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Combined cloud point-solid phase extraction by dispersion of TiO_2 nanoparticles in micellar media followed by semi-microvolume UV–vis spectrophotometric detection of zinc

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ABSTRACT

A new approach is presented in this paper by using dispersed TiO_2 nanoparticles (TiO_2-NPs) in a combined cloud point and solid phase extraction for the efficient preconcentration and determination of Zn^{2+} in various samples. In this method Zn^{2+} ions are adsorbed on TiO_2-NPs and transferred into surfactant rich phase. Subsequently the Zn^{2+} ions are desorbed from TiO_2-NPs by a dithizone solution via forming a color complex which could be detected colorimetrically. The influence of chemical variables such as pH of the sample solution, electrolyte, amount of TiO_2-NPs, type and volume of the eluent on the extraction system was studied. The calibration graph was linear in the range of 0.5–90.0 $\mu g\ L^{-1}$ of Zn^{2+} (r=0.9996). An enrichment factor of 80 was achieved and the limit of detection for Zn^{2+} was 0.33 $\mu g\ L^{-1}$. The relative standard deviation (RSD) for eight replicate measurements of 10 $\mu g\ L^{-1}$ and 60 $\mu g\ L^{-1}$ of Zn^{2+} was 1.8% and 1.5% respectively. The proposed method was successfully applied to the quantitative determination of Zn^{2+} in tap water, powder milk and Zinc sulfate tablet with satisfactory results.

1. Introduction

Zinc is an essential trace element for humans, animals and plants and plays an important role in some of physiological and pathological processes such as enzyme regulation, gene expression and catalytic function of the protein. The disorder of zinc metabolism in biological systems may lead to a variety of diseases such as Alzheimer, diabetes and epilepsy [1,2]. The symptoms of zinc deficiency lead to skin problems, slow healing of wounds, reduction in the senses of taste and smell, increased susceptibility to infections, decreased fertility and the loss of appetite and hair [3]. Therefore, there is an increasing need for simple, sensitive, and inexpensive methods for the determination of zinc at low level concentration in various samples such as food, biological and water.

Most analytical techniques do not present sufficient sensitivity for the trace determination of metal ions. Despite great improvements in the sensitivity of developed modern instrumental techniques there are still difficulties in the determination of trace heavy metals because of their low levels in the samples and the complexity of the sample matrices [4,5]. Therefore preliminary preconcentration/separation and matrix-removal steps are frequently required to ensure the accuracy and precision of the analytical results. Preconcentration/separation methods including solvent extraction [6], coprecipitation [7] stripping voltammetry [8], liquid–liquid microextraction [2], solid phase extraction (SPE) [9–14] and cloud point extraction (CPE) [15–17] have been utilized for analyte enrichment.

The powder nanoparticles (PNs) have been employed in SPE for the removal and preconcentration of trace amount of analytes in different samples [18–21] because of their high surface areas and high adsorption capacity towards different compounds. Among the current applications of the PNs in analytical chemistry is nanodispersion in batch extraction method or as a nanoadsorbent in SPE for concentration/separation of different analytes from aqueous solution.

Nevertheless, limitations of using nano-sized materials as adsorbents in SPE method is changing the shape and size of nanomaterials which redound to accumulation and decreasing of the surface area and also slow flow rate which leads to long process time. On the other hand, many studies have used the nanoparticles as adsorbents in batch extraction method for analytical purposes [22] in which the separation of the nanoparticles from high volume of aqueous sample is difficult and hence the preconcentration factor is small. To overcome the aforementioned problems, PNs could be used in CPE method for preconcentration of the analytes.

CPE using micelles is a well known methodology for designing new analytical procedures for different analytes such as organic

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compounds [23], metal ions [24], pharmaceuticals [25] and dyes [26]. CPE is a safe and green methodology which uses small amount of surfactant which limits the environmental pollution. Liu et al. have successfully evaluated the CPE of several nanomaterials with various sizes and different capping agents using non-ionic surfactant Triton X-114 [27]. Their suggested method has illustrated that CPE can be used for concentration and recycling of nanoparticles (NPs) in aqueous media.

In the present work, TiO_2-NPs were utilized as solid nanosubstrates for adsorption of Zn^{2+}, and for performing CPE method for preconcentration/separation of Zn^{2+}–TiO_2-NPs from aqueous solutions using Triton X-100 as a nonionic surfactant. The Zn^{2+}–TiO_2-NPs were easily transferred to the surfactant rich phase and the enriched surfactant phase was separated by centrifugation. The elution of Zn^{2+} ions from enriched TiO_2-NPs were performed using semi-microvolumes of dithizone solution through the formation of a colored complex. Subsequently, the colorimetric sensing of Zn dithizonate was carried out by measuring the absorbance at $\lambda = 530$ nm by UV–vis spectrophotometer.

2. Experimental section

2.1. Apparatus

Absorbance measurements were performed by GBC UV–visible spectrophotometer model Cintra 101 (Sidney, Australia) using 700 μL glass cells. A digital pH-Meter model 632, Metrohm (Herisau, Switzerland) with a combined glass electrode was used for pH measurements. A thermostat bath model Colora (England) maintained at the desired temperature was applied for the CPE temperature experiments.

2.2. Reagents

All chemicals were of analytical grade and doubled distilled water was used throughout. A stock solution of 1000 mg L^{-1} of Zn^{2+} was prepared by dissolving 0.4549 g of $Zn(NO_3)_2 \cdot 6\,H_2O$ (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. This solution was standardized by EDTA titration [28]. More diluted solutions were prepared daily using this stock solution. 1.0 mol L^{-1} of NaCl was prepared by dissolving 5.844 g of sodium chloride (Merck) in water and diluting it to 100 mL in a volumetric flask. 5% (v/v) of Triton X-100 was made by diluting 5 mL of Triton X-100 (Merck) to 100 mL. 5.85×10^{-4} mol L^{-1} of dithizone solution was prepared by dissolving 0.015 g of dithizone (Merck) in 100 mL of acetone/ethanol (3:7). This solution was provided weekly. Phthalate buffer solution pH 7 was prepared by adding 0.05 mol L^{-1} of NaOH (Merck) to 0.05 mol L^{-1} of phthalic acid (Merck) and adjusting the pH to 7 using a pH meter. TiO_2 nanoparticles (average size 50 nm) were purchased from Nanobond Technology (Tehran, Iran). Triton X-114 was purchased from Sigma (St. Louis, MO, USA). Ethanol and acetone were from Merck Company.

2.3. Recommended procedure

The colorimetric determination was carried out by performing the following steps. 5 mg of TiO_2-NPs was added to 8 mL of 5% (v/v) of Triton X-100 as the nonionic surfactant. The mixture was stirred for 1 min, causing further dispersion and suspension of the TiO_2-NPs. Then an aliquot of zinc solution (so that its final concentration would be in the range of 0.5–90 μg L^{-1}), 1 mL of phthalate buffer (pH 7) and 1 mL of 0.5 mol L^{-1} of NaCl, were added to the above mixture in a 50 mL volumetric flask and diluted to the mark with water. This solution was transferred to a 50 mL conical centrifuge tube and placed in a thermostat water bath at 80 °C for 40 min. Under this condition, the analyte was adsorbed on the TiO_2-NPs and the phase separation occurred. Subsequently, the solution was cooled in an ice-bath for 5 min. The TiO_2-NPs easily settled down in the surfactant phase and the aqueous phase was decanted. The enriched surfactant phase was separated from TiO_2-NPs by centrifugation (3 min). Next, 500 μL of dithizone (5.85×10^{-4} mol L^{-1}) was added to TiO_2-NPs and shaken for about 2 min to desorb the Zn^{2+} ions. Finally, the mixture was centrifuged (~3 min), the eluate (Zn dithizonate) was collected in a 700 μL glass cell and its absorbance was measured at $\lambda = 530$ nm by UV–vis spectrophotometer. A blank solution was also run under same conditions without adding any Zn^{2+} ion.

2.4. Sample preparation

2.4.1. Powder milk

1 g of powder milk sample was precisely weighted and transferred to a porcelain crucible and treated with 1.0 g of NaOH dissolved in few milliliters of water. The crucible content was gently heated at 110 °C to dryness and it was then placed in a furnace at 500 °C for 20 min. After cooling to room temperature, the residue was dissolved in 15 mL of water and 2 mL of concentrated nitric acid [29]. The solution was filtered through a filter paper and the pH of the solution was adjusted to 7 by suitable addition of 1.0 mol L^{-1} of sodium hydroxide solution. This solution was finally transferred to a 50 mL volumetric flask and made up to the mark with water. An aliquot of this solution was subjected to the general procedure.

2.4.2. Preparation of tablet sample

220 mg of zinc sulfate tablet was dissolved in 100 mL of water. Then, 0.2 mL of this solution was placed in a 100 mL volumetric flask and made up to the mark with water. An aliquot of this solution was subjected to the general procedure.

2.4.3. Preparation of tap water

Tap water sample was collected in the lab, boiled, filtered before use and its pH was adjusted to 7. An aliquot of the solution was subjected to the general procedure.

3. Result and discussion

It has been shown that PNs could be enriched into the surfactant rich phase at pH values about their point of zero charge (pH_{pzc} is the pH at which the surface charge of NPs is zero) [27]. The charge of NPs is negative if $pH > pH_{pzc}$ and positive if $pH < pH_{pzc}$. Therefore, any species existing in the aqueous phase, which could be adsorbed on the NPs surface and neutralize the charge of NPs, is concentrated into surfactant rich phase by CPE.

In this work, Zn^{2+} ion are adsorbed on the dispersed TiO_2-NPs as a solid phase in micellar media and then separated by performing CPE. In the absence of Zn^{2+} ions, the surface charge of TiO_2-NPs at pH~6.2 (reported pHpzc for TiO_2-NPs) [30] is neutral and they are enriched into non-ionic surfactant phase. At $pH > 6.2$ surface charge of TiO_2-NPs is negative; therefore when Zn^{2+} ions are present, they are adsorbed on the surface of TiO_2-NPs and the surface charge becomes neutral. Thus, Zn^{2+}–TiO_2-NPs are enriched into non-ionic surfactant phase. Our investigation indicated that the nonionic surfactant only transfers Zn^{2+}–TiO_2-NPs, and Zn^{2+} ions alone in solution are not transferred from the aqueous phase to ionic surfactant phase under these circumstances. After CPE, the surfactant phase is discarded and Zn^{2+}–TiO_2-NPs are treated with dithizone solution to strip Zn^{2+} ions by forming a color complex

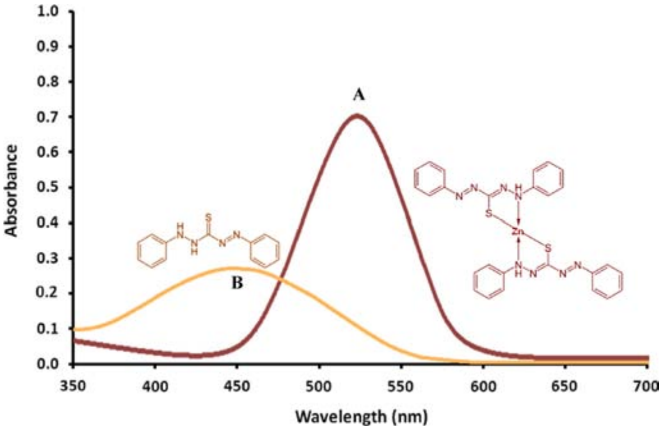

Fig. 1. Absorption spectra of (A) Zn dithizonate stripped from TiO_2-NPs and (B) the blank.

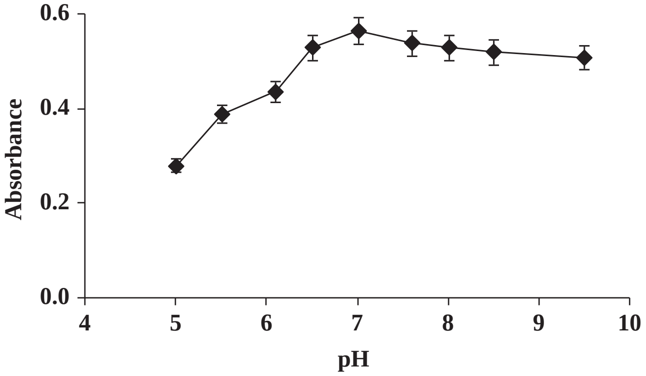

Fig. 2. Influence of pH on determination of 40 μg L^{-1} of Zn^{2+} with CPE–SPE using TiO_2-NPs in micellar media.

(Zn dithizonate) (Fig. 1). The absorbance of this complex at λ=530 nm is proportional to Zn^{2+} concentration.

3.1. *Effect of pH*

The pH of the sample solution is an important factor that influence the surface charge of TiO_2-NPs; therefore the effect of pH on the preconcentration of 40 μg L^{-1} of Zn^{2+} with CPE–SPE using TiO_2 NPs in micellar media was evaluated in the range of 5.0–9.5. The sample solutions were adjusted to the desired pH using 0.1–1.0 mol L^{-1} of hydrochloric acid and/or sodium hydroxide. The results of this investigation shown in Fig. 2 demonstrate that the highly effective adsorption of Zn^{2+} on the TiO_2-NPs is achieved when pH is above 6.5. As stated earlier this pH is above pH_{pzc} of TiO_2-NPs and thus its surface is negative and Zn^{2+} are adsorbed better on the surface of TiO_2-NPs. Thus pH=7 was selected for subsequent work. To maintain the pH of solution at 7, buffer solutions with pH 7 such as maleate, carbonate, phosphate, Britton–Robinson and phthalate were examined. It was found that the phthalate buffer at pH 7 was suitable because it did not change the absorbance. Therefore phthalate buffer was selected for this study and 1 mL of phthalate buffer was added to sample solutions to adjust the pH at 7.

3.2. *Effect of eluent type, concentration and volume*

The type, volume and concentration of eluent are important parameters for this kind of study. The Zn^{2+} ion reacts with dithizone in CCl_4 media to form a color complex with an absorbance peak at λ=530 nm. Due to the toxicity of carbon tetrachloride (CCl_4), it was replaced with less toxic solvents such as acetone, methanol or ethanol in this study. Thus 0.015 g dithizone was dissolved in 100 mL (5.85×10^{-4} mol L^{-1}) of aforementioned solvents alone or in mixtures with different volume fractions for desorption of Zn^{2+} ions from the TiO_2-NPs. The results of this investigation revealed that the highest absorbance is obtained when a mixture of acetone–ethanol with a ratio of 3:7 was used for preparation of dithizone solution. The effect of different volumes of this eluent in the range of 200–600 μL was investigated and the results showed that the absorbance was enhanced until it finally reached a plateau at 500 μL and the eluent volumes over 500 μL did not significantly affect the extraction efficiency. Thus 500 μL of 5.85×10^{-4} mol L^{-1} of dithizone in acetone/ethanol (3:7) was selected as the eluent for subsequent measurements.

3.3. *Effect of electrolyte*

It has previously been investigated that the addition of salts, alcohols and some organic compounds to a micellar aqueous solution can affect the extraction efficiency of the CPE process [31,32]. In order to assess the effect of the electrolytes in this work, the experiments were carried out by adding various salts with different concentrations (0.005–0.06 mol L^{-1}) to the solutions before CPE. It was specified that among the salts such as NaCl, KNO_3 and $CaCl_2$ that were examined, NaCl was a better electrolyte for this system because of providing higher absorbance at all concentrations. As can be ascertained from Fig. 3, the analytical signal was almost constant up to 2×10^{-2} mol L^{-1} of various salts and decreased above this concentration. Increasing the electrolyte concentration could neutralize the surface of the adsorbent resulting in less adsorption of the analyte in SPE. On the other hand due to the salting-out effect of electrolytes, more water goes to the dilute phase, decreasing the volume of the surfactant rich phase in CPE and increasing the concentration of analyte and hence its absorbance [33]. Therefore, the different behaviors of the salts in this study could probably be due to the dual role of electrolytes in the combined SPE and CPE method. Thus, in this study, NaCl (1×10^{-2} mol L^{-1}) which provided higher signal than other salts was chosen for the following experiments and 1.0 mL of 0.5 mol L^{-1} of NaCl was added to 50 mL solutions in order to achieve this concentration.

3.4. *Effect of mass of adsorbent*

The extraction efficiency is dependent on the amount of adsorbent. In order to estimate the optimum adsorbent quantity,

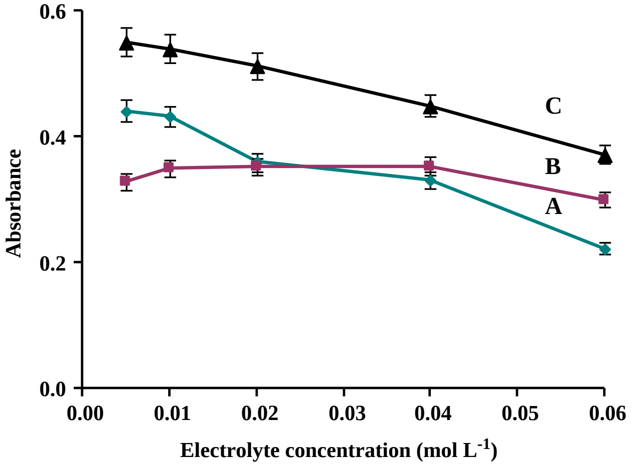

Fig. 3. Influence of electrolyte (A) $CaCl_2$, (B) KNO_3 and (C) NaCl on determination of 40 μg L^{-1} of Zn^{2+} with CPE–SPE using TiO_2-NPs in micellar media.

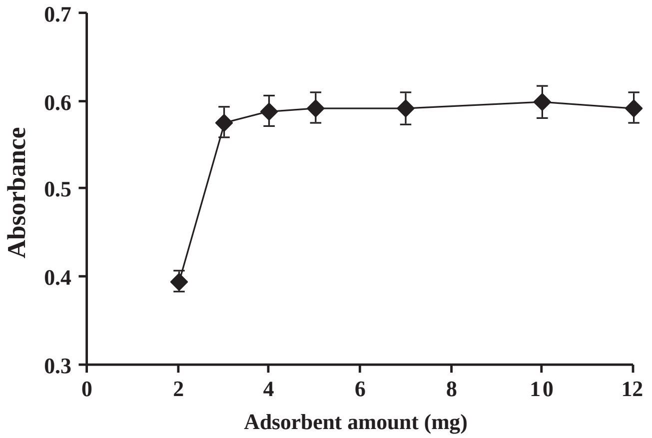

Fig. 4. Influence of adsorbent amount on determination of 40 μg L^{-1} of Zn^{2+} with CPE–SPE using TiO_2-NPs in micellar media.

different amounts of the adsorbent (TiO_2- NPs) in the range of 2–12 mg were used for the preconcetration of Zn^{2+}. The results shown in Fig. 4 indicate that the absorbance of the eluted samples is almost constant when the amount of the adsorbent is greater than 4 mg. Therefore in this procedure, 5 mg of TiO_2- NP was selected as the optimum amount of adsorbent.

3.5. *Surfactant selection and influence of its concentration*

The presence of a surfactant is vital in any CPE procedure in order to form two isotropic phases from aqueous solution. On the other hand, in this case, the surfactant also acts as a dispersing agent for TiO_2-NPs in aqueous solution. Therefore, a non-ionic surfactant was used as a dispersing and stabilizing agent and also for CPE process. In order to investigate the effect of non-ionic surfactant types on the system, surfactants such as Triton X-114 and Triton X-100 and mixture of both were examined. The results revealed that Triton X-100 shows higher analytical signal. Therefore, Triton X-100 5% (v/v) was selected and the influence of its volume on the extraction efficiency and sedimentation of the TiO_2 nanoparticles was investigated by adding different volumes of Triton X-100 5%(v/v) in the range of 4–10 mL. The obtained results demonstrate that the highest analytical signal was observed when the volume of Triton X-100 5% (v/v) was above 8 mL. Thus, this volume was selected as optimum in the subsequent studies.

3.6. *Effect of equilibrium temperature and time*

Two important parameters in CPE procedures are incubation time and equilibration temperature. It has been shown that increased temperature and prolonged reaction time result in more satisfactory extraction. Therefore the effects of equilibration temperature and incubation time on CPE of Zn^{2+}–TiO_2-NP were investigated in the range of 65–90 °C and 20–50 min, respectively. Maximum absorbance was obtained when the solution was equilibrated at 80 °C for an equilibration time of 40 min. The results also showed that the standing time of surfactant enriched phase in the ice bath had no significant effect on the extraction efficiency. Accordingly, a standing time of 5 min in ice bath was chosen for next experiments.

3.7. *Reusability of TiO_2 nanoparticles*

The reusability of the TiO_2-NPs was also investigated. For this purpose, after the elution of Zn^{2+}–TiO_2-NPs by dithizone solution and washing the nanoparticles with water, the recommended procedure was repeated many times. The results showed that each 5 mg of TiO_2-NPs can be used five times without any significant loss in the absorbance (less than 2% decrease in the absorbance).

3.8. *Interferences study*

In order to examine the selectivity of the method, the effects of other anions and cations on the analytical signal of Zn^{2+} were investigated in the system under the optimum experimental conditions. The experiments were performed at a constant concentration of Zn^{2+} (40 μg L^{-1}) and measuring the absorbance before and after adding the possible interfering ions. A relative error of $\pm 5\%$ in the absorbance measurement was considered as interference. The results of this study summarized in Table 1 demonstrate that most of the common coexisting ions did not show a serious effect on the separation and determination of Zn^{2+} ion. The interference of Ag^+ and Ni^{2+} up to 10 fold was overcome by the addition of thioglycolic acid. The reasonable selectivity obtained probably depends on both adsorption tendency of TiO_2-NPs for these cations and pH at which they are extracted by dithizone. It has been stated that the metal dithizonates are extracted in different pH media [34]. The most stable dithizonates (Cu, Hg, Pd, and Ag) can be extracted from strong acidic solutions. Some metals (Bi, In, and Zn) are extractable from weakly acidic media, whereas other metals such as CO, Ni, Pb and Tl are extractable from neutral or alkaline media.

3.9. *Analytical performance*

Under optimum conditions, the analytical characteristics of the developed procedure were evaluated. The calibration curve was linear in the range of 0.5–90.0 μg L^{-1} of Zn^{2+} ion with a correlation coefficient (*r*) of 0.9996. The equation of the line for Zn^{2+} was $A = 0.0162C + 0.0026$ where *A* is the absorbance and *C* is the concentration of Zn^{2+} in μg L^{-1} in the initial solution. The UV–visible absorption spectra of Zn-dithizonate after the elution from TiO_2-NPs at different concentrations and the corresponding calibration curve are shown in Fig. 5. The limit of detection (LOD) defined as the concentration giving a signal to noise ratio of 3:1 was found to be 0.33 μg L^{-1} and the relative standard deviation (RSD) for eight replicate measurements of 10 μg L^{-1} and 60 μg L^{-1} of Zn^{2+} ion were 1.8% and 1.5% respectively. An enrichment factor of 80 (defined as the ratio between the analyte concentration in the extract at the end of the extraction process and its initial concentration in the sample) was achieved. A comparison of the developed method with some of the previously reported methods for Zn^{2+} by different preconcentration procedures is shown in Table 2. From the table, it is observed that the proposed procedure presents analytical characteristics better or comparable to some of those previously reported in the literature.

3.10. *Application to environmental samples*

In order to evaluate the applicability of the proposed method, it was utilized for determination of Zn^{2+} concentration in tap water, powder milk and zinc sulfate tablet. These samples were also

Table 1
Effect of interfering ions on the determination of 40 ng mL^{-1} of Zn^{2+}.

Interfering ion	Tolerance ratio $[M]/[Zn^{2+}]$
Ca^{2+}, Mg^{2+}, Mn^{2+}, NH_4^+, SO_3^{2-}, acetate	1000
PO_4^{3-}, Br^-, I^-, F^-, NO_2^-, NO_3^-, citrate , tartarate,	100
CO_3^{2-}, $C_2O_4^{2-}$,	100
Al^{3+}, Mo^{2+}, Hg^{2+}, Cr^{3+} ,Pb^{2+} Ni^{2+}, Ag^+	10
Co^{2+}, Cu^{2+}, Fe^{2+}	5
Cd^{2+}	1

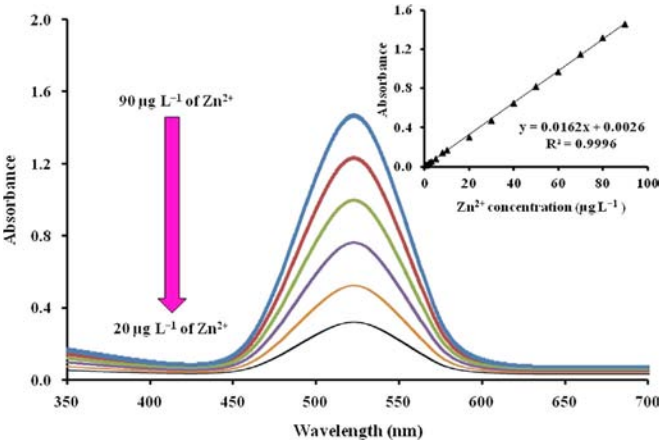

Fig. 5. UV–visible absorption spectra Zn dithizonate stripped from TiO_2-NPs at different concentrations and the corresponding calibration curve.

Table 2
Comparison of the proposed method with some of the methods reported in literature.

System	Enrichment factor	LOD ($\mu g\ L^{-1}$)	RSD (%)	Ref.
LLME	45	2.3	2.4	2
CPE–PAN	30	2.3	2.3	3
Ion imprinted polymer	118	0.48	2.5	10
Ionic liquid and Fe_3O_4@Si-OH	–	0.56	3.7	13
CPE–PBHA	74.2	0.42	2.65	16
MWCNTs impregnated with D2EHPA-TOPO	25	60	< 10	19
CPE-quinaldine	30	1.4	2.2	24
CPE–SPE–TiO_2	80	0.33	1.47	This work

LLME (Liquid–liquid microextraction).
PAN (1-(2-Pyridilazo)-2-naphthol).
PBHA (N-phenylbenzohydroxamic acid).
D2EHPA (di-(2-ethyl hexyl phosphoric acid)).
TOPO (tri-noctyl phosphine oxide).
MWCNTs (Multiwalled carbon nanotubes).

Table 3
Determination of Zn^{2+} in sample solutions.

Samples	Zn^{2+}added (ng mL^{-1})	Zn^{2+} found[a] (ng mL^{-1})	Recovery (%)
Tap water	–	20.6 ± 0.4	–
	10	30.6 ± 0.4	100.0
	20	40.9 ± 0.2	101.5
Powder milk	–	22.0 ± 0.2	–
	10	32.5 ± 0.6	105.0
	20	42.8 ± 0.9	104.0
Zinc sulfate tablet	–	10.1 ± 0.2	–
	10	19.6 ± 0.4	96.0
	20	30.7 ± 0.7	103.0

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence ($n=5$).

spiked with two concentration levels of Zn^{2+} and analyzed. The results of this determination and the recoveries for the spiked samples are listed in Table 3. As can be seen the proposed method provided acceptable recoveries in the range of 96–105%.

In order to estimate the accuracy of the procedure, two soil samples were also analyzed by both the proposed method and flame atomic absorption spectrometric (FAAS) method. The values obtained by both methods show that there is a good agreement among the results and there was no significant difference between them by performing a *t*-test at 95% confidence limit (Table 4).

Table 4
Determination of Zn^{2+} in samples and comparison by FAAS.

Sample	Proposed method[a] (mg g^{-1})	FAAS (mg g^{-1})
Powder milk	0.055 ± 0.004	0.054 ± 0.005
Zinc sulfate tablet	229.5 ± 10.0	227.3 ± 10.0

[a] $\bar{x} \pm ts/\sqrt{n}$ at 95% confidence ($n=5$).

4. Conclusions

In this investigation, the TiO_2-NPs were used in a new combined CPE–SPE method followed by semi-microvolume UV–vis spectrophotometric detection of Zn^{2+}. In this method TiO_2 nanoparticles were used as an assisted-solid phase for preconcentration of Zn^{2+} by CPE. The developed method has the advantages of simplicity, relative selectivity and high preconcentraion factor for Zn^{2+}. A small amount of adsorbent, low volume of solvent and surfactant are employed in this procedure. The procedure is inexpensive, because it does not require sophisticated equipment and uses instrument such as UV–vis spectrophotometer which is available in most laboratories. The determination of zinc in various samples was successfully performed using the proposed method

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References

[1] Y. Ma, H. Chen, F. Wang, S. Kambama, Y. Wang, C. Mao, X. Chen, Dyes Pigment. 102 (2014) 301–307.
[2] M. Shamsipur, M.M. Zahedi, G. De Filippo, V. Lippolis, Talanta 85 (2011) 687–693.
[3] R. Galbeiro, S. Garcia, I. Gaubeur, J. Trace Elem. Med. Biol. 28 (2014) 160–165 http://dx.doi.org/10.1016/j.jtemb.2013.12.004.
[4] Q.F. Hu, G.Y. Yang, J.Y. Yin, Y. Yao, Talanta 57 (2002) 751–756.
[5] C. Karadas, O. Turhan, D. Kara, Food Chem. 141 (2013) 655–661.
[6] A. Oliva, A. Molinari, F. Zuniga, P. Ponce, Mikrochim. Acta 140 (2002) 201.
[7] D. Citak, M. Tuzen, M. Soylak, Food Chem. Toxicol. 47 (2009) 2302–2307.
[8] B. Feier, D. Floner, C. Cristea, E. Bodoki, R. Sandulescu, F. Geneste, Talanta 98 (2012) 152–156.
[9] M. Tuzen, M. Soylak, L. Elci, Anal. Chim. Acta 548 (2005) 101–108.
[10] F. Shakerian, S. Dadfarnia, A.M. Haji Shabani, Food Chem. 134 (2012) 488–493.
[11] S. Rastegarzadeh, N. Pourreza, A.R. Kiasat, H. Yahyavi, Microchim. Acta 170 (2010) 135–140.
[12] N. Pourreza, K. Ghanemi, J. Hazard. Mater. 178 (2010) 566–571.
[13] C. Cui, B. Hu, B. Chen, M. He, J. Anal. Atom. Spectrosc. 28 (2013) 1110–1117.
[14] N. Pourreza, H. Parham, F. Habibzadeh, J. Iran. Chem. Soc. 10 (2013) 319–324.
[15] N. Pourreza, M.R. Fat'hi, A. Hatami, Microchem. J. 104 (2012) 22–25.
[16] R. Gürkan, N. Altunay, Anal. Methods 7 (2013) 1755–1763.
[17] N. Pourreza, S.h. Elhami, J. Iran. Chem. Soc. 6 (2009) 784–788.
[18] A.F. Barbosa, M.G. Segatelli, A.C. Pereira, A. de Santana Santos, L.T. Kubota, P.O. Luccas, C.R. Teixeira Tarley, Talanta 71 (2007) 1512–1519.
[19] N. Pourreza, K. Shaikhnajdi, Talanta 99 (2012) 507–511.
[20] S. Vellaichamy, K. Palanivelu, J. Hazard. Mater. 185 (2011) 1131–1139.
[21] N. Pourreza, S. Rastegarzadeh, A. Larki, J. Ind. Eng. Chem. 20 (2014) 127–132.
[22] X. Liu, X. Lu, Y. Huang, C. Liu, B.S. Zhao, Talanta 119 (2014) 341–347.
[23] E. Caballero-Díaz, B. Simonet, M. Valcárcel, Anal. Methods 5 (2013) 3864–3871.
[24] 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) 2548–2556.
[25] C. Kukusamude, A. Santalad, S. Boonchiangma, R. Burakham, S. Srijaranai, O. Chailapakul, Talanta 81 (2010) 486–492.
[26] N. Pourreza, M. Zareian, J. Hazard. Mater. 165 (2009) 1124–1127.
[27] J. Liu, R. Liu, Y. Yin, G. Jiang, Chem. Commun. (2009) 1514–1516.

[28] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd ed., Longman, London, 1961.
[29] S. Rastegarzadeh, V. Rezaei, Sens. Actuators B 129 (2008) 327–331.
[30] Y. Ku, I.-L. Jung, Water Res. 35 (2001) 135–142.
[31] C.C. Nascentes, M.A.Z. Arruda, Talanta 61 (2003) 759–768.
[32] L.M. Coelho, M.A.Z. Arruda, Spectrochim. Acta Part B 60 (2005) 743–748.
[33] M.K. Purkait, S. DasGupta, S. De, J. Hazard. Mater. B137 (2006) 827–835.
[34] Z. Marczenko, Spectrophotometric Determination of Elements, Ellis Horwood Ltd., Sussex, England, 1976.