Kashf Journal of Multidisciplinary Research
Vol:01 Issue10 2024
P-ISSN: 3007-1992 E-ISSN: 3007-200X
https://kjmr.com.pk

ENVIRONMENTALLY FRIENDLY DETECTION OF TRACE IRON IN REAL AND NATURAL SPECIMENS: METHOD DEVELOPMENT AND APPLICATION

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Article Info

Received: 24th Oct, 2024
Review 1: 30th Oct, 2024
Review 2: 30th Oct, 2024
Published: 31st Oct, 2024

Abstract

In this study, we have developed an easy and fast spectrophotometric procedure to analyse Iron in traces using a reagent 1-(2-thiazolylazo)-2-naphthol (TAN) in surfactant cetyltrimethylammonium bromide (CTAB) solution. Iron complexes with 1-(2-thiazolylazo)-2-naphthol to give bis[1-(2-thiazolylazo)-2-naphthol] Iron. Demonstrated 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 7.0 ngcm-2 and ε 1.59×104 L mol-1cm-1 at λmax 571.5 nm, respectively. The 1:2 ratio was observed for Fe-[TAN]2 development. Linear calibration curve was obtained within 0.25-4.0 µg mL-1. At pH 9.5, complex formation occurred and remained stable for 24 hrs. Our recommended procedure was applied successfully for the investigation of Iron from various alloy, ecological, pharmaceutical and biological specimens.

Keywords: *Iron; Cetyltrimethylammonium bromide; 1-(2-Thiazolylazo)-2-naphthol; Complexation*

Introduction

Trace metal ion detection is vital in several fields: environmental science, biology, and engineering [1]. Essential metallic ions like Ni(II), Fe(II), Zn(II), Mn(II) and Co(II) are critical for biological functions [2]. In contrast, toxic metal ions such as Hg, Pb, As, and Cd can harm living systems at certain concentrations [3]. Even essential metals can pose risks at higher concentrations [4]. Iron is an essential micronutrient for plants [5, 6]. It is a key component of several enzymes and proteins involved in fundamental metabolic pathways within plant cells [7]. One of the primary functions of iron in plants is its involvement in photosynthesis. Iron is a crucial component of the enzyme chlorophyllase, which catalyzes the biosynthesis of chlorophyll [8]. Iron also plays a vital role in electron transport chains within chloroplasts and mitochondria [9]. These electron transport chains are essential for generating adenosine triphosphate (ATP). Without sufficient iron, these energy-generating processes would be impaired, compromising the plant's ability to produce and utilize energy effectively [10]. Iron-containing enzymes are involved in the synthesis of nucleotides and in the regulation of gene expression, thereby influencing various aspects of plant physiology and metabolism [11]. Iron acts as a cofactor for enzymes involved in antioxidant defense systems, helping to neutralize harmful reactive oxygen species (ROS) that can damage cellular structures and impair cellular function under stress conditions [12]. Iron is indispensable for human life and health due to its crucial roles in various physiological processes. It is a vital mineral involved in the production of hemoglobin, the protein in red blood cells responsible for transporting oxygen from the lungs to tissues throughout the body [13]. This oxygen transport function is essential for cellular respiration, the process by which cells convert nutrients into energy. Additionally, iron plays a critical role in maintaining the structure and function of proteins and enzymes involved in energy metabolism, DNA synthesis, and immune function. Without adequate iron, these essential processes would be compromised, leading to detrimental effects on overall health and wellbeing [14].

Iron deficiency, commonly known as anemia, is a significant global health issue affecting individuals of all ages, particularly pregnant women, infants, young children, and women of childbearing age [15]. Symptoms of iron deficiency anemia include fatigue, weakness, pale skin, shortness of breath, and impaired cognitive function [16]. Severe or prolonged iron deficiency can lead to serious health complications, such as impaired growth and development in children and increased susceptibility to infections [17]. In some cases, iron supplementation may be recommended under medical supervision to correct deficiencies. Excess iron, also known as iron overload or hemochromatosis, poses significant health risks. When iron levels exceed it can lead to detrimental effects on multiple organ systems [18]. When there's too much iron, it can build up in organs like the liver, causing inflammation and possibly leading to cirrhosis [19]. It can also damage the heart, making it harder for it to pump blood properly [20]. Excessive iron might contribute to diabetes by harming cells in the pancreas that produce insulin [21]. Joints can be affected too, causing pain and stiffness similar to arthritis. Bones may weaken from too much iron, increasing the risk of fractures [22]. Changes in skin color and hormone imbalances are also common. In the brain, too much iron can lead to problems with movement, tremors, and memory loss, and it may worsen conditions like Parkinson's disease [23]. Iron overload also leads to more harmful chemicals in the body that can damage cells and cause inflammation. It can weaken the immune system, making it easier to get infections [24]. Iron pollution arises from the excessive deposition of iron into the environment as a result of human activities such as industrial operations and urban development [25]. Predominantly stemming from processes like steel production, mining, construction, and vehicular emissions, this pollution manifests when elevated levels of iron contaminate soil,

water, or the atmosphere [26]. This influx of iron can lead to several detrimental effects: in aquatic environments, it alters chemical balances and poses risks to aquatic organisms [27]; in soil, it diminishes fertility and impedes plant growth [7]; and in the atmosphere, iron particles contribute to pollution, thereby impacting both human and animal health [28].

Several spectrophotometric methods have been devised that use surfactants in place of traditional solvent extraction techniques [29]. Micellar systems enhance the analysis of metal ions due to the solubility of various metallic complexes [30]. These systems enhance the sensitivity and molar absorption, thereby replacing outdated extraction methods. Multiple spectrophotometric methods exist for iron estimation using different chelating agents [31-33]. We have designed a method using the TAN chelating agent in CTAB micellar system to detect Iron (II) in various real and natural samples, emphasizing its robustness, efficiency, and effectiveness. Previous studies had not explored Iron (II) metallic ions with TAN in CTAB micellar solutions. This method significantly enhances analytical parameters such as detection limit, molar absorptivity coefficient, Beer's law range, and Sandell's sensitivity in CTAB surfactant systems. The developed procedure finds extensive application in environmental, industrial, and medical research due to its accessibility, simplicity, and eco-friendliness, gaining recognition worldwide.

Material and Methods

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

Reagent Preparation

The CTAB solution of 0.02M was made by using 7.28g of CTAB in measuring flask of 1000 ml and deionized water was added until the final volume reached the mark [30]. Fe(II) 1000 μgL^{-1} solution was made from its salt $Fe(NO_3)_2$ (Merck Darmstadt, Germany) in graduated flask. 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 0.02M was added to make up the volume [30]. The solutions of buffers from pH 1 to 10 were made as per the procedures by adding suitable quantities of both HCl-KCl equimolar 0.2M for 1-4 pHs, CH_3COOH-CH_3COONa equimolar 0.2M 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 [34].

Iron(II) metal ion detection by general procedure

Iron 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 (0.02M) solution of CTAB were allowed to mix in a 10 mL volumetric flask and distilled water was added to make the final volume. Iron metal ion absorbance at optimal settings for the formation of metal complex was detected at specific λ_{max} using a UV-vis spectrophotometer.

Detection of Fe (II) from alloy specimens

The 0.1g of each alloys specimens were mixed 50-60mL HCl 6.0M and 30% H_2O_2 3-5mL volume and heated and added distilled water to get the 1L diluted solution. 10mL volume of each solution specimens was placed in graduated flagon of 250mL volume separately and added the distilled water to the mark. The specimens were reacted with 5×10^{-4} M TAN at 9.5 pH in 0.02M CTAB, then Iron-complexes absorbances were recorded. Results are presented in Table 4.

Fe (II) analysis from a tap water sampling

Tap water specimen was collected from the Pano Akil area of district Sukkur. The sample was then subjected to filtering with filter paper of 0.45µm and 1mL of concentrated HNO_3 was added to acidify the solution to prevent precipitations. Metal of Iron (II) was spiked into the specimen, 2mL of 5×10-4 M TAN, 2mL of buffer of 9.5 pH and 2mL of 0.02M CTAB were mixed in, after that, the Fe-$[TAN]_2$ complex absorption was recorded, results are presented in table 3.

Estimation of Fe(II) from pharmaceutical specimen

A powdered tablet was digested by adding the 10mL volume of 70% conc. perchloric acid and heated to dryness. The residues were dissolved with the mixing of 5mL volume of 0.1M HCl, solution was filtered and placed in calibrated flagon of 1000mL volume and added distilled water up to mark. The specimen was reacted with 5×10^{-4} M TAN at 9.5 pH in 0.02M CTAB, then Iron-complex absorbance was recorded. Results are presented in Table **4.**

Analyzing Fe (II) content from environmental water sampling

Samples containing 1 liter of wastewater from different locations in Sukkur, 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 2mL of 5×10^{-4} M TAN, 2mL of buffer of 9.5 pH and 2mL of 0.02M CTAB were mixed in, after that, the Fe-$[TAN]_2$ complex absorption was measured. Results are presented in Table 3.

Detection of Iron (II) from environmental specimens

The ecological specimens were mixed 50-60mL HCl 6.0M and 30% H_2O_2 3-5mL volume and heated to dryness. The residues were dissolved with the mixing of 10mL volume of 1M HCl, solutions were filtered and placed in calibrated flagon of 1000mL volume and added distilled water up to mark. The specimens were reacted with 5×10^{-4} M TAN at 9.5 pH in 0.02M CTAB, then Iron-complexes absorbances were recorded. Results are presented in Table **4**.

Results and Discussion

Spectrophotometric investigation of Iron using TAN

Iron 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 Iron metal ions in minute quantities.

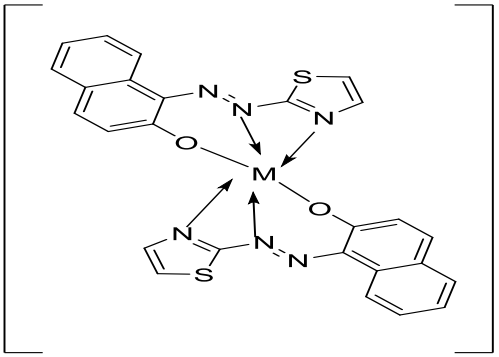

Figure 1. Structure proposed for metal(II)-$[TAN]_2$ chelate

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 UV-Vis spectrum of the Fe(II)-TAN chelate revealed absorbance bands at λ_{max} 571.5 nm, which shifted to longer wavelengths for the N=N and N=C moieties, indicating a bathochromic shift of 83 nm from π to π*. Additionally, ligand-to-metal charge transfer (LMCT) was noted from the unoccupied dπ orbital of iron (II) to the occupied pπ orbital of the -OH group in the ligand, as depicted in Figure 2(b).

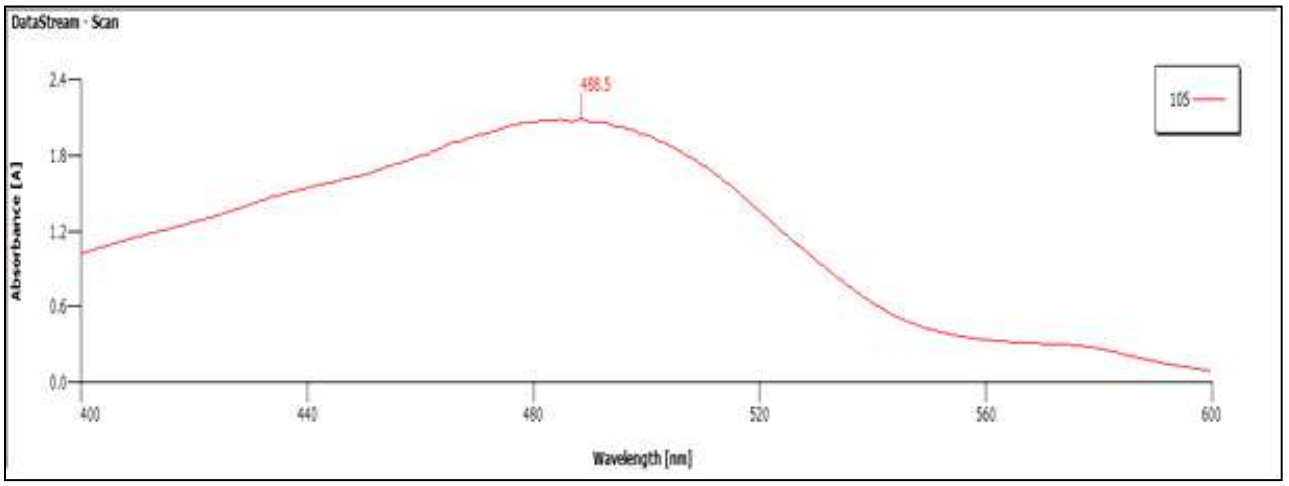

Figure 2(a). UV-Vis spectrum of complexing reagent TAN at $\square_{max}$488.5nm

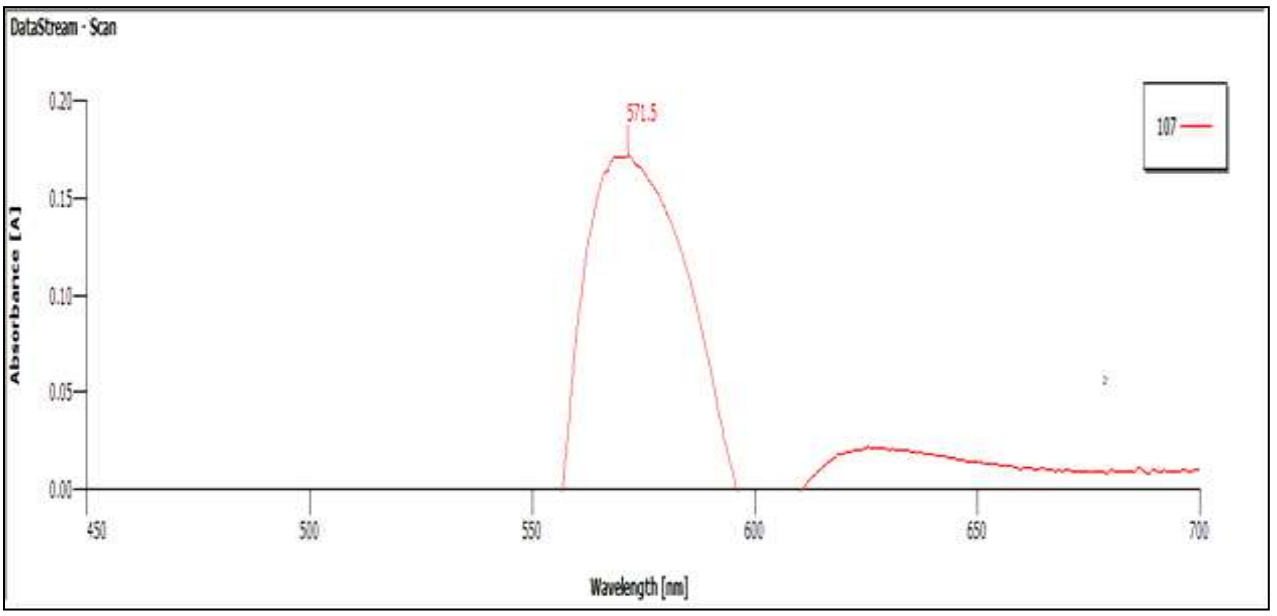

Figure 2(b). UV-vis spectrum of Fe (II)-$[TAN]_2$ complex at λ_{max}571.5 nm

Ratio of Metal to complexing reagent

The Molar ratio method was employed for the investigation of composition of metal chelate [35]. Metal Iron to reagent TAN ratio was obtained as 1:2 for the development of Fe(II)-$[TAN]_2$ complex (Table 1).

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

The surfactant CTAB 0.02M solutions of different quantities were investigated for complexation and absorbance maxima was observed when CTAB 0.02M 2mL volume was employed with fixed quantity of 2mg/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 Table 1.

pH and time influence

Impact of pH on extraction recovery was assessed while keeping other parameters constant. It was determined that the ideal pH for iron extraction is 9.5, which has been selected for further investigation, as illustrated in Figure 3 and Table 1.

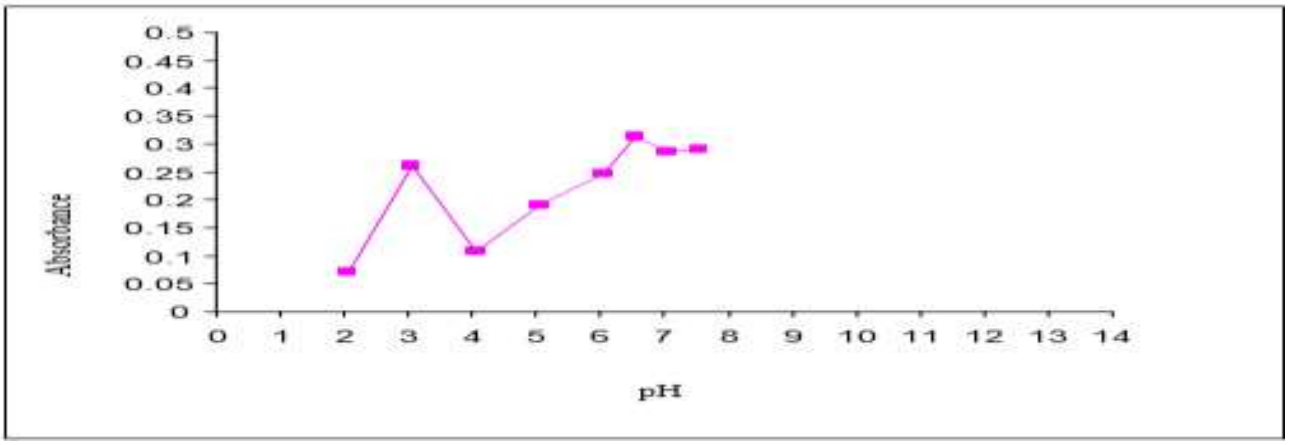

Figure 3. pH graph for the Fe-(TAN) complex in CTAB

Fe (II)-[TAN]$_2$ Calibration

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

The graph of calibration for Fe(II) at λ_{max}571.5 nm offered linear concentration ranges 0.25-4.0 mg/mL with R^2 0.9996 intercepting through zero as displayed in Figure 4.

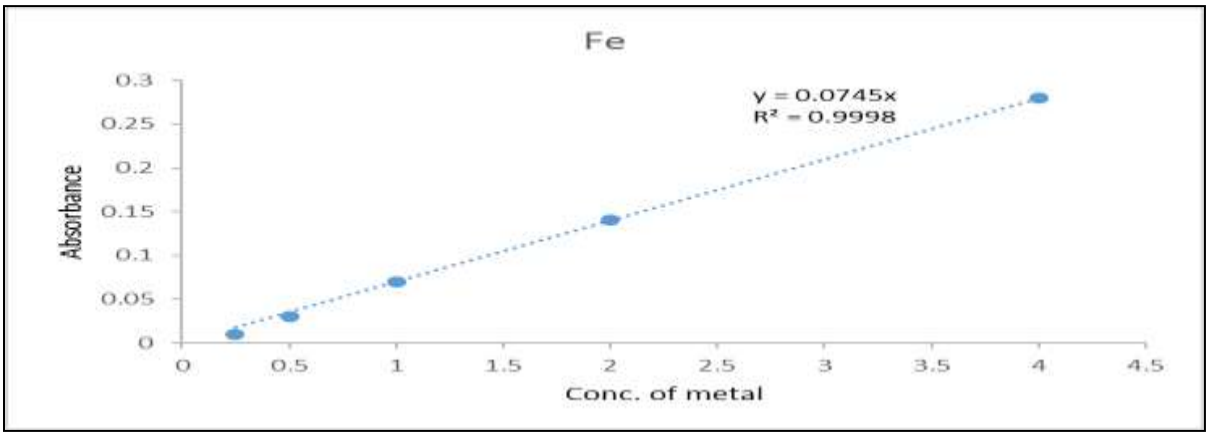

Figure 4. Calibration graph of Fe (II)-[TAN]$_2$

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

Linear calibration curve revealed the mean co-efficient of molar absorptivity for Iron(II) at λ_{max} 571.5 nm that was measured as 1.59×10^4 Lmol^{-1}cm^{-1}. Limit of detection was noted as 5.1 ngcm^{-2}. Sandell's sensitivity was observed to be 7.0 ngcm^{-2} (Table 1). Results obtained were analogous to the results indicated in literature reported.

Table 1. Characteristic parameters for Fe-TAN complex	
Parameters	**Iron**
Molar absorptivity	1.59×10^{4} $Lmol^{-1}cm^{-1}$
Limit of detection	5.1 $ngmL^{-1}$
Beer's law range	0.25-4.0 μgmL^{-1}
Concentration of TAN	5.0×10^{-4} M
Surfactant CTAB	2.0 mL
pH	9.5
L:M	2:1
Sandell's sensitivity	7.0 $ngcm^{-2}$
Wavelength (λ_{max})	571.5 nm
R^2	0.9998

Influence of different ions in Iron analysis

Solutions containing various proportions of multiple anions and cations, as well as 10 µg of iron (II), were prepared using the same method.

The interference limit of each ion was investigated by determining the ratio at which a ±2% variation in the absorbance of the complexes was observed, as presented in Table 2. The effect of ionic strength on the system was found to be negligible at 0.1 M concentrations of sodium chloride

Table 2. Foreign ions interference			
Ions	1×1	10× 1	100× 1
$PO4^{+3}$	N	N	I
Cl^{+1}	N	N	N
Cu^{+2}	N	I	I
Mn^{+2}	N	N	N
Ca^{+2}	N	N	N
Co^{+2}	I	I	I
Zn^{+2}	N	N	I
Al^{+3}	N	N	N
Ni^{+2}	N	I	I
Mg^{+2}	N	N	N

Validation of method

This recommended procedure was applied for estimation of Iron(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 4. 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 5).

Table 3. Percentage recoveries of iron (II) mixed to tap and waste water specimens

Specimens	**Iron mixed (µgmL^{-1})**	**Detected quantities (µgmL^{-1})**	**% Recoveries**
Tap water	1.5	1.4	93.33
Wastewater	00 2.0	1.00 2.91	 97.0

Table 4. Examination of Fe (II) from pharmaceutical, food and alloy specimens

Specimens	**Analytes**	**Present method (µg/mL)**	**% RSD**	**AAS technique (µg/mL)**	**% RSD**	**%Recoveries**
Pharmaceutical specimens						
Tablet Theragran-M 27 mg per tab.	Iron (II)	25.98	1.2	26.31	1.3	96.2
Food specimens						
Malus domestica (Apple)	Iron (II)	2.8	0.32	2.9	0.30	98.3
Alloy specimens						
	Standard values %		**Detected iron % ± SD**		**Relative error %**	
BY0110-1 (Steel)	4.13		3.96 ± 0.13		0.13	
NKK No.920	0.99		0.97 ± 0.03		0.12	
GSBD33001-94	9.53		9.48 ± 0.026		0.07	

Steel, S.A.E. No:6150	9.7	9.6 1± 0.037	0.14

Table 5. Comparison of detection method for of Fe(II) with TAN

Metal	Complexing agents	Procedures/Remarks	References
Fe(II)	HNAHBH	λ_{max}405 nm, Beer's law range 0.055–1.373µg/mL.	[31]
Fe(II)	PAR	λ_{max}718 nm, Beer's law obeyed 0.25-1.00 µgmL^{-1}.	[32]
Fe (II)	1,3-Diphenyl-4-carboethoxy pyrazole-5-one	ϵ 1.156 × 10^4 L mol^{-1}cm^{-1} at λ_{max}525 nm, pH 3.5–4.0.	[33]
Fe (II)	TAN	ϵ 1.59 x 10^4 L mol^{-1} cm $^{-1}$ at λ_{max}571.5 nm, linear calibration range 0.25-4.0 µg/mL, Sandell's sensitivity 7.0 ng/cm^2.	Present method

Conclusion

Conclusion

Developed recommended procedure was utilized to detect minute quantity of Iron(II) metal ions with complexing reagent 1-(2-thiazolylazo)-2-naphthol in surfactant CTAB solution instead of old method of solvent extraction. This procedure is more easy, speedy, sensitive, secure and ecofriendly for the detection of Iron (II) ions in very minute quantities. Developed suggested procedure has offered improvement in molar absorptivity, limit of detection, linear calibration range and Sandell's sensitivity than previous stated procedures as displayed in Table 5. Obtained outcomes were compared with values of certified substances, AAS method, official techniques and statistically validated results at confidence level of 95% comparable. This recommended procedure was applied for estimation of Iron(II) in natural, alloy, real, medicinal, environmental and biological specimens in minute quantities.

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