [36-38]. The effects of pH on to extract metal complexes are given in Fig2. In the pH range of 6.5-7.0, extraction was quantitative. The decrease in recoveries at pH >7.0 is probably due to the precipitation of metal ions in the form of hydroxide, and at pH < 6.5 may be due to competition from hydronium ion toward ions for complexation with IDPI or decomposition of complex at pH <7.0, which led to the decrease in recoveries. In later experiments a pH of 7.0 was selected.

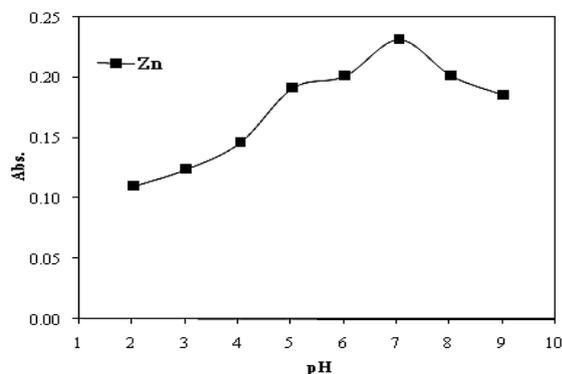


Fig. 2. Effect of pH on the extraction recovery of zinc ion. Conditions: 0.01 mg mL⁻¹, 0.26 mM IDPI, 0.1% (w/v) Triton X-114. Other experimental conditions are described in Procedures.

3.3. Effect of IDPI concentration

The absorbance of extracted metal ions as a function of the concentration of IDPI is shown in Figure 3. As can be seen, increasing IDPI concentration up to a 0.26 mM causes increasing absorbance. Thus, a IDPI concentration of 0.26 mM was

chosen to optimize other variables. At lower than 0.26 mM of IDPI, insufficient concentration leads to incomplete complexation. A possible explanation for the decrease in absorption with higher concentrations may be attributed to the formation of charged complexes with excess IDPI in the medium or with remaining excess IDPI in aqueous solution, competing with surfactant-rich phase for formation of complex with metal ions in aqueous phase.

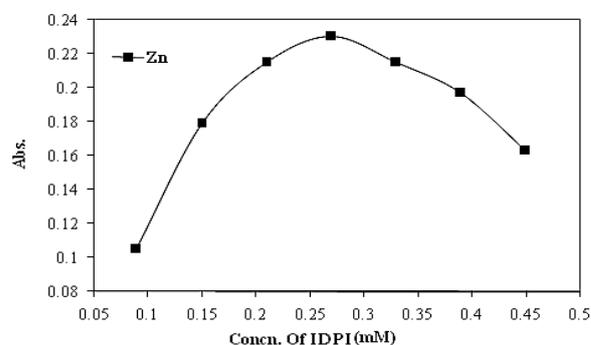


Fig. 3. Effect of IDPI concentration on the extraction recovery of zinc ion. 0.01 mg mL⁻¹, 0.1% Triton X-114, pH 7.0. Other experimental conditions are described in Procedures.

3.4. Effect of Triton X-114 concentration

Triton X-114 was used as extractant and the concentration of this surfactant affects both the extraction efficiency and the volume of the surfactant-rich phase. In order to obtain easy phase separation and maximum extraction efficiency the optimum amount of Triton X-114 should be determined [39]. The variation in absorbance of extracted Zn²⁺ ion within the Triton X-114 concentration range of 0.01 - 0.15% (w/v) was examined and results shown in Figure 3. The results show that quantitative extraction was obtained with an optimum Triton X-114 concentration of 0.1% (w/v), at which the highest absorbance for extracted Zn²⁺ ion was obtained. For concentrations lower than 0.1% (w/v), the preconcentration

efficiency of the formed complexes was very low, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Zn^{2+} ion[40]. The decreasing of absorbance at a concentration higher than 0.1% (w/v) is due to the remaining of some part of Triton X-114 and IDPI in aqueous solution as this phase can compete with surfactant-rich phase to draw analyte ions.

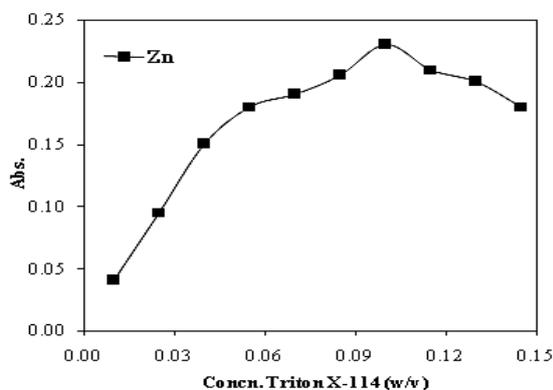


Fig. 4. Effect of Triton X-114 on zinc ion Recovery, Condition: 15 mL $1.0 \mu\text{g mL}^{-1}$ zinc ion at various Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2 % (w/v)KCl, eluting solution 0.5ml of 2.0 M HNO_3 in methanol.

3.5. Effect of temperature and equilibrium time on CPE

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range 30-70 °C and 5-30 min were thoroughly optimized, respectively[41]. Holding the sample solutions for 25 min at 50 °C was found to be satisfactory to achieve a small volume of the surfactant-rich phase, quantitative extraction and experimental convenience.

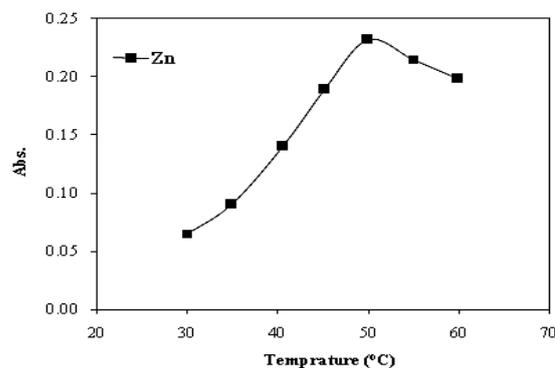


Fig. 5. Effect of temperature on zinc ion recovery, Condition: 15 mL $1.0 \mu\text{g mL}^{-1}$ zinc ion at various temperature, 0.1% (w/v) Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2 % (w/v) KCl, eluting solution 0.5ml of 2.0 M HNO_3 in methanol.

3.6. Effects of added electrolyte

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects) [42]. To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase [43,44]. In this way, 2.0 M KCl concentration was used in all further experiments.

3.7. Effect of methanol

Since the surfactant-rich phase obtained after the cloud point pre-concentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small (500 μl), methanol containing 2.0 mol L^{-1} HNO_3 was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase

without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (500 μ l) with respect to the zinc ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 500 μ l volume of methanol was therefore used throughout the remaining experiments.

3.8. Characteristics of the method

Calibration graphs were obtained by preconcentrating 2.0 mL of standard solution in the presence of 0.1% (w/v) Triton X-114, 0.26 mM IDPI with 0.2% (w/v) KCl, pH 7.0, under the experimental conditions specified in the optimized procedure section. The solutions were introduced into the flame by conventional aspiration. The characteristics of the proposed method are shown in Table 1.

Table 1. Optimum Conditions for the Presented CPE Method

Parameter	Optimum Value for ions
pH	7.0
IDPI concentration (mM)	0.26 mM
Triton X-114(w/v)	0.1 % (w/v)
Eluting agent	0.5 mL 2.0 mol L ⁻¹ HNO ₃ in methanol
Bath temperature	50 ^{0C}
Temperature time	20 min
Centrifuge time	15 min
Centrifuge rates	4000 rpm

Table 2, gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also

included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS.

Table 2. Specification of Method at Optimum Conditions for Each Element

Parameters	Ion
	Zn
Linear Range (μ g mL ⁻¹)	0/077-1/29
Correlation Coefficient	0/9990
Detection Limit (μ g.mL ⁻¹) (n =10)	0/14
Enrichment factor	33
Preconcentration factor	27
RSD % (n =5)	1/6
Recovery %	97

3.9. Interferences

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Cations that may react with IDPI, and anions that may form complexes with the metal ions were studied [45- 47]. The results were shown in Table 3. It was proved that zinc recoveries were almost quantitative in the presence of foreign cations.

Table 3. Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Ions	Added As	Tolerance Limit, mg L ⁻¹
Cl ⁻ , K ⁺ , Na ⁺ ,	KCl, NaCl, MgCl ₂	800
Cd ²⁺ , Ba ²⁺	Nitrate salts	300
PO ₄ ³⁻	Na ₃ PO ₄	800
Cu ²⁺ , Ni ²⁺ , Cr ³⁺ , Hg ²⁺	Nitrate salts	200
Ca ²⁺ , Mg ²⁺	Nitrate salts	50
Ti ⁺ , Al ³⁺ ,	Nitrate salts	150
HCO ₃ ⁻	NaHCO ₃	800

3.10. Determination of metal ions in real samples

To validate the proposed method, the

developed procedure was applied to the determination metal ions in real samples. For this purpose, 15 mL of each of the samples were pre-concentrated with 0.1%

(w/v) Triton X-114 and IDPI concentration of 0.26mM, following the proposed procedure. The results are shown in Table 4 and 5.

Table 4. Determination of analyte ions in soil, blood and vegetable

Ion	Added ($\mu\text{g.mL}^{-1}$)	Blood			Soil			Vegetable		
		Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %	Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %	Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %
Zn	0	0.8	1.4	-	1.2	0.9	-	1/3	1.2	-
	0.15	2.3	1.2	99.2	2.3	1.1	99	1/9	1/0	102

Table 5. Determination of analyte ions in Waste water (Hospital), River water and Tap water

Ion	Added ($\mu\text{g.mL}^{-1}$)	Waste water(Hospital)			River water			Tap water		
		Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %	Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %	Found ($\mu\text{g mL}^{-1}$)	RSD %	Recovery %
Zn	0	4/5	1/3	-	12/0	1/2	-	20.0	1/3	-
	0.15	11/2	1/1	99	33/0	0.9	99	32/0	1/1	102

4. CONCLUSIONS

The proposed cloud point extraction method, using ligand 2-(3-indolyl)-4,5-diphenyl imidazole (IDPI), as a stable and fairly selective complexing agent offers a simple, rapid, inexpensive and environmentally benign methodology for preconcentration and separation of Zn^{2+} ion in aqueous solutions. This method gives very low LOD, good RSD and was applied to the determination of trace amounts of Zn^{2+} ion in various real samples. In a full comparison of presented results in this paper with those previously reported, it is found that this method is superior in terms of linear range, detection limits and selectivity. For comparison, the analytical performance data of similar method reported in literature have been listed in Table 4 and 5. As it can be seen, the figures of merit of the developed method are comparable or better than the reported methods [1,3,48,49].

ACKNOWLEDGEMENTS

The authors gratefully acknowledge Bushehr Branch of Islamic Azad University, Iran.

REFERENCES

- [1] N. Dallali, M.M. Zahedi, Y. Yamini, *ScientiaIranica*. 14 (2007) 291.
- [2] N.F. Kolachi, T.G. Kazi, S. Khan, S.K. Wadhwa, J.A. Baig, H.I. Afridi, A.Q. Shah, F. Shah, *Food Chem. Toxicol.* 49 (2011) 2548.
- [3] A. Shokrollahi, H.E. Haghghi, E. Niknam, K. Niknam, *Quím. Nova São Paul.* 36 (2013) 273.
- [4] G. Mersal, M. Ibrahim, S. Fadlallah, S. El-Sheshtawy, M. Al-Malki, *Int. J. Electrochem. Sci.* 12 (2017) 710.
- [5] A.A. Gouda, *Talanta*. 146 (2016) 435.
- [6] Z. Bahadir, V.N. Bulut, D. Ozdes, C. Duran, H. Bektas, M. Soylak, *Ind. Eng. Chem.* 20 (2014) 1030.
- [7] P. L. Malvankar, V. M. Shined, *Analyst*. 116 (1991) 1081.
- [8] P. S. More, A. D. Sawant, *Analytical Letters*. 27 (1994) 1737.
- [9] S. Y. Bae, X. Zeng, G. M. Murray, *J. Anal. At.Spectrom.* 13 (1998) 1177.
- [10] N. Prakash, G. Csanady, *Mikrochim. Acta*. 3 (1989) 257.
- [11] M. Vircaus, V. Rone, A. Palne, D. Vircava, *Anal. Chim. Acta*. 299 (1994) 291.

- [12] R. Gurkan, S. Korkmaz, N. Altunay, *Talanta*. 155 (2016) 38.
- [13] J. L. Manzoori, A. Bavili-Tabrizi, *Microchem. J.* 72 (2002) 1.
- [14] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, A. Najibi, M. Soylak, *J. Hazard. Mater.* 168 (2009) 1022.
- [15] E. Pramauro, E. Pelizzetti, *Surfactants in Analytical Chemistry: Applications of Organized Amphiphilic Media*, Elsevier, NewYork, 1996.
- [16] M. Ghaedi, A. Daneshfar, A. Shokrollahi, H. Ghaedi, F. Arvin Pili, *Ann. Chim.* 97 (2007) 971.
- [17] A. M. Abdallah, M. A. Kabil, M. A. Akl, D.S. Ismael, *J. Iran. Chem. Soc.* 1 (2004) 79.
- [18] E. K. Paleologos, C. D. Stalikas, S. M. Tzouwara- Karayanni, G. A. Pilidis, M. I. Karayannis, *J. Anal. At. Spectrom.* 15 (2000) 287.
- [19] A. Shokrollahi, M. Shamsipur, F. Jalali, H. Nomani, *Cent.Eur. J. Chem.* 7 (2009) 938.
- [20] A. Shokrollahi, M. Ghaedi, R. Shabani, M. Montazerzohori, F. Chehreh, M. Soylak, S. Alipour, *Food Chem. Toxicol.* 48 (2010) 482.
- [21] M. Ghaedi, A. Shokrollahi, R. Mehrnoosh, O. Hossaini, M. Soylak, *Cent.Eur. J. Chem.* 6 (2008) 488.
- [22] C.G. Yuan, G.B. Jiang, Y.Q. Cai, B. He, J. F. Liu, *At. Spectrosc.* 25 (2004) 170.
- [23] R. Carabias-Martinaz, E. Rodriguez-Gonzalo, B. Moreno- Cordero, J. L. Perez-Pavon, C. Garcia-Pinto, E. F. Laespada, *J. Chromatogr.* 902 (2000) 251.
- [24] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, M. Soylak, *Cent. Eur. J. Chem.* 7 (2009) 148.
- [25] M. Ghaedi, A. Shokrollahi, K. Niknam, M. Soylak, *Sep. Sci. Technol.* 44 (2009) 773.
- [26] F. Shemirani, M. Baghdadi, M. Ramezani, M. R. Jamali, *Anal. Chim. Acta.* 534 (2005) 163.
- [27] S. A. Kulichenko, V. A. Doroshchuk, *J. Anal. Chem.* 58 (2003) 524.
- [28] K. Niknam, D. Saberi, *J. Can. J. Chem.* 88 (2010) 167.
- [29] M. Ghaedi, H. Tavallali, M. Zahedi, K. Niknam, M. Soylak, *J. Clean.* 37 (2009) 45.
- [30] F. Ahmadi, E. Niknam, K. Niknam, *Arabian Journal for Science and Engineering.* 36 (2011) 47.
- [31] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, S. Derki, M. Soylak, *J. AOAC Int.* 92 (2009) 35.
- [32] M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, *J. Chinese Chem. Soc.* 56 (2009) 150.
- [33] A. Shokrollahi, M. Ghaedi, R. Shabani, M. Montazerzohori, F. Chehreh, M. Soylak, S. Alipour, *Food Chem. Toxicol.* 48 (2010) 482.
- [34] A. Shokrollahi, M. Ghaedi, M. Montazerzohori, A. Kianfar, H. Ghaedi, N. Khanjari, S. Noshadi, S. Joybar, *E-J chem.* 8 (2011) 495.
- [35] A. Shokrollahi, M. Ghaedi, S. Alipour, *Eur. J. Chem.* 2 (2011) 324.
- [36] M. Bahram, S. Khezri, S. Khezri, *Current Chemistry Letters.* 2 (2013) 49.
- [37] M. Soleimani, B. Raei, Z. H. Siahpoosh, *J. Anal. Chem.* 7 (2015) 794.
- [38] C. Duran, D. Ozdes, E. Celenk Kaya, H. Kantekin, *Turk J Chem.* 36 (2012) 445.
- [39] M. Koluman, F. Tokay, S. Bagdat, *Turk J Chem.* 40 (2016) 953.
- [40] A. A. Satti, I. Durukan Temuge, S. Bektas, *Turkish Journal of Chemistry.* 40 (2016) 979.
- [41] M. A. Salehi, S. A. Milani, N. Rahgozar, *Journal of Chemical and Petroleum Engineering, University of Tehran.* 46 (2012) 135.

- [42] M. Ghaedi, K. Niknam, M. Soylak, J. Anal. Environ. Chem. 12 (2011) 42.
- [43] H. Abdolmohammad-Zadeh, E. Ebrahimzadeh, J. Braz. Chem. Soc. 22 (2011) 517.
- [44] C. Fan, S. Lue, R. Liu, Adv. 5 (2015) 65321.
- [45] R. Rahnema, M. Najafi, Environ. Monit. Assess. 188 (2016) 150.
- [46] A. Safavi, H. Abdollahi, M.R.H. Nezhad, R. Kamali, spectrochim Acta. 60 (2004) 2897.
- [47] M. S. Karacan, N. J. Aslantas, Hazard. Mater. 155 (2008) 155.
- [48] E. L. Silva, P. Roldan, M. F. Gin, J. Hazard. Mater. 171 (2009) 1133.
- [49] M. M. Hassanien, A.M. Hassan, W. I. Mortada, A. A. El-Asmy, J. Anal. Chem. 2 (2011) 697.