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A Unique and Green Method Designed for the Detection of Minute Quantities of Zinc in Real and Natural Specimens

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Abstract

In this study, we have developed an easy and fast spectrophotometric procedure to analyze zinc in trace amount using a reagent 1-(2-thiazolylazo)-2-naphthol (TAN) in surfactant cetyltrimethylammonium bromide (CTAB) solution. Zinc reacted with 1-(2-thiazolylazo)-2-naphthol to give bis[1-(2-thiazolylazo)-2-naphthol]zinc. Designed spectrophotometric method has been of great significance as using the micellar system instead of toxic, expensive and time taking extraction method. This method presented an improved detecting efficacy, sensitivity and coefficient of molar absorption. The Sandel's sensitivity and molar absorption coefficient were determined to be 4.5 ngcm^{-2} and ε 1.96×10^4 L mol^{-1}cm^{-1} at λ_{max} 581.4 nm, respectively. The 1:2 ratio was observed for Zn-[TAN]$_2$ development. Linear calibration curve was obtained within 0.12-4.0 µg mL^{-1}. At pH 6.5, complex formation occurred and remained stable for 24 hrs. Our recommended procedure was applied successfully for the investigation of Zinc from various alloy, ecological, pharmaceutical and biological specimens.

Keywords: Zinc; Cetyltrimethylammonium Bromide; 1-(2-Thiazolylazo)-2-naphthol; Complexation

1. Introduction

The detection of trace metal ions is of paramount importance across diverse domains, including biology, environmental science, and industrial applications. Metallic ions such as Cu (II), Zn (II), Fe (II), Co (II), and Mn (II) are not only integral to various biochemical processes but are also essential for the physiological functioning of living organisms (May, Linder, & Williams, 1977), whereas metal ions, such as arsenic (As), cadmium (Cd), lead (Pb), and Mercury (Hg), are poisonous to living systems at certain concentrations (Stankovic, Kalaba, & Stankovic, 2014), while valuable metals are hazardous at much greater concentrations. Zinc (Zn) ion is vital for entire systems of animals, plants and humans, participates in numerous living roles (Natasha et al., 2022), its chief function is the formation of numerous enzymes and co-enzymes. It behaves as both metalloenzyme and enzymes activator. It is involved in the production of deoxyribonucleic acid (DNA) and ribosomal ribonucleic acid (RRNA) (Shankar & Prasad, 1998). They are essential for the nerve systems and DNA synthesis (Gower-Winter & Levenson, 2012). Zinc imparts core role in person's blood scattered 3%, 75% - 85% and 12% - 22% in leukocytes, erythrocytes and plasma respectively

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(Reddy & Reddy, 2011). Zn is commercially available and is utilized in the pharmaceutical industry as vitamins, balms, eye drops and lotions (Mohiuddin, 2019). Zinc (II) ions contain vitamins utilized in nutrients as a supplement for vitamins, which is essential to improve tissue formation, heal wounds, traumatic injury, sex and hair growth (Grada & Phillips, 2022). Zn (II) ion deficiency indicates forfeiture of sexual hormones and hair growth (Wong, Thomas, Merkus, Zielhuis, & Steegers-Theunissen, 2000), diminution in collagen production, procrastinating soothing of injuries, and detrimental DNA creation (Hara et al., 2017). Its deficiency also causes growing obstruction, lesser food proficiency, ulcers, and skin scaling (Prasad, 1995). Though, high consumption of zinc is unsafe but its moderate consumption is vivacious to healthy life. Zinc sulphate capsule (220 mg) causes nausea and vomiting (Reddy & Reddy, 2011). It is utilized in dry batteries, photoengraving, protection against corrosion and lithography (Prkić, Giljanović, Petričević, Brkljača, & Bralić, 2013).

During the spectrophotometric study of metallic ions, the reaction of metals with a chelating agent and their dissolution in a surfactant system offers an efficient and rapid approach for metal ion analysis (Soomro & Shar, 2014).

A range of spectrophotometric methods have been introduced as alternatives to the conventional solvent extraction technique, incorporating the use of surfactants (Yun & Choi, 2000). The micellar systems because of solubility of different metallic complexes show enhancement in the analysis of metal ion techniques (Olkowska, Polkowska, & Namieśnik, 2012). The micellar system is acquaint with improve molar absorption and sensitivity and substitute old extraction solvent method. Numerous spectrophotometric approaches are available for zinc estimation with different chelating agents. Some most recent established spectrophotometric approaches of analysis have least sensitivity and selectivity (Allan, 1961; Ghaedi et al., 2009; Rao, Balaji, Rao, Babu, & Naidu, 2002; Sammut et al., 2008). We have developed a novel, robust, efficient, and effective method for detecting zinc (II) in various real and natural samples using the 1-(2-thiazolylazo)-2-naphthol (TAN) chelating agent in cetyltrimethylammonium bromide (CTAB) aqueous micellar solutions. Previous research has not investigated zinc (II) ions using TAN in CTAB aqueous micellar systems. This newly developed method demonstrates improvements in several analytical characteristics, including the limit of detection, molar absorptivity coefficient, Beer's law range, and Sandell's sensitivity when applied to CTAB surfactant solutions. The proposed procedure has significant applications in natural, environmental, industrial, and medicinal studies and is widely recognized worldwide for its accessibility, simplicity, and eco-friendliness.

2. Material and Methods

Ultra-violate visible spectrophotometer, FT-IR spectrophotometer, pH/conductivity meter and Atomic absorption spectrophotometer were used.

2.1. Reagent Preparation

The CTAB solution of 0.02 M was made by using 7.28 g of CTAB in measuring flask of 1000 ml and deionized water was added until the final volume reached the mark (Korai et al., 2022). Zn (II) 1000 μgL^{-1} solution was made from its salt zinc nitrate $Zn(NO_3)_2$ (Merck Darmstadt, Germany) in graduated flask (Abdolmohammad-Zadeh & Sadeghi, 2009). The 4×10^{-3} M solution of reagent TAN was made up with addition of 0.50 g of TAN containing 25 ml of methanol into volumetric flask of 500 mL and CTAB 0.02 M was added to make up the

volume (Korai et al., 2022). The solutions of buffers from pH 1 to 10 were made as per the procedures by adding suitable quantities of both HCl-KCl equimolar 0.2 M for 1-4 pHs, CH_3COOH-CH_3COONa equimolar 0.2 M for 5-6 pHs, KH_2PO_4-NaOH equimolar 0.1 M for 6.5-8 pHs and 0.025 M sodium borate - 0.1 M HCl for 9-10 pHs solutions (Perrin, 2012).

2.2. Zinc (II) metal ion detection by general procedure

Zinc ion concentrations ranging 0.06-10 μgmL^{-1}, 2 mL (5×10^{-4} M) solution of TAN, 2 mL of different pHs buffer solutions and 1-2 mL (0.02 M) solution of CTAB were allowed to mix in a 10 mL volumetric flask and distilled water was added to make the final volume. Zinc metal ion absorbance at optimal settings for the formation of metal complex was detected at specific λ_{max} using a UV-vis spectrophotometer.

2.3. Detection of Zn (II) from alloy specimens

The 0.1g of each alloys specimens were mixed 50-60 mL HCl 6.0 M and 30% H_2O_2 3-5 mL volume and heated and added distilled water to get the 1 L diluted solution. 10 mL volume of each solution specimens was placed in graduated flagon of 250 mL volume separately and added the distilled water to the mark. The specimens were reacted with 5×10^{-4} M TAN at 6.5 pH in 0.02 M CTAB, then zinc-complexes absorbances were recorded. Results are presented in Table 3 & 6.

2.4. Zn (II) analysis from a tap water sampling

Tap water specimen was collected from the Sukkur area. The sample was then subjected to filtering with filter paper of 0.45 µm and 1mL of concentrated HNO_3 was added to acidify the solution to prevent precipitations. Metal of zinc (II) was spiked into the specimen, 2 mL of 5×10^{-4} M TAN, 2 mL of buffer of 6.5 pH and 2 mL of 0.02 M CTAB were mixed in, after that, the Zn-$[TAN]_2$ complex absorption was recorded, results are presented in Table 4.

2.5. Estimation of Zn (II) from pharmaceutical specimen

A powdered tablet was digested by adding the 10 mL volume of 70% conc. perchloric acid and heated to dryness. The residues were dissolved with the mixing of 5 mL volume of 0.1 M HCl, solution was filtered and placed in calibrated flask of 1000 mL volume and added distilled water up to mark. The specimen was reacted with 5×10^{-4} M TAN at 6.5 pH in 0.02 M CTAB, then zinc-complex absorbance was recorded. Results are presented in Table 5.

2.6. Investigation of zinc (II) from vegetable specimen

The specimen of vegetable *caymopsis psoralides* locally known as Guwar was gathered from the vegetable market in Pano Akil, Pakistan, washed and oven dried at 110 ^{0}C. The specimen was powdered using mortar and pestle. 5 g of powdered specimen was taken and digested by mixing 2 mL of H_2O_2 30% and 10 mL of HNO_3 conc. on hot plate heating until decreased to 2-3 mL volume then filtered it and added distilled water up to 25 mL volume and adjusted the required pH. Then, the 5 mL of specimen solutions were transferred to a graduated beaker and 2 mL of 5×10^{-4} M TAN, 2 mL of buffer of 6.5 pH and 2 mL of 0.02 M CTAB were mixed and absorbance was recorded. Results are presented in Table 5.

2.7. Analyzing Zn (II) content from environmental water sampling

Samples containing 1 liter of wastewater from different locations in Pano Akil, Sukkur district, and Mirpur Mathelo industrial area, Ghotki district, Pakistan, were collected. Specimens were subjected to filtering and acidification with addition of H_2O_2 (30% concentrated) 2 mL and HNO_3 (conc.) 4 mL. Then the resulting solutions were pre-concentrated by heating in an oven at 110 °C to obtain 25 mL of solutions finally. Then, the

specimen solutions were transferred to a graduated beaker and 2 mL of 5×10^{-4} M TAN, 2 mL of buffer of 6.5 pH and 2 mL of 0.02 M CTAB were mixed in, after that, the Zn-$[TAN]_2$ complex absorption was measured. Results are presented in Table 5.

2.8. Detection of zinc (II) from environmental specimens

The 1-5 g of each oven dried ecological solid specimens were mixed 50-60 mL HCl 6.0 M and 30% H_2O_2 3-5 mL volume and heated to dryness. The residues were dissolved with the mixing of 10 mL volume of 1 M HCl, solutions were filtered and placed in calibrated flask of 1000 mL volume and added distilled water up to mark. The specimens were reacted with 5×10^{-4} M TAN at 6.5 pH in 0.02 M CTAB, then zinc-complexes absorbances were recorded. Results are presented in Table 6.

3. Results and Discussion

3.1. Spectrophotometric investigation of Zinc using TAN

Zinc produced coloured metal chelate when it was reacted with reagent 1-(2-thiazoylazo)-2-naphthol (TAN) in the presence of surfactant CTAB. The derivatizing agent TAN is tridentate having three lone pair of electron donating sites as given in Figure 1. The surfactant solution was employed for metal chelate solublization as to estimate the zinc metal ions in minute quantities.

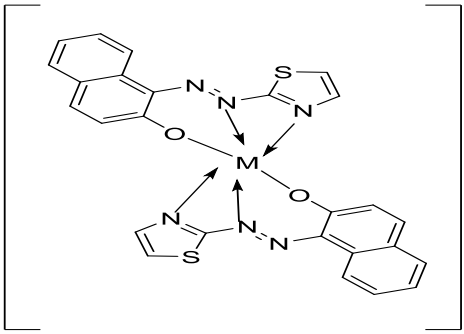

Figure 1 Structure proposed for metal (II)-$[TAN]_2$ chelate

3.2. UV-Vis spectra

Complexing reagent 1-(2-thiazoylazo)-2-naphthol solution displayed orange-red color and exhibited absorption sharp peak at λ_{max}488.5 nm in region of UV-Vis spectrum due to electronic transition $\pi\rightarrow\pi^*$, in fact, the charge transfer took place from ligand to ligand L→LCT. The complexing reagent (TAN) UV/Vis spectrum is given in Figure 2(a).

The chelate Zn (II)-$[TAN]_2$ spectrum in UV-vis region represented enhanced longer absorbance bands for N=N and N=C bathochromic sharp band shifted to 92.9 nm from $\pi\rightarrow\pi^*$. L→MCT took place to unoccupied zinc (II) dπ orbital and occupied chelate pπ orbital at λ_{max}581.4 nm. It was perceived that the oxygen of O-H and nitrogen of N=C groups on de-protonation contributed in developing bonds for the creation of Zn (II)-$[TAN]_2$ chelate as presented in Figure 2(b).

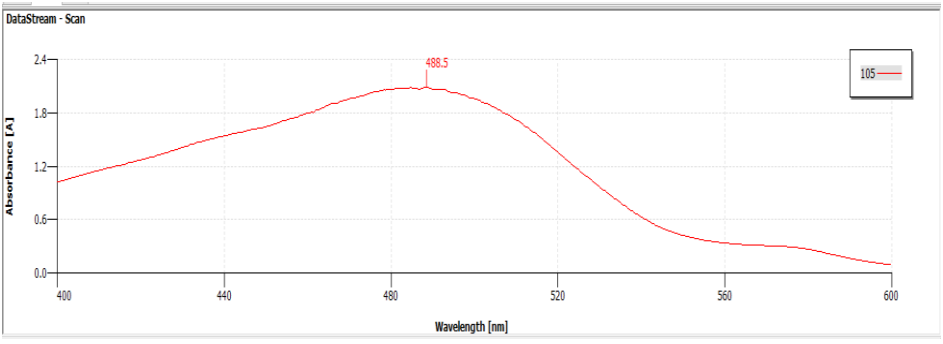

Figure 2(a) UV-Vis spectrum of complexing reagent TAN at λ_{max}488.5 nm

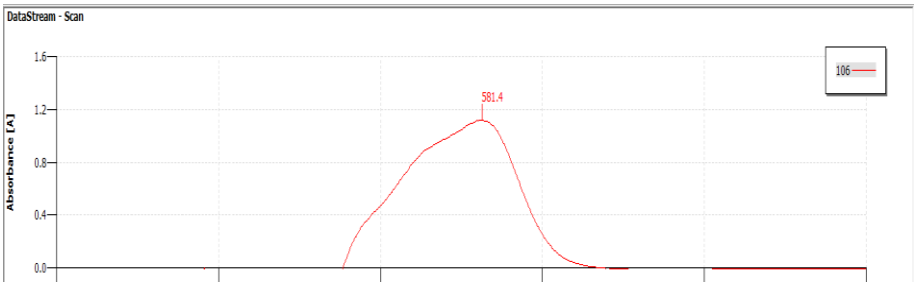

Figure 2(b) UV-vis spectrum of Zn (II)-$[TAN]_2$ complex at λ_{max}581.4 nm

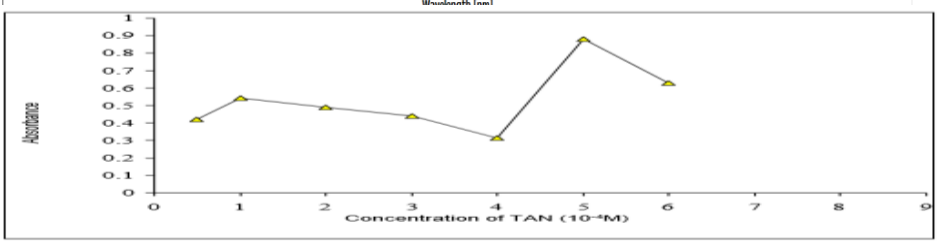

Figure 3. Influence of comlexing agent TAN concentration

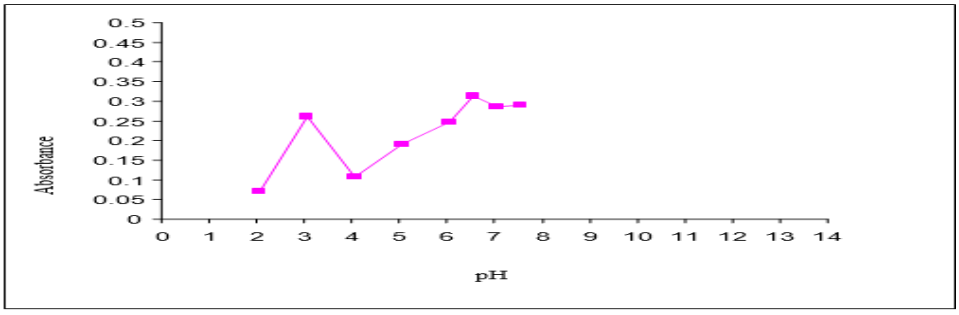

Figure 4. pH graph for the Zn-(TAN) complex in CTAB

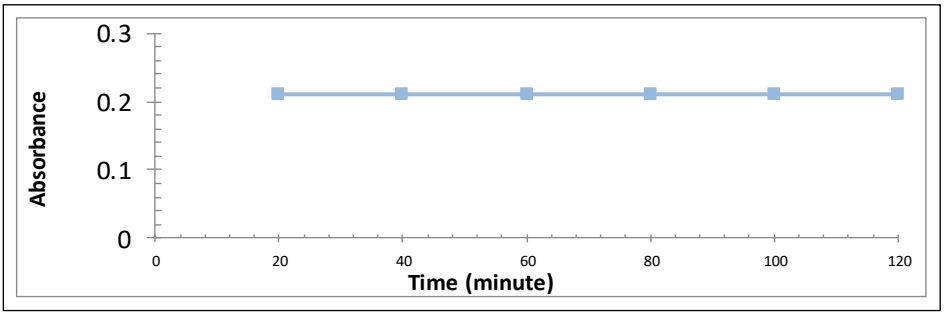

Figure 5. Metal -TAN complex stability

3.3. Ratio of Metal to complexing reagent

The Molar ratio method was employed for the investigation of composition of metal chelate (Malik & Rao, 2000). Metal zinc to reagent TAN ratio was obtained as 1:2 for the development of Zn (II)-$[TAN]_2$ complex (Table 1).

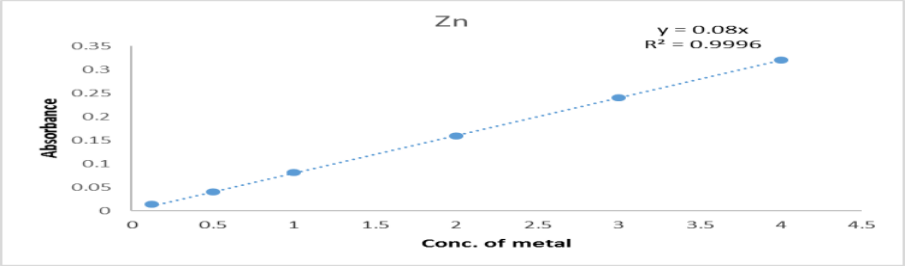

Figure 6 Calibration graph of Zn (II)-$[TAN]_2$

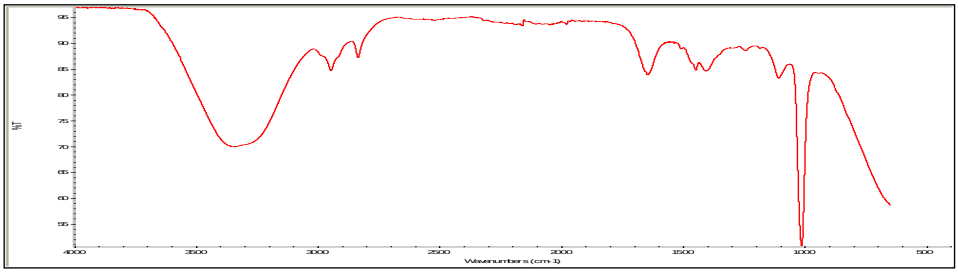

Figure 7(a) FT-IR spectrum of complexing reagent TAN

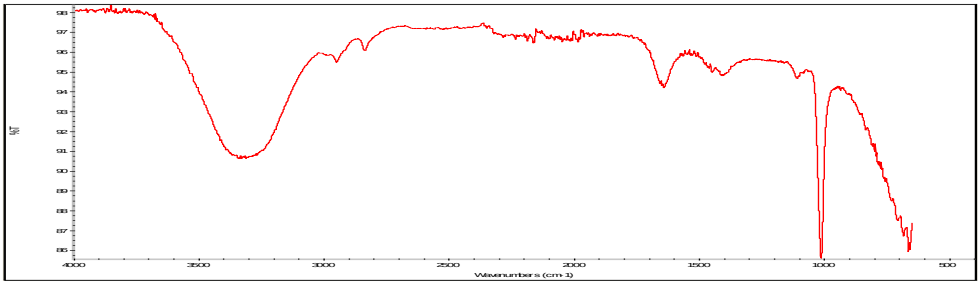

Figure 7(b) FT-IR spectrum of Zn (II)-$[TAN)_2$ compound

3.4. Effect of concentrations of surfactant cetyltrimethylammonium bromide (CTAB) and complexing reagent TAN

The surfactant CTAB 0.02 M solutions of different quantities were investigated for complexation and absorbance maxima was observed when CTAB 0.02 M 2 mL volume was employed with fixed quantity of 2 mg/L of metallic ion. The TAN complexing reagent concentrations from 0.5 to 8×10^{-4} M influenced on complexation of metal with chelating agent, absorbances were noted using different concentrations and absorbance maxima for metal chelate was observed at 5×10^{-4} M concentration that was taken as optimum condition and was utilized throughout the research as given in Figure 3 and Table 1.

3.5. pH and time influence

pH influence on retrieval extraction in general investigation was carried with fixed values of other parameters. Optimal pH for zinc was detected 6.5 and it was selected for more research as given in Figure 4 and Table 1.

Metal chelate formation was examined; the complexation was quick and offered fixed maximum absorbance at room temperature and remained unchanged until 2hrs as displayed in Figure 5.

Table 1 Characteristic parameters for Zn-TAN complex

Parameters	Zinc
Molar absorptivity	1.96×10^4 $Lmol^{-1}cm^{-1}$
Limit of detection	5.1 $ngmL^{-1}$
Beer's law range	0.12-4.0 μgmL^{-1}
Concentration of TAN	5.0×10^{-4} M
Surfactant CTAB	2.0 mL
pH	6.5
L:M	2:1
Sandell's sensitivity	4.5 $ngcm^{-2}$
Wavelength (λ_{max})	581.4 nm
R^2	0.9996

3.6. Zn (II)-$[TAN]_2$ Calibration

The graph of calibration for Zn (II) at λ_{max}581.4 nm offered linear concentration ranges 0.12-4.0 mg/mL with R^2 0.9996 intercepting through zero as displayed in Figure 6.

3.7. Sandell's sensitivity, limit of detection and coefficient of molar absorptivity

Linear calibration curve revealed the mean co-efficient of molar absorptivity for zinc (II) at λ_{max} 581.4 nm that was measured as 1.96×10^4 $Lmol^{-1}cm^{-1}$. Limit of detection was noted as 5.1 $ngcm^{-2}$. Sandell's sensitivity was observed to be 4.5 $ngcm^{-2}$ (Table 1). Results obtained were analogous to the results indicated in literature reported.

3.8. Influence of different ions in Zinc analysis

The solutions with zinc (II) of 10 µg and varied contents of several ions (cations & anions) were prepared and charted process. The limit of interference of ion was set as the ratio in which ± 2% deviation in absorbance was calculated. Bi (III), Al (III), Mn (II), Ba (II), Mg (II), Ca (II), nitrate, carbonate, phosphate and chloride ions were with no any interfering effect as a lowest 100:1 mass ratio (Reddy, Reddy, & Reddy, 2011). More influences were noted as in Table 2.

Table 2 Foreign ions interference

Added ions	Tolerance Range (µg)
Mo (VI)	50
Bi (III)	60
As (III)	65
Pd (II); Sn (IV); Fe (III)	80
Co (II); Ni (II); Cu (II)	100
Al (III)	150
Pt (IV); Au (III)	200
Mg (II)	300
Cr (VI); Ba (II)	400
Sodium sulphate	500
Ascorbic acid; Sodium potassium tartate	1000
Ammonium phosphate; Sodium thiosulphate	2000
NaF	2100
$NaNO_3$	3100
Sodium citrate; Dimethylglyoxime	5000
KCl	8100
Thiourea; Potassium thiocyanate	10000
KI	11000

3.9. FT-IR spectra

The reagent TAN FT-IR spectrum offered bands of absorption for *v* (O-H), *v* (C-H)(C-N) groups and aromaticity at 3342.70, 2948.39 and 1651.39 cm^{-1} respectively as presented in Figure 7(a). Bands ranges 1500 cm^{-1} to 4000 cm^{-1} indicated the stretching whereas 550 cm^{-1} to 1500 cm^{-1} indicated finger print area. Complex Zn-$[TAN]_2$ exhibited bands of absorption for *v* (O-H), *v* (C-H)(C-N) groups and aromaticity at 3332.92, 2942.38 and 1655.13 cm^{-1}. These different bands proposed M-O-H and M-

Table 3 Analysis of Zn (II) from alloys specimens

(%) Certified Alloys	Metallic ions	Metal existent	Metal obtained	% RSD	% Relative errors	% Recoveries
BCR-191	Zinc (II)	1.5 µg	1.38 µg	0. 79	0.13	92.00
Bronze PUC-2	Zinc (II)	4.55%	4.31	0.53	0.24	94.73

Table 4 % recovery of Zn (II) in tap H_2O

Metals	Mixed (µg/mL)	obtained (µg/mL)	% Recovery
Zn (II)	1.75	1.69	96.57

N bonding in Zn-$[TAN]_2$ as displayed observed for metallic ion in H_2O, and % in Figure 7(b).

Table 5 Examination of Zn (II) from real and pharmaceutical specimens

Specimens	Analytes	Present method (μgmL^{-1})	% RSD	AAS procedure (μgmL^{-1})	% RSD	%Recoveries
Surbex Z tablet	Zn (II)	22.41	0.3	22.45	0.4	99.3
Vegetable sample (mg/kg) (field vetch) *caymopsis psoralides*	Zn (II)	15.37	0.51	15.42	0.46	98.3
Municipal water (mg/L)	Zn (II)	13.78	0.7	14.1	0.5	99.0
Industrial Wastewater (mg/L)	Zn (II)	27.5	0.2	28.0	0.4	97.5

Table 6 Study of Zn (II) content from certified material and environmental specimens

Certified Reference Material				
(%) Certified	**Metallic ions**	**Present (µg/g)**	**Obtained (µg/g)**	**%Recovery**
IRMM-3702	Zinc (II)	14	13.98	99.85

Environmental specimens		
Specimens	**Present method (mg/g) Zinc obtained**	**A.A.S method (mg/g) Zinc obtained**
Soil near Pano Akil	24.71 ± 0.4	24.80 ± 0.5
Fly ash near Mirpur Mathelo	126.2 ± 3.2	126.5 ± 3.25

3.10. Accuracy and precision

IRMM-3702 certified reference material and Bronze PUC-2 alloy were investigated to validate the methodology. In addition, to obtain the result reliability of the current procedure was ensured via percentage recovery process by usage of identified quantity of ion in specimens, recovery was 96.57% (Table 3-6).

3.11. Validation of method

This recommended procedure was applied for estimation of zinc (II) metal in natural, alloy, real, medicinal, environmental and biological specimens. Obtained results presented good agreements with the results of AAS as displayed in Table 5-6. This procedure

was compared with existing procedures. Developed suggested procedure has offered improvement in molar absorptivity, limit of detection, linear calibration range and Sandell's sensitivity than previous stated procedures (Table 7).

Table 7 Comparison of detection method for of zinc (II) with TAN

Metal	Complexing agents	Procedures/Remarks	References
Zinc (II)	PPT	ϵ 1.6×10^4 $Lmol^{-1}cm^{-1}$ at λ_{max}430 nm, Sandell's sensitivity $4.085\times10^{-3}\mu g/cm^{2,}$ Linear range up to 6.0 µg/mL.	(Sarma, Kumar, Reddy, Thriveni, & Reddy, 2006)
Zinc (II)	BPT	ϵ 1.8×10^4 L $mol^{-1}cm^{-1}$ at λ_{max}430 nm, limit of detection 0.064 μgmL^{-1}, Beer's law range 0.26 to 2.61 µg/mL.	(Reddy et al., 2011)
Zinc (II)	HPHOPD	ϵ 0.156×10^3 L $mol^{-1}cm^{-1}$ at λ_{max}415 nm, linear calibration range 1 to 20 ppm.	(Tekale, 2012)
Zinc (II)	DBHQ	ϵ 1.62 x 10^5 L mol^{-1} cm^{-1} at λ_{max}391nm, LOD 5.0 µg/L, Linear range 0.02-4.0 mg/L.	(Islam & Ahmed, 2013)
Zinc (II)	TAN	ϵ 1.96 x 10^4 L/mol.cm at λ_{max}581.4 nm, linear calibration range 0.12-4.0 µg/mL, Sandell's sensitivity 4.5 ng/cm^2.	Present method

4. Conclusion

The developed recommended procedure was employed to detect trace amounts of zinc (II) metal ions using the complexing reagent TAN in a CTAB surfactant, as opposed to the previous solvent extraction method. This new procedure is more efficient, quick, sensitive, secure, and environmentally pleasant for detecting zinc (II) ions in minute quantities. The proposed method demonstrates significant improvements in molar absorptivity, limit of detection, linear calibration range, and Sandell's sensitivity compared to the previously described techniques, as presented in Table 7. The obtained results were compared with those from certified reference materials, the AAS method, official techniques, and statistically validated at a 95% confidence level, demonstrating comparability. This recommended procedure has been successfully applied for the estimation of zinc (II) in a variety of samples, including natural, alloy, real, medicinal, environmental, and biological specimens, at trace levels.

5. Statements & Declarations

5.1. Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

5.2. Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

5.3. Availability of data and material

Corresponding authors will provide data on request.

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