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Efficiency Enhancement of the Spectrophotometric Estimation of Zinc in Water, Food, Tobacco and Pharmaceutical Preparations Samples Utilizing Cloud Point Extraction

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Abstract

To increase the analytical effectiveness of spectrophotometric detection of zinc (Zn (II)) in water, food, tobacco, and pharmaceutical preparations samples, cloud point extraction (CPE) and a new chromogenic reagent were used in this study. The proposed methodology is based on measuring the absorbance of a Zn(II) complex with 2-amino-4-(4-nitrophenyl) diazenyl) pyridine-3-ol (ANPDP) at pH 9.0 in Triton X-114 at maximum 595 and maximum 605 nm for methods without and with CPE. Investigation and optimization were done on the key variables determining CPE effectiveness. For techniques without CPE and with CPE, respectively, the calibration graph was linear under ideal conditions in the ranges of 10-140 µg mL^{-1} and 0.01-0.8 µg mL^{-1}, with R^2 = 0.9989 and 0.9997, respectively. For techniques without CPE and with CPE, the detection limits were 3.0 µg mL-1 and 0.003 µg mL^{-1} with a preconcentration factor of 50, respectively. As precision, the relative standard deviation (RSD %) is 4.0%. The interactions of various cations and anions have been studied. The proposed CPE method was successfully used to estimate Zn (II) in a variety of samples, including water, food, tobacco, and pharmaceutical preparations.

Keywords: Zinc; Water, food, tobacco and pharmaceutical preparations samples; Cloud point extraction; Spectrophotometry.

1. Introduction

For people, animals, and plants alike, zinc is a crucial trace element [1]. Superoxide dismutase is also found in zinc because it is essential for the body's defence against activated oxygen species [2]. Therefore, if there is a high amount of zinc, it plays a significant role in the progression of various health problems that affect the human body, such as an increase in oxidative stress or changes in energy metabolism. In addition, this metal serves as a cofactor for over 200 enzymes and plays a structural role in many Zn finger proteins. Premature pregnancy, growth retardation, weight loss, impaired immunological response, and anorexia were all caused by Zn deficiency. Zn excess can be harmful, impairing the body's ability to maintain homeostasis and causing oxidative stress, whereas Zn deficiency can result in biochemical and histological abnormalities [3, 4]. The immunological, digestive, and brain systems all depend on zinc for normal operation, and it is found in many foods [5]. Zinc is also important in enzymes. Lack of zinc (Zn) can alter the nervous system's perceptions, reduce sperm count, impair cognitive processes, stop growth, take longer for wounds to heal, compromise the immune system, and lead to dermatitis. Growth arrest, infertility, nausea, diarrhoea, hemoglobinuria, liver and renal failure, and anaemia can all be brought on by a zinc deficiency [6]. Zn has been identified by the EPA as a non-mandatory water quality standard pollutant with a "secondary maximum contaminant level" (SMCL) of 5 mg L^{-1}, at which impacts on metallic taste are indicated [7]. At the SMCL, this contamination is not thought to pose a threat to

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human health.

Analytical chemistry finds the determination of trace metal ions in water, food, and environmental samples to be intriguing and crucial [8]. A wide range of methods, such as FAAS [9], ICP-MS [10], and electrochemical [11, 12], have been used to measure Zn(II) ions in different samples. Despite the fact that these procedures yield quantitative results, they are not suitable for the direct examination of Zn (II) ions in samples due to traces and matrix interference. They also have fundamental restrictions on the price, difficulty, sample processing, and run times of the equipment. Due to these factors, it is usually necessary to perform preliminary preconcentration and matrix-removal processes to guarantee the precision and accuracy of the analytical data.

Improved Zn detection in real samples requires and benefits from a pre-concentration and enrichment process. Due to its safety, environmental friendliness, simplicity, speed, single-stage operation, and affordability, the CPE technique is regarded as a pre-concentration and enrichment phase [13–15].

Liquid-liquid micro-extraction [13, 14], solid-phase extraction [15, 16], and chemical partitioning extraction [17-26] are the three most popular preconcentration techniques for finding Zn(II) in various materials right now. Because these processes can reduce or stop the usage or manufacture of harmful compounds, separation and preconcentration based on CPE have received a lot of attention recently. It adheres to the tenets of "green chemistry." Additionally, as compared to the traditional liquid-liquid extraction technique, the CPE methodology has gained popularity because to its high enrichment factor, high recovery, quick phase separation, low cost, minimal use of organic solvents, and ability of be combined with other detection methods. To quantify the concentration of metal elements in various samples, CPE has been employed in conjunction with a range of modern analytical techniques, including FAAS and spectrophotometry [27-33].

The current work seeks to propose a novel, sensitive, easy, affordable, green, and valid CPE methodology for preconcentration and measurement of tiny quantities of Zn(II) in various water, food, tobacco, and pharmaceutical preparation samples to improve the analytical efficiency of spectrophotometric estimation of Zn(II) in these samples. A novel chelating agent, 2- amino-4-(4-nitrophenyl) diazenyl) pyridine-3-ol (ANPDP), was used to chelate the trace amount of Zn(II), and the produced complex was found in Triton X-114 as a nonionic surfactant, which is less expensive and less harmful. Investigation and optimization were done on the experimental variables impacting CPE effectiveness.

2. Experimental

2.1. Apparatus

JASCO V-670 double-beam UV-Vis spectrophotometer (Tokyo, Japan) with wave length 200-800 nm and a 10 mm quartz cell was used to measure the absorbance. For measuring the pH of solutions, an Orion Research Model 601 A/digital ionalyzer pH meter was used. To hasten the phase separation procedure, a centrifuge with 25 mL centrifuge tubes (Isolab, Germany) was employed. For the CPE tests, a thermostated water bath with precise temperature control was employed. A Nicolete IS10 FTIR spectrophotometer was used to record the IR spectra on KBr discs in the 4000-400 cm-1 region in order to describe the produced reagent. The 1HNMR spectra were collected using a JEOL (500 MHz) spectrometer in DMSO-d_6 solvent.

2.2. Chemicals and reagents

Unless otherwise noted, all chemicals were of analytical-reagent grade, and water was double-distilled.

Standard stock solution for zinc (II)

The appropriate amount of $ZnCl_2$ (Merck, Darmstadt, Germany) was dissolved in 100 mL of deionized water to make a stock of standard solution (1.0×10-3 mol L^{-1} and 1000 mg L^{-1}) of Zn(II).The working standard solutions were made fresh by dilution with water. Every day, a new version of the solution was created.

As previously advised, acetate, citrate, borate, phosphate, and universal buffer solutions with pH ranges of 2.0 to 12 were made.

Triton X-114, was provided by Fluka, Buches, Switzerland, and utilised without additional purification. The Triton X-114 solution was made into an aqueous (2.0%, v/v) form by swirling 2.0 ml of Triton X-114 into 100 ml of bidistilled water in a volumetric flask. The following surfactants were made in 100 mL of water: Cetyltrimethylammonium

Bromide (CTAB), Triton X-100, Sodium Lauryl Sulfate (SLS), and Tween 80 at a concentration (5.0%). In order to make 0.6 mol L^{-1} of sodium dodecyl sulphate (SDS), 86.514 g of pure SDS were dissolved in 500 mL of distilled water. Direct dilution of the concentrated solutions in deionized water. Using methanol, acetone, and ethanol (Merck), the surfactant-rich phase's viscosity was decreased. By carefully diluting the various cations and anions (Sigma-Aldrich, USA) in bidistilled water, the solutions of different cations and anions employed for the interference investigation were prepared.

2.3. Synthesis of ANPDP reagent

The p-nitroaniline (0.01 mole) in the aromatic amines was converted to the hydrochloride form by adding the least amount of concentrated hydrochloric acid, which was then diluted with bidistilled water and cooled at -5°C. The amine salt is progressively mixed with a cooled solution of $NaNO_2$ (0.01 mole) while being continuously flipped. The resultant diazonium salt solution is added gradually to a solution of 2-amino-3-hydroxypyridine (0.01 mole) dissolved in 10% NaOH and chilled at -5°C after being let stand for 15 minutes in an ice bath with continual flipping. To obtain brown crystals, the ained azo compound is filtered out, dried, and then recrystallized in alcohol/water to produce (88%) with a melting point of 230 °C. The synthesized reagent's (ANPDP) chemical composition was identified (Figure 1) [30].

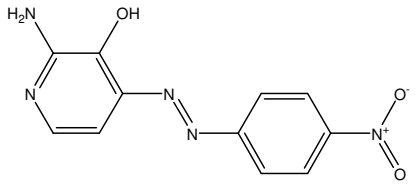

Figure 1: The structural formula of 2-amino-4-(4-nitophenyl)diazenyl)pyridine-3-ol (ANPDP)

As shown from Figure 2 IR(KBr) spectra of the ANPDP reagent shows 3497 cm^{-1} (OH), 3383 cm^{-1} (NH2), 1624 cm^{-1} (C=C), 1583 cm-1 (N=N) and 1520 cm^{-1} (NO_2). ^{1}H-NMR(DMSO-d_6): δ=6.60 (d, 1H, J=9.5 Hz, Hpy), 7.36 (bs, 2H, NH_2), 7.52 (m, 3H, Haryl and py.), 8.17(d, 2H, J=9.5 Hz, Ar-H), 11.27 (bs, 1H, OH).

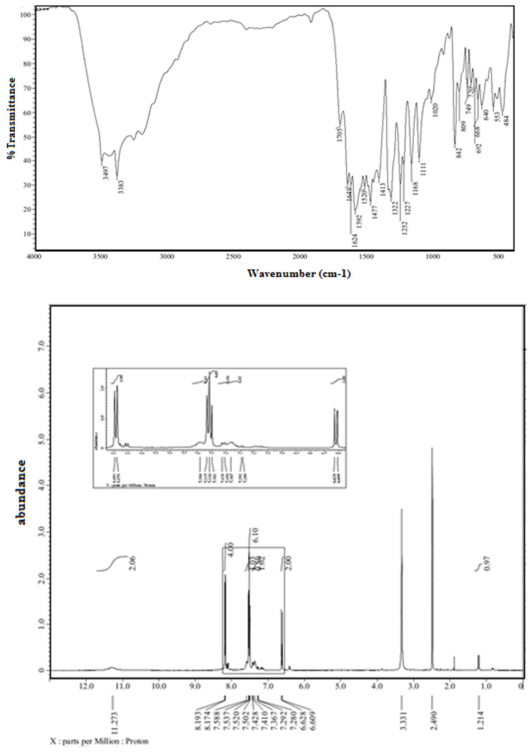

Figure 2: FT-IR and 1H-NMR spectra for the synthesized ANPDP reagent

By dissolving an adequate weight (0.0026 g) of the ANPDP reagent in 10 mL of ethanol and then adding the same solvent to the mark in a 100 mL calibrated flask, the desired concentration of the reagent (1.0×104 mol L^{-1}) was achieved.

2.4. General procedures

2.4.1. Without CPE

A 2.5 mL of the ANPDP solution (1.0×104 mol L-1) was added to an aliquot of Zn(II) standard solution (10-140 µg mL-1) in a set of 10 mL measuring flasks. About 4.0 mL solution of universal buffer with a pH of 9.0. Then, 1.0 mL of (0.6 mol L-1) SDS solution was added, and the required amount of bidistilled water was added to finish the mixture. For two minutes, the mixture was left at room temperature. In comparison to a reagent blank prepared under the same experimental conditions but without Zn, the absorbance was measured at 595 nm (II). Calculating the concentration of Zn(II) and performing the calibration graph.

2.4.2. With CPE

ANPDP solution (1.0×104 mol L^{-1}) and a

universal buffer solution (pH 9.0) were both added to an aliquot of Zn(II) standard solution (10-800 µg L^{-1}) that had been transferred to a 50 mL centrifuge tube. 1.0 mL of (2.0% v/v) Triton X-114 solution was then added, and the required volume was then filled with bidistilled water. To get the mixture to the cloud point temperature, it was sonicated in an ultrasonic bath for 10 minutes at 40°C. The mixture was centrifuged for 5.0 min at 3500 rpm to separate the two phases. The resulting turbid solution was then chilled in an ice bath for 5.0 min to make the surfactant-rich phase more viscous. Zn(II) concentration was estimated. By inverting the tubes, the surfactant-rich phase transformed into a viscous phase, which could then be separated from the watery phase. With the use of ethanol, the remaining micellar phase was thinned out to a final volume of 1.0 mL. At a wavelength of 605 nm, the absorbance was measured in comparison to a bidistilled water-prepared reagent blank. The same procedures were used to prepare and process a blank solution that contained every ingredient but Zn(II). Calculating the concentration of Zn(II) and performing the calibration graph.

2.5. Application for water samples

2.5.1. Water samples

Various water samples, including tap, well, and industrial waste water samples, were subjected to the suggested methodology. The samples were gathered in polyethylene bottles from a natural pond in the city and vicinity of Benha, Egypt. To remove any suspended particles, the water samples were filtered through a Millipore cellulose membrane filter with a 0.45 m pore size. Then, 100 mL of each filtered water sample was precisely transferred into a 250 mL round bottom flask, and 10 mL of a solution consisting of HNO3 and H2O2 (1:9, v/v) were added. These samples were heated under reflux for two hours to facilitate digestion. The samples were placed in 100 mL volumetric flasks after cooling, filled to the prescribed level with deionized distilled water, mixed well, and then had the pH of the samples corrected to pH 9.0 by buffer solution before being placed in a dark refrigerator. Water aliquots were tested using the CPE approach in accordance with the basic protocol mentioned above.

2.5.2. Food and tobacco samples

Various fresh food samples (carrot, potato, and clove), and tobacco samples were collected from the markets in Benha, Egypt. The samples are homogenised by grinding in an agate porcelain mortar and drying at 90°C for 24 hours. Firstly, food samples (1.0 g), and tobacco samples (0.5 g) were weighed in glass beakers, treated with 10 mL of a mixture of concentrated HNO_3–H_2O_2 (2:1, v/v) in Teflon tubes and the tubes were sealed. Microwave digestion procedure has been applied for sample preparation [34]. Then, the digested samples were subjected to the proposed procedures.

2.5.3. Pharmaceutical formulations

A weighed sample of the Care by Care (2.0% ZnO) cream (1.0 g) was dissolved in ether, then in a little quantity of diluted HCl, heated for a few minutes, and the aqueous layer separated. Cool the solution before filtering off the insoluble material and washing it three times in deionized water. In a measuring flask, the filtrate was diluted to a total of 100 mL. In order to evaluate Zn(II) as previously described, an aliquot was obtained.

3. Results and discussion

3.1. Absorption spectra

The spectra of the Zn(III)- ANPDP complex solution have a maximum absorbance at 595 and 605 nm against reagent blank in an aqueous ethanolic and surfactant-rich phase using procedures without CPE and with CPE, respectively (Figures 3 and 4).

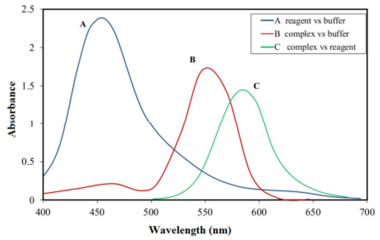

Figure 3: The absorption spectra of Zn(II) (140 µg mL^{-1}) complexed with ANPDP reagent (1.0×10^{-4} mol L^{-1}) at pH 9.0 using procedure without CPE against reagent blank

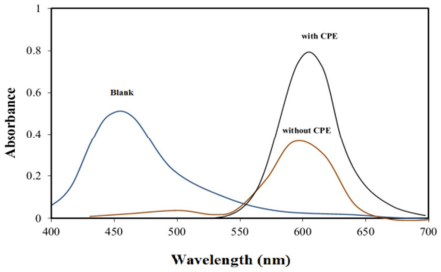

Figure 4: Absorption spectra for Zn(II) (800 ng mL^{-1}) complexed with ANPDP reagent (1.0 x 10^{-4} mol L^{-1}) at pH 9.0 using procedure with CPE against reagent blank

3.2. Optimization of the cloud point extraction conditions

By using the CPE process outlined above, the analytical variables including pH, reagent and surfactant concentrations, temperature, and centrifugation periods were optimised.

3.2.1. pH Effect

Due to its direct connection to the emergence of metal-ligand species, the pH of the aqueous solution plays a significant role in the determination of Zn(II). Complexation was done with various buffer solution types. The optimal one, which provides the maximum absorbance value in addition to the stability of the colour complex, was maintained using the universal buffer solution. While maintaining the other conditions constant, the effect of pH on the CPE efficiency of Zn(II) was investigated, with the findings displayed in Figure 5. As can be seen, pH 9.0 produced the highest absorption. The impact of the buffer volume was also evaluated. The outcomes indicated that 4.0 ml of the universal buffer solution was the best choice for achieving the highest level of sensitivity.

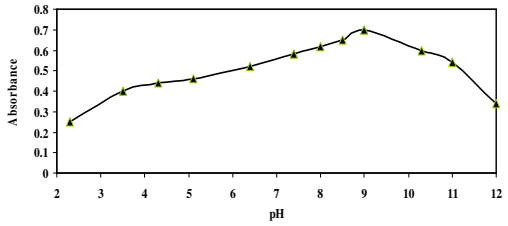

Figure 5: Effect of pH on the Zn(II)-ANPDP complex formation

3.2.2. Impact of the reagent concentration

For Zn(II) solution and various concentrations of the reagent in the range of 5.0 x 10^{-5} – 5.0 x 10^{-4} mol L^{-1}, the impact of ANPDP concentration on analytical performance was examined. The complex's absorbance increased as the reagent concentration increased, and it was found to be constant between 8.0 × 10^{-5}–2.0 × 10^{-4} mol L^{-1} of ANPDP reagent (Figure 6). The complex's ideal absorbance in conjunction with the lowest blank measurement was discovered to be 1.0×10^{-4} mol L^{-1}. When the reagent was used at a higher concentration, the absorbance remained constant or decreased. In the subsequent studies, 1.0×10^{-4} mol L^{-1}, was sufficient for the best outcomes. This concentration guarantees enough excess to offset the reagent use of other metals. Therefore, 2.0 mL of ANPDP (1.0×10^{-4} mol L^{-1}) solution was chosen as the ideal volume that gives the greatest complex formation yield for all subsequent investigations.

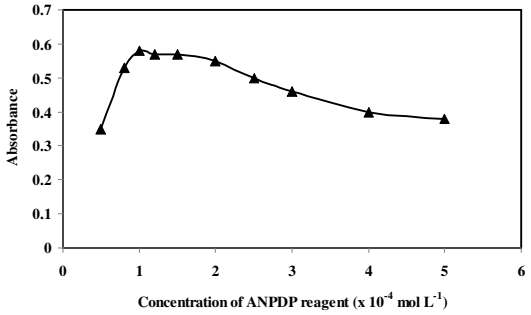

Figure 6: Effect of ANPDP reagent concentration on the absorbance of Zn(II)-ANPDP complex

3.2.3. Impact of surfactant concentration

The impact of different types of surfactants (non-ionic, cationic, and anionic) was examined. In the method without CPE, the anionic surfactant (SDS) was the best one. The highest absorbance was obtained at concentration. Different volumes (0.25–3.0 mL) of SDS (0.6 mol L^{-1}) was tested, by increasing volume to 1.0 mL, the absorbance was increased. The amount of surfactant needed as an ion-pairing agent in the surfactant-rich phase and the strength of the solubilization increase with the addition of 1.0 mL of CTAB, increasing the extraction efficiency. Therefore, 1.0 mL of SDS (0.6 mol L^{-1}) was chosen for the tests that followed (Figure 7).

One of the non-ionic surfactants that is frequently utilised in CPE is Triton X-114. This is because of its benefits, including commercial availability, with high purity, a relatively low cloud point temperature, low toxicity, a low cost, and a high density of the phase rich in surfactants that makes phase separation by centrifugation possible. The CPE effectiveness of Zn(II) ions is affected by the non-ionic surfactant content in the Triton X-114 (2.0%, v/v) volume in a range of 0.25–3.0 mL. According to Figure 7, adding up to 1.0 mL of metal ions to the (2.0%, v/v) Triton X-114 solution improved the complex's absorbance. When the surfactant level is increased above 2.0%, v/v, the absorbance is seen to significantly drop. This is explained by a rise in the micellar phase's volume and viscosity. Because there aren't many molecules of the surfactant available to quantitatively entrap the Zn(II)-ANPDP complex at concentrations below this threshold, the extraction efficiency of complexes is low. Therefore, 1.0 mL of Triton X-114 (2.0%, v/v)

was used for the investigations that followed.

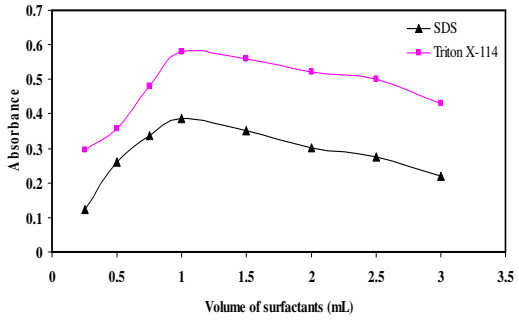

Figure 7: Effect of SDS (0.6 mol L^{-1}) and Triton X-114 (2.0 %, v/v) volume on absorbance of Zn(II)-ANPDP complex at pH 9.0 and ANPDP (1.0 x 10-4 mol L^{-1})

3.2.4. Temperature and equilibration time effects

Optimizing the incubation time and temperature is essential for achieving simple phase separation and effective preconcentration in CPE processes. As a compromise between successful extraction and effective phase separation, it was preferable to use the shortest incubation time and lowest equilibration temperature possible. Investigations on the effects of incubation time and temperature were conducted in the ranges of 2.0–20 min and 25–70°C. The outcomes show that a temperature of 40°C and an incubation period of 10 min were selected for subsequent studies. The metal-ANPDP complex's extraction effectiveness remained steady. So, 40°C was chosen as the equilibrium temperature for the separation procedure. The complex decomposes at higher temperatures, which lowers the extraction yield. The optimal centrifuge time was found to be 5.0 min at 4000 rpm since total separation happened during this time and no discernible benefits were seen for longer times.

3.2.5. Effect of diluting agent

In order to achieve a homogeneous solution with compatible viscosity for the CPE method, the surfactant-rich phase frequently requires the addition of a diluent. As diluent solvents, various solvents such as methanol, ethanol, acetone, and acetonitrile were investigated. In order to have an adequate volume of sample for transferring, measuring the sample's absorbance, and also having a proper preconcentration factor, the high viscosity of the surfactant-rich phase is substantially reduced used ethanol as a diluting agent. As a result, 1.0 mL of ethanol was added to the end of the surfactant-rich phase. The preconcentration factor was 50 as a result.

3.2.6. Complexity of the System

The molar ratio and continuous variation approaches were used to determine the Zn(II) - ANPDP complex's composition. Both methods' results indicated that molar ratios of (1: 1) and (2: 1) were present. For at least 10 hours, the chromogenic system could stabilise.

3.3. Analytical performance

Under the ideal circumstances of the general method with CPE, the calibration graphs were linear in the range of 0.01-0.8 µg mL^{-1} Zn(II). A = 0.0233 + 0.7269C (R^2 = 0.9997), where A is the absorbance and C is the metal concentration in solution, served as the regression equations for the measurement of Zn(II) (ng mL^{-1}). The linear ranges for the batch spectrophotometric technique, however, were 10-140 µg mL^{-1}, and the regression equations were A = 0.0184 + 0.0047C (R^2 = 0.9989). The thresholds for detection and quantification are C_L = 3 S_B/m, LOD = 3.3 S_B/m, and LOQ = 10 S_B/m, respectively (where C_L, S_B and m are the limit of detection, the standard deviation of the intercept, and the slope of the calibration graph, respectively). Using a technique without CPE, the LOD and LOD limit were 3.0 and 10 µg mL^{-1}, respectively. The LOD and LOD limit for the technique using CPE, however, were 0.003 and 0.01 µg mL^{-1}, respectively. The ratio of the initial sample volume (50 mL) to the final measurement volume (1.0 mL) after the CPE was 50 is known as the preconcentration factor. The ratio of the calibration graph's slope with the preconcentration CPE method to its slope without the operation was used to calculate the enhancement factor, which came out to be roughly 154.66. The consumptive index (CI) was 0.32 and is calculated as the sample volume in millilitres needed to produce one unit of enrichment factor (EF): CI = Vs (mL)/EF. When six replicate measurements were made in solutions containing 10 and 0.5 µg mL^{-1} of Zn(II) at intra-day and inter-day repeatability, the relative standard deviation (RSD) and relative error were calculated to determine the procedure's precision (RSD%= 2.40 and 2.20 for the method without CPE, respectively, and (RSD%= 1.90 and 1.70 for the method with CPE, respectively) (Table 2). To compare the accuracy and precision of the proposed approach and the reported methods instead, a significance test was used [25]. In every case, the estimated t- and F-values were lower than the theoretical values (Table 1).

Table 1
Features of the proposed methods' analysis

Parameters	Without CPE	With CPE
λ_{max} (nm)	595	605
Calibration range (µg mL^{-1})	10 –140	0.01– 0.8
Molar absorptivity (L mol^{-1} cm^{-1})	7.342×10^3	4.216×10^5
Regression equation [a]		
Slope		
Intercept (a) ± S*a* [b]	0.0184± 0.0043	0.0233± 0.0022
Slope (b) ± S*b* [b]	0.0047± 0.00005	0.7269± 0.0053
$S_{y/x}$ [b]	0.0079	0.0039
Correlation coefficient (r^2)	0.9989	0.9997
Preconcnetration factor (PF)	50	-
Enrichment factor (EF)	154.66	-
Consumptive index (CI)	0.32	-
Intra-day precision (RSD%; n=6) [b]	2.40	1.90
Inter-day precision (RSD%; n=6) [b]	2.20	1.70
Limit of detection (µg mL^{-1})	3.0	0.003
Limit of quantification (µg mL^{-1})	10	0.01
Student t-test/(2.57)[c]	1.02	1.64
F-value/(5.05)[c]	2.10	3.20

[a]: A = a + bC, where C is the concentration of Zn(II) in mg mL^{-1}

3.4. Foreign ions effect

Tests were conducted on the impacts of representative putative interfering species. These tests used synthetic solutions with 800 µg L^{-1} of Zn(II) and varying concentrations of other interfering ions, and they followed the suggested method for determining Zn(II). It was deemed acceptable for the absorbance reading to have a 5.0% in accuracy. A smaller concentration of foreign ions was then generated for any metal ions that were discovered to interfere. Table 2 lists the tolerance limitations.

Table 2
Effect of interfering ions on seoaration and recoveries of 140 and 0.8 µg mL-1 Zn(II) for methods without and with CPE, respectively (N=3)

Ions	Without CPE		With CPE	
	Maximum Tolerable amount (µg mL^{-1})	Recovery (%)± SD [a]	Maximum Tolerable amount (µg mL^{-1}	Recovery (%)± SD [a]
K^+	4000	97.0 ± 2.0	10	95.0 ± 3.0
Na^+	3200	98.0 ± 2.0	10	96.0 ± 4.0
Al^{3+}	2000	96.0 ± 1.0	2.0	96.0 ± 2.0
Cr^{3+}	2000	95.0 ± 3.0	1.0	97.0 ± 1.0
Ca^{2+}	2000	97.0 ± 2.0	2.0	96.0 ± 3.0
Mg^{2+}	3200	96.0 ± 3.0	1.0	96.0 ± 2.0
$^{BA}2^+$	2800	97.0 ± 2.0	2.0	95.0 ± 3.0
Pb^{2+}	3000	95.0 ± 2.0	1.0	97.0 ± 3.0
Ni^{2+}	3500	96.0 ± 2.0	1.0	98.0 ± 3.0
Bi^{3+}	700	96.0 ± 1.0	1.0	96.0 ± 1.0
Co^{2+}	2500	96.0 ± 2.0	0.5	95.0 ± 3.0
NO_3^-	2200	95.0 ± 3.0	5.0	97.0 ± 2.0
SO_4^{2-}	3000	96.0 ± 4.0	5.0	96.0 ± 3.0
Cl^-	3000	95.0 ± 3.0	10	98.0 ± 2.0
F^-	1000	97.0 ± 1.0	10	95.0 ± 2.0

[a] Mean ± standard deviation

3.5. Analytical applications

The application of the suggested procedures to the estimation of Zn(II) from various samples was done to evaluate their dependability (water, food, tobacco and pharmaceutical preparations). To validate the devised procedure reliability and accuracy, certain amounts of Zn(II) ions were spiked to the sample solutions utilizing addition/recovery test and the recoveries and RSD% were determined as shown in Tables 3 and 4. The developed preconcentration method was tested for its ability to recognize and separate Zn(II) ions in a variety of real water, food, tobacco and pharmaceutical preparations samples. The Zn(II) analyte had excellent quantitative recoveries, ranging from 95.0–97.60% with RSD% ≤ 3.40% for water samples (Table 3) and 95.0–98.50% with RSD% ≤ 3.80% for food, tobacco and pharmaceutical preparations samples (Table 4). As a result of these findings, the methods may be used to separate, preconcentrate, and analyse Zn(II) in real samples at trace levels.

Table 3
Zn(II) extraction in water samples using the described methods, addition/recovery test (N=3)

Sample	Added (µg mL^{-1})	Found [a]± SD (µg mL^{-1})	Recovery± RSD(%)
Without CPE			
Tap water	0	< LOD[b]	-
	50	48.50 ± 0.60	97.0±1.24
	100	96.90 ± 1.70	96.90±1.70
Well water	0	< LOD[b]	-
	50	47.50 ± 0.40	95.0±0.84
	100	96.0 ± 1.40	96.0±1.46
Industerial waste water	0	10.0 ± 0.12	-
	50	57.50 ± 0.45	95.80±0.78
	100	107.25±0.92	97.50±0.86
With CPE			
Tap water	0	< LOD[b]	-
	0.3	0.291 ± 0.01	97.0±3.40
	0.6	0.58 ± 0.02	96.70±3.45
Well water	0	< LOD[b]	-
	0.3	0.29 ± 0.008	96.80±2.75
	0.6	0.573 ± 0.014	95.50±2.44
Industerial waste water	0	0.02 ± 0.005	-
	0.3	0.312 ± 0.01	97.60±3.21
	0.6	0.595±0.02	96.0±3.36

[a] Mean ± standard deviation
[b] LOD: limit of detection

4. Conclusion

In the proposed work, CPE system coupled to spectrophotometry was developed for the preconcentration and determination of trace amount of Zn(II) in various water, food, tobacco and pharmaceutical preparations samples. ANPDP is a

very stable and fairly selective new complexing reagent. Triton X-114 has a relatively low cost, low toxicity, and is readily available in most laboratories. The CPE approach is convenient, safe, sensitive, rapid, simple, and economic, accurate, precise, has lower detection and quantification limits, a better preconcentration factor, and a wider linear range. It also offers the advantage of isolating the analyte from the sample matrix, allowing for interference-free analysis. The proposed method can be applied to the analysis of trace amounts of Zn(II) in various samples with good results.

5. Conflicts of interest

There are no conflicts to declare.

Table 4
Addition/recovery test for extraction of Zn(II) in food, tobacco and cream samples using the developed approaches (N=3)

Sample	Added (μg mL^{-1})	Found [a]± SD (μg mL^{-1})	Recovery± RSD(%)
Without CPE			
Carrot	0	4.0 ± 0.07	-
	50	51.73 ± 0.45	95.80±0.87
	100	99.84 ± 1.45	96.0±1.45
Potato	0	6.0 ± 0.12	-
	50	54.32±0.61	97.0±1.12
	100	103.88±1.56	98.0±1.50
Clove	0	7.0±0.10	-
	50	54.72±0.57	96.0±1.04
	100	102.20±1.33	95.50±1.30
Tobacco	0	5.0±0.08	-
	50	53.46±0.20	97.20±0.37
	100	101.33±0.70	96.50±0.69
Cream care by care	0	10.0±0.10	-
	50	57.0±0.48	95.0±0.85
	100	105.60±1.16	96.0±1.10
With CPE			
Carrot	0	0.01±0.007	-
	0.3	0.304±0.009	98.0±2.80
	0.6	0.595±0.018	97.50±3.10
Potato	0	0.012±0.005	-
	0.3	0.30±0.01	96.0±3.40
	0.6	0.603±0.022	98.50±3.70
Clove	0	0.01±0.008	-
	0.3	0.3007±0.008	97.0±2.70
	0.6	0.580±0.017	95.0±3.0
Tobacco	0	0.013±0.009	-
	0.3	0.307±0.011	98.0±3.50
	0.6	0.588±0.022	96.0±3.80
Cream care by care	0	0.02±0.008	-
	0.3	0.308 ± 0.008	96.40±2.60
	0.6	0.60 ± 0.018	96.80±3.0

[a] Mean ± standard deviation

[b] LOD: limit of detection

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