



Dual-wavelength β -correction spectrophotometric determination of trace concentrations of cyanide ions based on the nucleophilic addition of cyanide to imine group of the new reagent 4-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-6(3H)-one

A. Hamza^a, A.S. Bashammakh^b, A.A. Al-Sibaai^a, H.M. Al-Saidi^c, M.S. El-Shahawi^{a,*}

^a Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

^b The Centre of Excellence in Environmental Studies, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia

^c Department of Chemistry, Teachers College, Umm AL-Qura University, Makkah, Saudi Arabia

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ABSTRACT

A simple, fast, low cost and sensitive direct β -correction spectrophotometric assay of cyanide ions based on its reaction with the reagent 4-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-6(3H)-one, abbreviated as HOTT in aqueous media of pH 7–10 is described. The electronic spectrum of the produced brown-red colored species showed well defined and sharp peak at $\lambda_{\max} = 466$ nm. The effective molar absorptivity for the produced cyano compound was 2.5×10^4 L mol⁻¹ cm⁻¹. Beer's law and Ringbom's plots were obeyed in the concentration range 0.05–2.0 and 0.30–1.5 $\mu\text{g mL}^{-1}$ cyanide ions, respectively. The proposed method offers 16.0 and 50.3 $\mu\text{g L}^{-1}$ lower limits of detection (LOD) and quantification (LOQ) of the cyanide ion, respectively. The analytical utility of the method for the analysis of cyanide ions in tap and drinking water samples was demonstrated and the results were compared successfully with the conventional cyanide ion selective electrode. The short time response and the detection by the naked eye make the method available for the detection and quantitative determination of cyanide in a variety of samples e.g. fresh and drinking water. Moreover, the structure of the produced colored species was determined with the aid of spectroscopic measurements (UV-Vis, IR, ¹H and ¹³C NMR) and elemental analysis.

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1. Introduction

Recent years have seen growing interest in anion recognition because of its importance in a wide range of clinical, chemical and biological applications [1]. Among various anions, cyanide is one of the most concerned anions because it is being widely used in synthetic fibers, resins, herbicides, and the gold-extraction process [2]. Thus, monitoring of cyanide ions in industrial effluents is highly demanded for environmental control, in particular in electroplating, precious metal refining and metal cleaning industries. Cyanide ions either in free or metal-complexed form enter the environment from various human activities e.g. metal finishing, electroplating, steel, petroleum and chemical industries and mining operations [3]. The high toxicity of cyanide ions arises from its complexing ability 'towards iron (III) in the respiratory enzyme, cytochrome c oxidase. On the other hand, due its acute toxicity, environmental protec-

tion authorities such as Australian and New Zealand Environmental and Conservation Council (ANZECC) issue guidelines allowing a maximum permissible concentration limit of 5.0 $\mu\text{g L}^{-1}$ cyanide in fresh and marine waters for protection of aquatic ecosystems [4]. Therefore, considerable attention has been focused on monitoring cyanide concentrations in a variety of samples such as fresh, marine and industrial wastewater by low cost procedures [5,6].

Several methods have been reported for the determination of cyanide ions at low concentration levels, e.g. chromatography [7,8], fluorimetry [9], electro analysis [10–12], indirect determination of cyanide-complexed metal with atomic absorption spectrometry [13]. On the other hand a series of direct and indirect spectrophotometric methods have been reported for the assessment of cyanide ions [13,14]. Most of these methods are based upon the conversion of cyanide ion into cyanogens chloride or bromide followed by the selective chromogenic reactions with pyridine solution of barbituric acid [13,14], pyrazolone [15], isonicotinic acid-barbiturates [16,17], 1,2-phenylenediamine [18], and benzide [19]. The decoloration of some colored complexes such as Cu²⁺/N,N-diethyl-1,4-phenylenediamine [20], and Ni²⁺/2-(5-bromopyridylazol)-5-diethylaminephenol [21] has been

* Corresponding author. Permanent address: Department of chemistry, Faculty of Sciences at Damietta, Mansoura University, Mansoura, Egypt.

E-mail address: mohammad.el.shahawi@yahoo.co.uk (M.S. El-Shahawi).

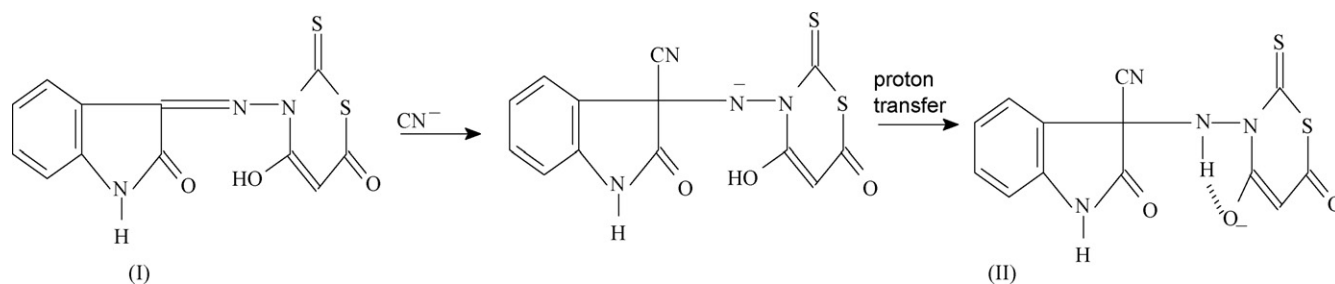


Fig. 1. Nucleophilic addition of cyanide anion to the free reagent HOTT.

widely employed as indirect methods for cyanide assessment. A simple indirect simultaneous spectrophotometric determination method for the cyanide and thiocyanate ions after separation on a melamine–formaldehyde resin has been developed by Gumus et al. [22]. However; the low level of cyanide in industrial wastewaters is not compatible with the detection limit of some of these methods [13,14]. Moreover, some of these methods are too expensive [14,18], unselective, considerably suffered from the time consuming of color development [19,22], interferences by most of the common anions [13,15], require careful experimental conditions and the produced colored species of the cyanide ions are unstable and/or the reagent is carcinogenic.

Recently, particular attention has been focused on the utilization of chemo sensors based on the strong nucleophilicity of cyanide in aqueous media for the determination of cyanide ions through specific chemical reaction between the guest molecules and the target species. In a routine screening, Drochioiu [23] has reported a specific reaction between cyanide ions and 2,2-dihydroxy-1,3-indanedione in alkaline media. Ren et al. [24] and Sun et al. [25] have also used fused indoline and benzoxazine fragment and nucleophilic addition of cyanide to the imine group of a new type of probe molecule bearing hydrazone functionality for highly selective determination of cyanide ions in water. However, these two methods are suffered from the interference of the excess chromogenic reagent which limits the sensitivity and selectivity. Therefore, in continuation to our previous work on the dual-wavelength β -correction spectrophotometry [26] on the reagent HOTT containing numerous active sites e.g. C=O, C=S and C=N (Fig. 1), the present article is focused on the use of the title reagent 4-hydroxy-3-(2-oxindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one for the determination of cyanide ions in various water samples. The study was also aimed to fully characterize the structure and mechanism of the produced cyano compound by spectroscopic techniques e.g. IR, ^1H NMR and ^{13}C NMR and elemental analysis.

2. Experimental

2.1. Reagents and materials

Unless otherwise stated, all chemicals and solvents used were of analytical reagent-grade quality and were used without further purification. A stock solution of cyanide ions ($1000\ \mu\text{g mL}^{-1}$) was prepared from potassium cyanide (BHD, USA). More diluted standard ($0.01\text{--}20\ \mu\text{g mL}^{-1}$) solutions were prepared by dilution of the stock solution and stored in low density poly ethylene (LDPE) bottles. An accurate weight (0.05 g) of the pure reagent HOTT was dissolved in a minimum volume of N, N-dimethyl-formamide (3–5 mL, DMF), followed by dilution with absolute ethanol (100 mL). A series of Britton–Robinson (B–R) buffer (pH 2–11.7) was prepared as reported earlier [27].

2.2. Apparatus

The UV–Vis (190–1100 nm) and IR (200–4000 cm^{-1}) spectra were recorded on a PerkinElmer (model Lambda 25, USA) and a Perkin Mattson 5000 FTIR spectrophotometers, respectively. The absorbance of the reagent and its compound with cyanide ions were also measured with A PerkinElmer (Lambda 25, USA) spectrophotometer (190–1100 nm) with 10 mm (path width) quartz cell. A Bruker NMR (model Vance DPX 600 MHz) was used for recording the ^1H and ^{13}C NMR spectra of the reagent and its cyanide compound in deuterated DMSO solution using TMS as an internal standard. A digital-micro-pipette (Volac) and an Orion pH-meter (model EA 940) were employed for the preparation of the standard cyanide and test solutions and pH measurements, respectively. A scientific melting point SMP1 (UK) was used for recording the melting of the reagent and its cyanide compound. Carbon, hydrogen, nitrogen and sulfur contents were determined by a PerkinElmer 2400C series elemental analyzer, USA.

2.3. Synthesis of the reagent, HOTT

The HOTT reagent was prepared by direct condensation of isatin with dithioic formic acid hydrazide in DMF for 1 h. The reaction product was then poured onto an ice bath and the resultant solid precipitate was separated out, washed with ethanol and ether and finally dried. The dried precipitate (10.0 mmol) was refluxed with diethyl-malonate (10.0 mmol) in ethanol (50.0 mL) in the presence of sodium ethoxide (20.0 mmol) for 4 h. The reaction mixture was cooled, poured onto an ice bath and filtered off. The solid was separated out, washed with ether and acetone, recrystallized from ethanol as a yellow powder with an average yield of 63% and melting point of $242\ ^\circ\text{C}$. Finally elemental analysis of the crystallized compound [$\text{C}_{12}\text{H}_7\text{N}_3\text{O}_3\text{S}_2$] required: 47.2% C, 2.3% H, 13.8% N, and 21% S; found 47.8% C, 2.5% H, 14.1% N, and 21.6% S. The characteristics IR frequencies of the solid reagent in KBr disk were observed at 3353, 3147, 1682, 1655, 1585, 1350, 1098, 977 cm^{-1} and are safely assigned to $\nu\text{O-H}$, $\nu\text{N-H}$, $\nu\text{C=O}$, $\nu\text{C=O}$ (oxindole ring), $\nu\text{C=N}$, $\nu\text{NC=S}$, $\nu\text{C-S}$, ν substituted aromatic nucleus [28], respectively. Moreover, ^1H NMR spectrum of the reagent (I) (Fig. 1) in d_6 -DMSO showed the characteristics signals at δ 10.71 (1H, OH), 10.5 (1H, NH of thioxo-1,3-thiazin-4-one), 9.5 (s, 1H, cyclic H–C=O–H) and 7.8–8.2 ppm (m, 4H, Ar–H). Fine structure of the compound I was also deduced from ^{13}C NMR signals at 163 (1C=S), 139 (2 C=O) of 2,6-tautomeric indole and thiazine, 127, 126, 123, 122 (4 C of benzene ring), 117 (=C–OH), 110 (C=N) and at 66 ppm ($\text{C}_3=\text{C}$) (Fig. 1).

2.4. Preparation of the cyano compound

An accurate amount (0.02 mol) of the reagent HOTT was refluxed with an excess of potassium cyanide in methanol (50 mL) for 1 h. The reaction mixture was then cooled in an ice bath and the pro-

duced brown-red colored precipitate was separated out, filtered off, washed with ether and acetone, and finally recrystallized from ethanol.

2.5. Recommended analytical procedure

An appropriate concentration ($0.05\text{--}2.0\ \mu\text{g mL}^{-1}$) of the test cyanide solution was transferred to 25 mL measuring flasks containing B–R buffer of pH 7–10 and the reagent HOTT solution (2 mL, 0.05%, w/v). The test solutions were completed to the mark with deionized water and shaken. The solution mixtures were allowed to stand at room temperature for 2–5 min and the absorption spectra were measured from 300 to 600 nm. The absorbance of the produced brown-red colored species at 336 nm (λ_1) and $\lambda_{\text{max}} = 466\ \text{nm}$ was finally measured. Calibration plot of the cyanide concentration versus the corrected absorbance of dual-wavelength ($\lambda_1 = 336$, and $\lambda_{\text{max}} = 466\ \text{nm}$) β -correction spectrophotometric method was used for all subsequent measurements of cyanide test and interference test solutions. The spectrophotometric data were measured in triplicate.

2.6. Analytical applications

2.6.1. Determination of cyanide ions in tap and drinking water

Tap water collected from the laboratories of the Chemistry Department, King AbdulAziz University, Jeddah city, KSA, and drinking bottled water, commercially available in Saudi Arabia markets, were filtered through $0.45\ \mu\text{m}$ cellulose membrane filter prior to their analysis and stored in LDPE sample bottles (250 mL). The recommended general spectrophotometric procedure used in preparing the standard curve was followed and the concentration of cyanide ions was then determined from the standard curve using the equation:

$$\text{cyanide concentration} = \frac{C_{\text{std}} \times A_{\text{samp}}}{A_{\text{std}}} \quad (1)$$

where, C_{std} is the standard concentration and A_{samp} and A_{std} are the corrected absorbance of the sample and the standard, respectively.

Alternatively, the method of standard addition was carried out as follows: transfer known volume (5.0 mL) of the unknown water samples to the volumetric flask (25.0 mL) adjusted to pH 7–10 with B–R buffer (5 mL). An accurate volume (2 mL) of the reagent was then added to the test solution and the reaction mixture was then made up to the mark with distilled water. Repeat the same procedures after adding various known concentrations ($0.1\text{--}1.0\ \mu\text{g mL}^{-1}$) of the cyanide ions. Measure the true absorbance displayed by the test solutions before and after addition of the standard cyanide solution employing β -correction spectrophotometric method. The cyanide concentration was then determined via the calibration curve of the standard addition procedure. The average of five independent measurements was taken and the precision in most cases was $\pm 2\%$.

3. Results and discussion

3.1. Preliminary and spectroscopic studies

In aqueous media, on mixing the reagent HOTT with the cyanide ions, a brown-red colored product was developed immediately. The electronic spectrum of the reagent HOTT against water showed one absorption peak at 366 nm (Fig. 2) assigned to $n \rightarrow \pi^*$ transition [28]. In the reaction with cyanide ions in the pH range of pH 7–10, significant changes in the energies were noticed, where a new absorption band at 466 nm was observed on the electronic spectrum versus water. This band was safely attributed to the nucleophilic addition of the cyanide anion to the imine group of

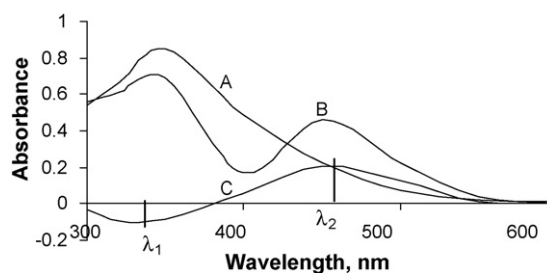


Fig. 2. Electronic spectra of the reagent HOTT and its cyanide compound at pH 9. Curve A is the spectrum of the reagent blank (reference water); curve B is the spectrum of the reagent with cyanide ion (reference, water); and curve C is the spectrum of cyanide-HOTT compound (reference reagent blank).

the reagent HOTT as reported earlier [25] and cleavage of the C–O bond of tautomeric indole and thiazine (Fig. 1) [29,30]. Therefore, solid cyano compound was prepared and isolated as described in the experimental section and subjected to spectroscopic studies to give strong proofs consistent with the proposed structure II (Fig. 1) and to assign the most probable reaction mechanism.

The characteristics IR frequencies of the solid reagent (I) (Fig. 1) in KBr disk changed dramatically after the addition of the cyanide anion. Two new bands were noticed at 3310 and $2088\ \text{cm}^{-1}$ and are safely assigned to $\nu\text{NN-H}$ (amine) and $\nu\text{C}\equiv\text{N}$ [29], respectively. This assignment was also confirmed by the absence of the vibration band at $1585\ \text{cm}^{-1}$ ($\nu\text{C}=\text{N}$) in the IR spectrum of the cyano compound II (Fig. 1). Moreover, the IR spectrum of the cyano compound (II) (Fig. 1) showed also vibration bands at 3353 (νOH), 1656 ($\nu\text{C}=\text{O}$), 1585 ($\nu\text{C}=\text{N}$), 1347 ($\nu\text{NC}=\text{S}$), 1096 ($\nu\text{C}-\text{S}$) and at $974\ \text{cm}^{-1}$ (substituted aromatic nucleolus) which are observed in the IR spectrum of the free reagent I (Fig. 1) confirming the involvement of the C=N group in the cyanide ion attack.

The ^1H NMR spectrum of compound I after the addition of the cyanide ion was dramatically changed, where the proton of OH group was shifted up field to 2.2 ppm confirming the occurrence of proton transfer of the OH group to the developing cyanide anion. This behavior is most likely close to the nucleophilic addition of cyanide anion to imine group (Fig. 1) as reported earlier [25]. The observed signals at $\delta 9.2$, 7.9–6.8 ppm were noticed and were safely assigned to H–C=C–OH and benzo protons, respectively. ^{13}C NMR spectrum of compound II revealed signals at 164 (C=S), 139 (C=O), 129, 124, 123, 122 (4 C of benzene), 118 (=C–OH), 110 (C=N), 79 (C≡N) and 40 ppm (N–C–CN) as shown in Fig. 1. The relatively low value of the OH signal is most likely attributed to intra molecular hydrogen bonding. The chemical structure of the produced cyano compound (Fig. 1, II) was also determined by the method of continuous variations at various concentrations of the cyanide ions and reagent [28]. A plot of the true absorbance of the produced colored solution at 466 nm versus the mole fraction of the HOTT reagent revealed the formation of a compound of 1:1 cyanide to reagent molar ratio. These data confirm the presence of numerous active sites in the structure of the HOTT reagent e.g. C=O, C=S and C=N (Fig. 1) and the nucleophilic addition of the cyanide anions to the imine group of the reagent. Elemental analysis of the cyanide-HOTT compound [$\text{C}_{13}\text{H}_6\text{N}_4\text{O}_2\text{S}_2$] required 49.68% C, 1.91% H, 17.8% N, and 20.4% S; Found 48.5% C, 1.64% H, 19.2% N, 21.2% S.

3.2. Application of β -correction spectrophotometry

Most of the reported spectrophotometric methods [15–23] are suffered from the lack of sensitivity due to the significant interference of the excess chromogenic reagent with the analyte at λ_{max} . This problem can be solved employing β -correction spectrophotometric method to calculate the real absorbance of the formed colored species [30–32]. Thus, the electronic spectra of

the reagent and its compound with cyanide anions were recorded (Fig. 2). The spectrum of the reagent versus water, showed one well defined peak at 336 nm (λ_1), while in the spectrum of cyano compound against the reagent blank at pH 7–10, a well defined absorption peak (λ_2) at 466 nm with a molar absorptivity (ϵ) of $7.8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ was observed (Fig. 2). These results suggest the possible application of the β -correction spectrophotometric technique to improve the sensitivity of the proposed reaction for the determination of cyanide ions the subsequent work. Moreover, the interference caused by the excess chromogenic reagent in the reaction mixture will be eliminated. Therefore, the real absorbance (A_c) of the produced cyanide-HOTT species in solution was calculated employing the equation [31,32]:

$$A_c = \frac{\Delta A - \Delta A'}{1 - \alpha\beta} \quad (2)$$

The spectrophotometric parameters α , β were also calculated employing the equations [31,32]:

$$\beta = \frac{A_o}{A'_o} = \frac{\epsilon_L^{\lambda_2}}{\epsilon_L^{\lambda_1}} \quad (3)$$

$$\alpha = \frac{A'_\alpha}{A_\alpha} = \frac{\epsilon_M^{\lambda_1}}{\epsilon_M^{\lambda_2}} \quad (4)$$

where, $\Delta A'$ and ΔA , are the absorbance's of the produced cyano compound versus reagent blank at λ_1 and λ_2 , respectively., The values of A'_o and A_o represent the absorbance's of the blank solution against water at λ_1 and λ_2 , and A'_α and A_α are the absorbance's of the cyano compound formed in the solution versus water at λ_1 and λ_2 , respectively. Moreover, it should be noted that, the sensitivity of the developed dual-wavelength β -correction method become better than that of the single wavelength method by selecting the wavelengths λ_1 and λ_2 at the valley and the peak of the electronic spectrum of the cyanide compound versus blank solution [32–34], respectively. Thus, curve C in Fig. 2 shows the minimum and maximum absorption of cyanide-HOTT compound at pH 7–10 at 336 nm (λ_1), and 466 nm (λ_2), respectively. Thus, the absorbance of cyanide compound formed at λ_2 versus reagent blank (ordinary single wavelength) was found less than the corrected absorbance by β -correction spectrophotometric technique. Based on the reported equations [33,34], the parameter β was calculated from curve A and was found equal 0.31 while, the value of α_{466} calculated from Fig. 2 (curve B) was 1.1.

3.3. Optimization of chemical variables

The influence of pH on the reaction of the reagent HOTT with cyanide anion can be predicated from the relation: $\text{HCN}/\text{CN} = 10^{9.2}/10^{\text{pH}}$ [35]. The availability of free cyanide ions required completing the addition reaction increases on raising the pH of the aqueous solution. The effect of pH on the real absorbance of the addition product at 466 nm was investigated and the results are presented in Fig. 3. Maximum absorbance was achieved on the pH range 7–10. At pH > 10, the absorbance decreased which is most likely attributed to the formation of hydroxo-species that minimizes the formation of cyanide compound. The stability of the produced cyano compound could be low at pH > 10. Thus, in the subsequent work, the pH of the aqueous solution was adjusted at pH 7–10.

The influence of the reagent (HOTT) concentration on the formation of the cyano compound was studied at pH 7–10. Various volumes (1–6 mL) of the reagent (0.05%, w/v) solution were added to the test solutions. A 2 mL of the reagent (0.05%, w/v) was found sufficient for quantitative determination of cyanide ions up to $2.0 \mu\text{g mL}^{-1}$ in the aqueous solution.

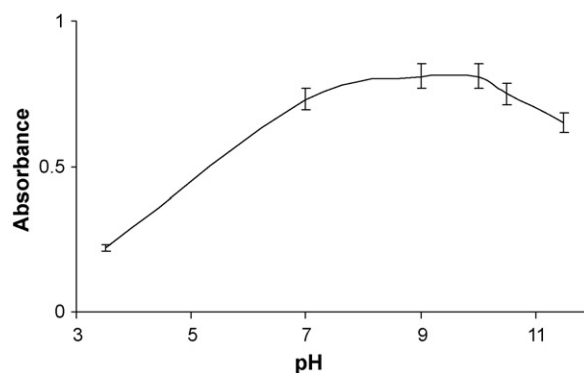


Fig. 3. Plot of the pH of the test aqueous solution versus the true absorbance of the cyanide-HOTT compound. [HOTT] = 0.004% (w/v) and cyanide ion = $1 \mu\text{g mL}^{-1}$.

3.4. Interference study

The determination of cyanide ions at concentration $0.6 \mu\text{g mL}^{-1}$ in the presence of a relatively high excess (0.05–1.0 mg) of some diverse ions relevant to water e.g. Na^+ , Li^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , I^- , NO_3^- , NO_2^- , PO_4^{3-} , Fe^{3+} , Al^{3+} , Zn^{2+} , and Mn^{2+} and ions was critically investigated by the developed procedure. The tolerance limit (w/w) was defined as the concentration of the diver's ions added causing a relative error within $\pm 3\%$ in the true absorbance of cyanide-HOTT compound. The presence of excess amounts (100-fold) of the foreign ions: Na^+ , K^+ , Ca^{2+} , NH_4^+ , Li^+ and Mg^{2+} , Mn^{2+} , Zn^{2+} and the anions PO_4^{3-} , NO_2^- and NO_3^- to the cyanide ions showed no significant change of the corrected absorbance. The anions SO_4^{2-} , I^- and Cl^- at 100-fold excess to the cyanide ions also did not interfere. The interference of the ions Fe^{3+} and Al^{3+} which probably react with the HOTT and/or cyanide forming stable complexes was eliminated by the addition of sodium fluoride (0.5%, w/v). Thus, the method can tolerate the foreign species tested in satisfactory amounts. Hence, the method is adequately selective for the cyanide determination in water and other matrices.

3.5. Analytical performance of the developed procedure

The analytical utility of the developed procedure was determined in terms the dynamic linear range, LOD, and LOQ, repeatability, recovery and specificity for the determination of the cyanide ions under the established experimental conditions. The effective molar absorptivity (ϵ) and the Sandell's sensitivity index [36] of the cyanide compound with and without the use of the dual-wavelength β -correction spectrophotometry were found equal $2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $7.8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.002 \mu\text{g cm}^{-2}$ and $0.0033 \mu\text{g cm}^{-2}$, respectively. The linear dynamic range was $0.05\text{--}2.0 \mu\text{g mL}^{-1}$ employing β -correction spectrophotometry. The regressions of the linear plots without and with the use of β -correction spectrophotometry were given by the equations:

$$A = 0.269C_x + 0.011 \quad (r^2 = 0.997) \quad (5)$$

$$A_c = 0.454C_x + 0.0097 \quad (r^2 = 0.999) \quad (6)$$

respectively, where, C is the concentration of the cyanide ions in (g mL^{-1}). The effective concentration range of cyanide ions evaluated by the Ringbom's plot [37] was obeyed in the range $0.15\text{--}1.5 \mu\text{g mL}^{-1}$. The precision and accuracy of the developed procedure was evaluated by the recovery studies of five replicate measurements of cyanide ions at concentration of $1.0 \mu\text{g mL}^{-1}$ using the developed β -correction method. The relative standard

Table 1

Analytical features of the developed and some of the reported spectrophotometric methods for the cyanide determination.

Reagent	λ_{\max} (nm)	pH	Linear dynamic range ($\mu\text{g mL}^{-1}$)	Limit of detection ($\mu\text{g mL}^{-1}$)	Ref.
Hydroxybenzamide/Ag ⁺ phenolphthalein.	552	10.3	0.6–4	0.10	[39]
CNBr/pyridinium chloride/sulfanilic acid	460	–	0.5–3	0.50	[40]
Chloramine-T/pyridine barbituric acid	578	6–8	0.3–5	0.10	[41]
Phenolphthalein/CuS	552	10.3	0.6–4	0.60	[35]
Oxazine	411	7.6	Up to 0.26	0.026	[24]
2,2'-Dipyridyl-2-quinolyldiazone/Cu ²⁺	353	9.5	0.04–1.2	0.020	[35]
Aquacyanocobyrinic acid heptamethyl ester					
4-Hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one	466	7–10	0.05–2	0.016	Present work

Table 2Analysis of cyanide ions in tap-, bottled- and underground water samples by the proposed (A) and the potentiometric (B) methods^a.

Sample	Cyanide added ($\mu\text{g mL}^{-1}$)	Cyanide found ($\mu\text{g mL}^{-1}$)		Recovery (%)	
		A	B	A	B
Tap water	0.0	ND	ND	–	–
Tap water	1	1.04 ± 0.13	1.06 ± 0.3	104 ± 3.0	106 ± 0.01
Bottled water	0.0	ND	ND	–	–
Bottled water	2	2 ± 0.06	2.05 ± 0.1	99 ± 2.5	105 ± 1.57
Ground water	0.0	ND	0.008 ± 0.03	–	–
Ground water	1	1.05 ± 0.5	1.09 ± 0.4	105 ± 5.02	109.0 ± 3.2

^a Average of five measurements ± standard deviation.

deviation (RSD) and the relative error of the developed β -correction method were 2.3% and 1.9%, respectively.

The values of LOD and LOQ were calculated using the formula $\text{LOD} = 33\sigma/b$ and $\text{LOQ} = 103\sigma/b$ where σ is the standard deviation of the blank and b is the slope of the calibration plot [38]. Employing the ordinary single wavelength spectrophotometry, the values of LOD and LOQ were found 0.16 and 0.52 $\mu\text{g mL}^{-1}$ cyanide ions, respectively. Such limits of LOD and LOQ were improved to 0.016 and 0.050 $\mu\text{g mL}^{-1}$, respectively employing the developed β -correction method. A comparison of the main analytical features of the proposed method was made with many of the previously published spectrophotometric methods [24,35,39–41] is summarized in Table 1. Some of these method exhibited high detection limit (0.1–0.6 $\mu\text{g mL}^{-1}$) and serious interferences by halides ions [39–41]. Thus, it can be concluded that, the developed method is more selective and sensitive than the reported methods

3.6. Analytical applications

The validation of the proposed method for the assay of the cyanide ions in tap and drinking bottled water was critically investigated by the direct calibration plot and the standard addition method. The tested water samples (Tap- and drinking water) were processed at the optimum experimental conditions of the developed as mentioned in the experimental section. Moreover, different concentrations of the cyanide ions at concentration range 0.1–2.0 $\mu\text{g mL}^{-1}$ were also spiked onto the tested water samples. The cyanide content in each sample was then determined via the developed method and the standard solid state cyanide ion selective electrode (ISE) method [42]. The results are summarized in Table 2. The percentage recoveries of both methods were in good agreement and always higher than 95% confirming the accuracy of developed procedure and its independence from matrix interference. The statistical evaluations involving F test revealed no significant differences between the two the variances of the developed and the ISE methods [38]. The calculated value of $F(2.78)$ is less than the tabulated F value (6.39) for five replicate measurements. Therefore, there is no significant difference in the precision of the two methods at the 95% confidence level. The student t test was also applied to the analytical data obtained from the developed and ISE methods [43]. The results revealed no statistical difference

between methods. The tabulated t value at 95% confidence limit was found equal 2.306 while the calculated t value of t calculated by applying t test to the results obtained analyzing the bottled water sample was found 0.79 ($n = 5$) at 2 $\mu\text{g mL}^{-1}$ concentration of cyanide ions. Moreover, the method was applied for the analysis of cyanide ions in industrial wastewater samples of electroplating baths after prior distillation with HCl (1.0 mol L⁻¹). The liberated cyanide ions were absorbed on alkaline KOH (1.0 mol L⁻¹). The average recovery (98.6%) of cyanide ions was compared successfully with the data obtained by potentiometry using a solid state cyanide ion selective electrode [42].

4. Conclusions

The reaction of the HTTO reagent with cyanide ion at pH 7–10, develops an intense brown-red color due to the nucleophilic addition of cyanide to imine group. The described method has the advantage of virtual freedom from interference from extraneous ions and can therefore serve as an alternative to the widely used methods for rapid and precise determination of trace amounts of cyanide in natural water and effluent samples. The method requires no complex pretreatment of chromatographic separations and/or preconcentration of the analyte and represents a highly selective and sensitive chemo sensor for the cyanide determination because color change appears rapidly within less than 30 s and remains quite stable for up to 1 h. The detection limit of the developed method was compared successfully with that of some published spectrophotometric procedures (Table 2). However, work is still continuing for investigating the influence of memory effect, organic material present in the investigated fresh water samples, competitive complexing agents in addition to the on-line determination of cyanide in industrial wastewater after preconcentration on solid sorbent immobilized with the title reagent.

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