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Part 1. Spectrophotometric determination of trace mercury (II) in dental-unit wastewater and fertilizer samples using the novel reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one and the dual-wavelength β-correction spectrophotometry

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ABSTRACT

A simple and low cost method was developed and validated for the determination of trace mercury (II) ions in dental-unit wastewater and fertilizer samples. The method was based upon the reaction of mercury (II) ions with the novel reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one, the formed complex shows an absorption maximum at 505 nm (λ_{max}) in Britton–Robinson (B–R) buffer (pH 4–6).The corrected absorbance of the formed complex at λ_{max} was obtained employing β-correction spectrophotometric method. Beer's–Lambert law and Ringbom's plots of the colored Hg–reagent complex were obeyed in the concentration range of 0.2–2.0 and 0.32–0.96 $\mu g\,mL^{-1}$ mercury (II) ions, respectively with a relative standard deviation in the range of 2.1±1.3%. The limits of detection (LOD) and quantification (LOQ) of the procedure were 0.026 and 0.086 $\mu g\,mL^{-1}$ Hg^{2+}, respectively. The proposed method was applied for the analysis of mercury (II) in dental-unit wastewater and fertilizer samples. The validation of the method was tested by comparison with the data obtained by the inductively coupled plasma-mass spectrometry (ICP-MS). The statistical treatment of data in terms of Student's *t*-tests and variance ratio *f*-tests has revealed no significance differences.

1. Introduction

Mercury is one of the most toxic heavy metal in the earth and it exists in nature at trace and ultratrace amounts in three valence states [1]. Mercury (0, I, II) species and are able to combine with most inorganic and organic ligands to form various complexes, e.g. $HgX_4{}^{-2}$ (where X = Cl, Br and I) and methyl mercury [1,2]. Mercury can accumulate in animals and plants and also enters into human body through the food chain causing damage to central nervous system [3]. Due to the toxicological effects and potential accumulation of mercury onto human bodies and aquatic organisms, the determination of mercury (II) or organo mercury (II) has seen an upsurge of interest in the last few years [4]. According to WHO, the allowed limits of mercury in drinking water are less than 1.0 $ng\,mL^{-1}$ [5].

The determination of low concentrations of mercury is a vital task. Therefore, considerable efforts and progress have been carried out to develop accurate, low cost and reliable methods for mercury determination in contaminated samples without any complicated processing steps [6]. The most common techniques in natural samples are ICP-MS [7,8]; atomic fluorescence [9,10]; cold vapour atomic absorption [11–13]; GC [14]; stripping voltammetry [15,16]; X-ray fluorescence spectrometry [17]; neutron activation analysis [18] and atomic fluorescence spectrometry [19]. The determination and chemical speciation of mercury (II) and/or methyl mercury in a series of complicated matrices, e.g. Mushroom from Tokat-Turkey, water and fish have been reported by Tuzen et al. [20,21]. Moreover, the use of Lichen (Xanthoparmelia conspersa) biomass and Streptococcus pyogenes loaded Dowex optipore SD-2 has been reported as efficient materials for the removal of mercury (II) and methylmercury from aqueous media [22,23]. Among these techniques, visible absorption spectrophotometry represents the most convenient technique because of the availability of the instrumentation, simplicity, speed, precision, accuracy and low cost.

A series of chromogenic reagents has been reported for mercury (II) determination in different samples [24–28]. Most of these methods are suffered from the lack of sensitivity due to the significant interference of the excess of chromogenic reagent with the analyte at λ_{max}. This problem was solved by employing the β-correction

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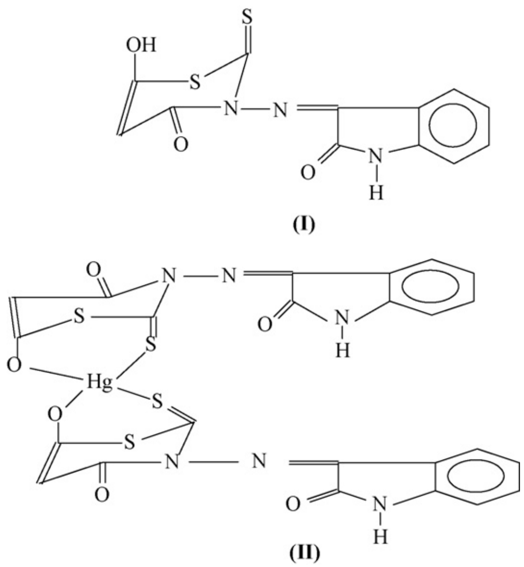

Fig. 1. Chemical structure of the reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one (I) and the proposed structure of its mercury (II) complex (II).

spectrophotometric method to calculate the real absorbance of the complex [29,30].

A recent literature on the analytical applications of the entitled reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one abbreviated as HOTT (Fig. 1) has revealed no study on the use of the reagent for mercury (II) determination and/or other trace metal ions. Therefore, the goals of the present manuscript are focused on the synthesis and spectroscopic characterization (UV–Vis, IR and ^{1}H NMR) of the HOTT reagent. Moreover, the stiochiometry of the formed mercury (II)-HOTT chelate was elucidated in an attempt to develop an accurate method for the analysis of mercury (II) in different water and fertilizer samples. The effect of different parameters that control the absorbance of the formed complex was determined.

2. Experimental

2.1. Reagents and materials

Unless otherwise stated, all chemicals and solvents used were of analytical reagent grade and were used without further purification. A stock solution of mercury (1000 μg mL^{-1}) was prepared from mercury (II) chloride (BDH, Poole, England). More diluted standard (0.05–20 μg mL^{-1}) solutions were then prepared by dilution and were stored in low density polyethylene (LDPE) bottles. An accurate weight (0.05 g) of the pure reagent HOTT (Fig. 1) was dissolved in a minimum volume of N,N-dimethyl-formamide (DMF), followed by dilution with absolute ethanol (100 mL). A series of Britton–Robinson (B–R) buffer (pH 2–11) was prepared by mixing equal proportions of BDH acetic (0.04 mol L^{-1}), phosphoric (0.04 mol L^{-1}) and boric (0.04 mol L^{-1}) acids in deionized water and the pH of the solutions were then adjusted to the required pH by adding various volumes of NaOH (0.2 mol L^{-1}) solution as reported earlier [31].

2.2. Apparatus

The UV–Vis (190–1100 nm) and IR (200–4000 cm^{-1}) spectra were recorded on a Perkin Elmer (Lambda 25, Shelton, CT, USA) and a Perkin Mattson 5000 FTIR spectrophotometers, respectively. The absorbance measurements of the reagent and its mercury (II) complex were also measured with a Perkin Elmer (Lambda 25, USA) spectrophotometer (190–1100 nm) with 10 mm (path width) quartz cell. A Bruker NMR (model Vance DPX 400 MHz) was used for recording the proton NMR spectra of the reagent and its mercury (II) complex in deuterated DMSO solution using TMS as internal standard. A digital micro-pipette (Volac), an Orion pH-meter (model EA 940) and the scientific melting point SMP1 (UK) were employed for the preparation of the standard and test solutions, pH measurements and melting point, respectively. De-ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and was used for the preparation of all solutions. Carbon, hydrogen, nitrogen and sulfur content was determined by a Perkin Elmer 2400 C series elemental analyzer, USA. A Perkin Elmer ICP-MS spectrometer (model Elan DRC II, USA) was used under the optimum experimental conditions.

2.3. Synthesis of the chromogenic reagent, HOTT

The reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one 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, ether and finally dried. The resultant dried precipitate (10.0 mmol) was then refluxed with diethyl malonate (10.0 mmol) in ethanol (50.0 mL) in presence of sodium ethoxide (20.0 mmol) for 4 h. The reaction mixture was then cooled, poured onto an ice bath and filtered off. The solid was separated out, washed with ether and acetone, recrystallized from ethanol and finally characterized.

2.4. Recommended procedure

In a series of volumetric flasks (25 mL), an appropriate concentration (0.2–2.0 μg mL^{-1}) of mercury (II) solution was added to the reagent solution (1.50 mL, 0.05%, w/v). To the test solution, an approximate volume (5 mL) of B–R buffer of pH 4–5 was added and finally the solution was made up to the mark with distilled water. The solution mixtures were allowed to stand at room temperature for 5 min before measuring the absorbance at 336 nm (λ_1) and λ_2 505 nm.

2.5. Analytical application

2.5.1. Determination of mercury (II) in tap and mineral water

Tap water collected from the laboratories of Chemistry Department, King AbdulAziz University, Jeddah city, KSA, and mineral water, commercially available in Saudi market, were filtered through 0.45 μm cellulose membrane filter prior to analysis and stored in LDPE sample bottles (250 mL). The recommended general spectrophotometric procedure used to prepare the standard curve was followed and the concentration of mercury (II) ions was then determined from the standard curve using the equation:

$$\text{Mercury (II) concentration} = C_{\text{std}} \times A_{\text{samp}}/A_{\text{std}} \tag{1}$$

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 standard addition method was employed as follows: transfer known volume (5.0 mL) of the unknown water samples to the volumetric flask (25.0 mL) adjusted to pH 5–6 with B–R buffer (10 mL). An accurate volume (1.5 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 concentrations (0.2–1.0 μg mL^{-1}) of mercury (II). Measure the true absorbance displayed by the test solutions before and after the addition of the standard (0.2–1.0 μg mL^{-1}) mercury (II) solution employing

Table 1
Analytical features of some spectrophotometric methods employed for mercury determination.

Reagent/Ref.	λ_{max}	pH	Linear dynamic range ($\mu g\,mL^{-1}$)	Molar absorptivity ($L\,mol^{-1}\,cm^{-1}$)	Remarks
Thiobenzoylacetone/[38]	345	4	0.6–12	1.7×10^{4a}	Sensitive but interference from Ag^+ and excess of chromogenic reagent. Using toxic organic solvents.
Variamine Blue B/[39]	605	2.5–4	0.64–4.4	4×10^{4b}	Sensitive but using toxic organic solvents. Time-consuming.
Phenanthroline and eosin/[33]	550	4.5	0.2–1.2	8×10^{4}	Sensitive, but interference from Al^{3+}, Co^{2+}, Ni^{2+} and excess of dye.
Thiacrown ether and Bromocresol Green/[40]	420	–	0.5–12	–	Less sensitivity and interference from. Cu^{+2}, $Cd^{2+}$and Ag^+. Time-consuming.
Diphenylthiocarbazone/[41]	488	Acidic media	0.1–25	2.5×10^{4}	Low sensitivity
Present work	505	4–6	0.2–2	4×10^{4c}	Sensitive, selective and free from the interference of Al^{3+}, Ag^+, Co^{2+}, Ni^{2+} and excess chromogenic reagent. No need for organic solvent.

[a] In benzene.
[b] In nitrobenzene.
[c] With β-correction spectrophotometry.

β-correction spectrophotometry method. The concentration of mercury (II) was then determined via the calibration curve of the standard addition procedure.

2.5.2. Analysis of mercury in dental-unit (DU) wastewater

DU wastewater samples were collected from dental chair, King AbdulAziz Hospital, Makkah city, KSA, at the end of working day. An accurate volume of sample was digested by UV-digester in the presence of suitable volumes of both concentrated HNO_3 and H_2O_2 (30%) for 1 h. the obtained solution was neutralized by NaOH (5 mol L^{-1}) and 10 mL of this solution was treated under the conditions of recommended procedure.

2.5.3. Determination of mercury (II) in fertilizer

In a 50 mL beaker, an accurate weight (4.50–5.70 g) of the local fertilizer (Broxals 1 and 2) was dissolved in de-ionized water after constant stirring for few minutes. The aqueous solution was then completed to 250.0 mL with double distilled water. An accurate volume of the test solution (5.0 mL) was then adjusted to pH 5 with B–R buffer, transferred into the measuring flask (25.0 mL) in the presence of the reagent (1.5 mL, 0.05%, w/v) and various concentrations (0.2–1.0 $\mu g\,mL^{-1}$) of mercury (II) were added separately. The solutions were then completed to the mark with doubly de-ionized water and the absorbance of the test solutions was measured by dual-wavelength β-correction spectrophotometer. The concentration of mercury (II) was finally determined via the standard addition curve. The results were compared with the analytical data obtained from ICP-MS under the conditions described in Table 1. The measurements are the average of three independent measurements and the precision in most cases was ±2%.

3. Results and discussion

The characteristics IR vibrations of the solid reagent in KBr disk are observed at 3353, 3147, 1682, 1655, 1585, 1350, 1098, and 977 cm^{-1} and are safely assigned to ν O–H, ν N–H, ν C=O , ν C=O, ν C=N, ν NCS, ν C–S, ν substituted aromatic nucleus [32], respectively. ^1H NMR spectrum of the reagent in d_6-DMSO show signals at δ 7.15, 9.5, 10.5 and 10.71 ppm and are safely assigned to (*m*, 4H, aromatic protons), 9.5 (s, 1H), 10.5 (s, 1H, OH) and 10.71 (s, 1H, NH) protons [32], respectively. The relatively low value of the OH signal is most likely attributed to intramolecular hydrogen bonding. Elemental analysis of the reagent after solvent evaporation and crystallization from ethanol for the structure $[C_{12}H_7N_3O_3S_2]$ 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. In complex formation, the ligand has numerous coordination sites which gave variable bonding modes and behaves as a mononegative dentate fashion (Fig. 1). A careful comparison of the IR spectrum of the reagent HOTT with the spectrum of its mercury (II) complex in KBr disk revealed that, the ligand is bonded through the thione sulfur as indicated from the observed shift of ν(C=S) vibration to lower wave number with simultaneous appearance of new band at 395 cm^{-1} due to ν(Hg–S) [32]. Deprotonation of the enolic OH of the reagent in the complex formation was also confirmed by the disappearance of ν(OH) and the appearance of ν(N–O) at 1100 cm^{-1} and ν(Hg–O) at 549 cm^{-1} and provides an additional support for the oxime oxygen donation. Elemental analysis of the formed mercury (II) complex $[Hg\,(C_{12}H_7N_3O_3S_2)_2]$ required 35.5% C, 1.73% H, 10.4% N, and 15.8% S, and 24.7% Hg; Found 36.5% C, 1.44% H, 9.2% N, 16.2% S, and 25.1% Hg.

3.1. Absorption spectra of the reagent and its mercury (II) chelate

Preliminary screening investigation on the interaction of the title reagent HOTT (Fig. 1) with mercury (II) ions in the aqueous media and shaking has revealed the formation of a red colored complex. The absorption electronic spectra of the reagent and its mercury (II) complex are shown in Fig. 2. The spectrum of the reagent versus water, showed one well defined peak at 336 nm (λ_1), while in the spectrum of its mercury (II) complex against the reagent blank at pH 4–5 a well defined absorption peak (λ_2) at 505 nm with a molar absorptivity (ε) of $2.5 \times 10^4\ L\,mol^{-1}\,cm^{-1}$ was observed (Fig. 2). These results suggest the possible applica-

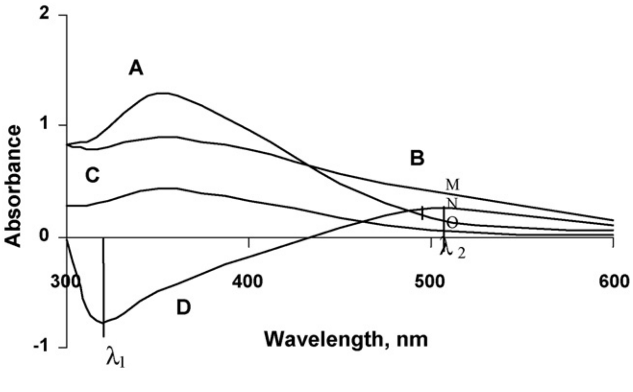

Fig. 2. Absorption spectra of the reagent HOTT and its mercury (II) complex at pH 5. Curve A is the spectrum of the reagent blank (reference water); B is mercury (II) complex (reference, water); C is the excess of reagent (reference water) and D is mercury (II) complex (reference, reagent blank).

tion of the β-correction spectrophotometric technique to improve the sensitivity of the proposed reaction for the determination of mercury (II) on 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 mercury (II) complex in solution was calculated using the equation:

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

where ΔA and $\Delta A'$ are the absorbance's of the mercury (II) chelate at λ_2 and λ_1, respectively versus reagent blank as a reference. The spectrophotometric parameters α and β were calculated employing the equations:

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

$$\alpha = \frac{A'_\alpha}{A_\alpha} = \frac{\varepsilon_{ML}^{\lambda_1}}{\varepsilon_{ML}^{\lambda_2}} \qquad (4)$$

where A'_o and A_o are the absorbance's of the blank solution at λ_1 and λ_2, respectively, against water as a blank; A_α and A'_α are the absorbance's of the complex formed in the solution at λ_2 and λ_1 versus water, respectively. Moreover, it should be noted that, the sensitivity of the developed β-correction method was improved 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 chelate versus blank solution [29,30], respectively. Thus, curve C in Fig. 2 demonstrates the theoretical absorption spectrum of the excess reagent. Curve D shows the minimum and maximum absorption of mercury (II)–HOTT complex at pH 4–5 at 336 nm (λ_1), and 505 nm (λ_2), respectively. Thus, the absorbance of mercury (II) complex formed at λ_2 when blank was used as a reference (single-wavelength method) was found less than the corrected absorbance by β-correction spectrophotometric technique. Thus, the real absorbance will be equal to the interval MO but not MN. From Fig. 2 (curve A), the calculated parameter β was found equal 0.24 while, the correction coefficient, α_{505}, calculated from Fig. 2 (curve B) was 1.3.

3.2. Influence of different parameters on the determination of mercury (II)

The influence of pH of the aqueous solution employing B–R buffer (pH 2–11) on the developed colored complex was studied by measuring the real absorbance of the solution containing mercury (II) ions at a suitable mercury concentration (1.0 μg mL^{-1}) in the presence of the reagent HOTT. The results are shown in Fig. 3, where it was clearly seen that, maximum absorbance of the produced colored complex was obtained at pH 4–6 and the central value of this range was achieved at pH 5. On the other hand, in the aqueous solution of pH ≤ 4, the absorbance was found low since the equilibrium moves to the left and the quantity of the dissociated species of the reagent available to form complex with mercury (II) decreased. In the aqueous solution of pH ≥ 5.5, the absorbance of the produced colored complex decreased dramatically. The hydrolysis of the colored complex and the formation of non-colored complex species of mercury (II), e.g. hydroxo complex species of mercury (II) are most likely minimize the colored complex and may account for the observed trend [35]. Thus, in the subsequent work, the aqueous solution was adjusted at pH 5–6 to ensure complete color formation.

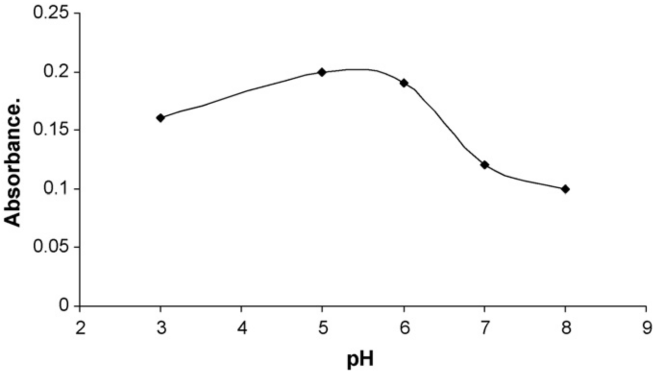

Fig. 3. Influence of pH of the aqueous test solution on the real absorbance of mercury (II)–HOTT complex. Conditions are: reagent concentration = 0.003% (w/v) and mercury (II) = 1 μg mL^{-1}.

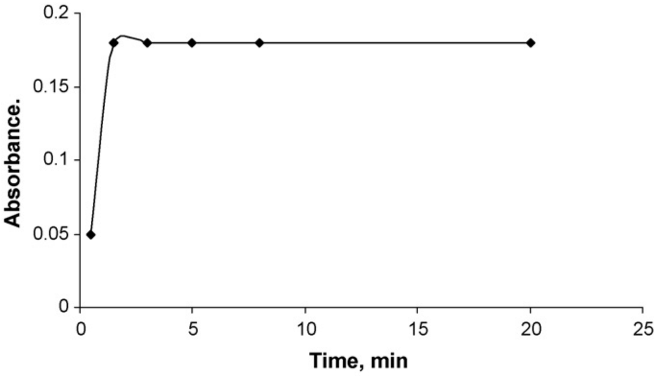

Fig. 4. Plot of the absorbance (stability) of the formed mercury (II)–HOTT complex versus time. Reagent concentration = 0.003% (w/v); mercury (II) = 1 μg mL^{-1} and the aqueous solution pH 5.

The influence of the reagent HOTT concentration on the formation of the complex species of mercury (II) ions (1.0 μg mL^{-1}) was studied at pH 5–6. Various volumes of the reagent (0.05%, w/v) solution were added to the test solutions. A 1.5 mL of the reagent (0.05%, w/v) was found sufficient to quantitatively determine mercury (II) up to 1.0 μg mL^{-1} in the aqueous solution. A large excess of the reagent decreased the absorbance possibly owing to the increased acidity of the aqueous phase which minimizes the complex formation.

The stability of the formed complex was examined (Fig. 4) at the optimum conditions. The results showed that, the complex was stable after 0.5 min for periods longer than 20 min and therefore, this reaction is suitable for quantitative measurements.

3.3. Interference study

The determination of mercury (II) ions at concentration 0.6 μg mL^{-1} in the presence of a relatively high excess (0.05–1.0 mg) of some diverse ions relevant to water, e.g. alkali and alkaline earth metals, Al^{3+}, Ag^+, Au^{3+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, VO_3^-, AsO_2^-, SO_4^{2-}, and PO_4^{3-} 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 ±3% in the true absorbance of mercury (II)–HOTT complex. The results revealed that the presence of large amounts of the following foreign ions: Ag^+, Ca^{2+}, NH_4^+, Li^+ and Mg^{2+} and the anions PO_4^{3-}, CH_3COO^- and NO_3^- did not cause any significant change in the corrected absorbance of the Hg complex even at 1:1000 tolerable concentrations of Hg (II) to the foreign ions, respectively. The ions Co^{2+}, Ni^{2+}, Cd^{2+}, Au^{3+}, F^- and Cl^- at 100-fold excess to the mercury (II) ions also did not interfere. The ions Pb^{2+} and Fe^{3+} at concentrations 50 times higher than those of the analyte interfered seriously. Addition of few drops of NaCl (0.1%, w/v) and NaF (1.0%, w/v) to the aqueous solution eliminates the positive interferences caused by the ions Pb^{2+} and Fe^{3+}, respectively. Addition of NaCl and NaF to the aqueous solution containing mercury (II) and the HOTT reagent forms white precipitate of $PbCl_2$ and colorless anionic complex species $[FeF_6]^{3-}$ with Fe^{3+}. The interference of $MnO_4{}^-$ was also eliminated by the addition of sodium azide to reduce manganese (VII) to manganese (II). After employing these modifications, the tolerance level of the interfering ions was improved to acceptable limit (98 ± 2%). These results extend the possible use of the method for the determination of mercury (II) ions in various matrices.

3.4. *Stiochiometry of the mercury (II) complex*

The chemical structure of the produced mercury (II) complex species was determined by the method of continuous variations at various concentrations of the mercury (II) ions and reagent [34]. A plot of the true absorbance of the produced colored solution at 505 nm versus the mole fraction of the reagent revealed a graph that indicated the formation of complex having mercury (II) to a reagent molar ratio of 1:2. These data confirmed that, the colored species is most likely fit with the molecular formula of mercury (II)–reagent.

3.5. *Analytical performance*

At the optimum experimental conditions of the reaction of the reagent HOTT with mercury (II) in the aqueous solution of pH 4–5, the effective molar absorptivity (ε) calculated from Beer's–Lambert plot and the Sandell's sensitivity index [35] of the mercury (II)–complex with and without the use of β-correction spectrophotometry were found to be equal to $4.0 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ and $2.5 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ and $0.005\,\mu\mathrm{g\,cm^{-2}}$ and $0.008\,\mu\mathrm{g\,cm^{-2}}$, respectively. The plot of the absorbance's of the mercury (II) complex at 505 nm versus mercury (II) concentrations employing β-correction spectrophotometry was obeyed Beer's–Lambert law in the concentration range of $0.2–2.0\,\mu\mathrm{g\,mL^{-1}}$. The regressions of the linear plots without and with the use of β-correction spectrophotometry were given by Eqs. (5) and (6), respectively:

$$A = 0.101C_x + 0.002 \quad (r^2 = 0.995) \tag{5}$$

$$A_c = 0.183C_x + 0.004 \quad (r^2 = 0.999) \tag{6}$$

The effective concentration range of mercury (II) ions as evaluated by the Ringbom's plot [35] was obeyed in the range $0.2–0.96\,\mu\mathrm{g\,mL^{-1}}$. The precision and accuracy of the developed procedure was evaluated by the recovery studies of four replicate measurements of mercury (II) in distilled water at concentration level of $1.0\,\mu\mathrm{g\,mL^{-1}}$ using β-correction and the ordinary single-wavelength spectrophotometry methods. The relative standard deviation and the relative error of the developed β-correction method were 1.3% and 1.0% while 3.2% and 6.0% for the single-wavelength spectrophotometry, respectively. The level of precision was found suitable for the routine analysis of the mercury (II) in various water samples. Under the conditions established for mercury (II) ions, the lower limits of detection (LOD) and quantification (LOQ) of mercury (II) were determined by employing the equations [36]:

$$\mathrm{LOD} = \frac{3\delta}{b} \tag{7}$$

and

$$\mathrm{LOQ} = \frac{10\delta}{b} \tag{8}$$

where δ is the standard deviation ($n = 4$) of the blank and b is the slope of the calibration plot. The values of LOD and LOQ of the developed procedure without using β-correction absorbance values were found are 0.16 and $0.52\,\mu\mathrm{g\,mL^{-1}}$ mercury (II), respectively. Such limits were improved to lower detection and quantification limits of 0.026 and $0.086\,\mu\mathrm{g\,mL^{-1}}$ mercury (II), respectively employing the developed β-correction method at the optimum experimental conditions. Such limits are comparable to most of the spectrophotometric methods involving pre concentration step on solid sorbent [37]. The analytical features of the proposed method were also compared with many of extractive spectrophotometric methods [33,38–41]. The data given in Table 1 revealed that, the developed method is simple, less toxic, reliable and free from interference of the ions Al^{3+}, Ag^+, Co^{2+}, and Ni^{2+} and the excess reagent compared to the reported methods [33,38–41].

3.6. *Validation and analytical applications of the developed method*

The validity of the proposed method was tested by the analysis of mercury (II) in tap, mineral and DU wastewater samples. For this purpose, different concentrations of mercury (II) ions at concentration range $0.2–2.0\,\mu\mathrm{g\,mL^{-1}}$ were spiked onto the tested water samples. The mercury content in each sample was then determined via the developed method and the results are summarized in Table 2.The obtained results were compared with the standard

Table 2
Analysis of mercury (II) ions in tap, mineral and DU wastewater samples by the developed (A) and the ICP-MS (B) methods[a].

Water sample	Mercury (II) added (μg mL^{-1})	Mercury (II) found (μg mL^{-1})[a]		Recovery (%)[a]	
		A	B	A	B
Tap water	–	ND	ND	–	–
Tap water	1	1.04 ± 0.03	1.06 ± 0.003	104 ± 3.0	106 ± 0.01
Mineral water	0.0	ND	ND	–	–
Mineral water	2	1.98 ± 0.0.05	2.1 ± 0.0.02	99 ± 2.5	105 ± 1.57
DU wastewater	0.0	3.83 ± 0.67	3.76 ± 0.56	–	–
DU wastewater	1	4.62 ± 0.52	4.30 ± 0.8	96 ± 2.02	90 ± 1.45

[a] Average of three measurements ± standard deviation.

Table 3
Analysis of mercury (II) ions in the fertilizer samples by the proposed procedure (A) and ICP-MS (B)[a].

Fertilizer sample	Mercury (II) added (μg mL^{-1})	Mercury (II) found (μg mL^{-1})		Recovery (%)	
		A	B	A	B
Broxal 1	0.450	0.452 ± 0.03	0.44 ± 0.03	100.4 ± 6.6	97.8 ± 0.03
Broxal 2	0.250	0.25 ± 0.03	0.26 ± 0.03	100.0 ± 3.3	104 ± 0.03

[a] Average of three measurements ± standard deviation.

ICP-MS method in terms of Student's *t*-test (3.03–5.89) and *f*-test (0.53–0.96). The results summarized in Table 2 revealed that, 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.

Moreover, the validity of the proposed method was also tested by the analysis of mercury (II) on the Broxal fertilizer under the conditions described in Section 2.5.2. The true absorbance of the test solutions calculated via the proposed dual-wavelength β-correction spectrometry was plotted versus the concentrations of mercury added. The spiked mercury (II) concentration was determined via the standard addition curve and the results were successfully compared with the value of mercury (II) determined by ICP-MS (Table 3).

4. Conclusions

The method described provides a simple and reliable means of determination of trace amounts of mercury (II) ions in aqueous media by spectrophotometry. The method is sensitive ($\varepsilon = 4.0 \times 10^4\ \mathrm{L\,mol^{-1}\,cm^{-1}}$), inexpensive and less toxic than most of the reported extractive spectrophotometric methods [33,38–41]. Moreover, the method also has the advantage of virtual freedom from interference from extraneous ions. Thus, it can act as an alternative approach to the widely used flameless AAS and ICP-OES in rapid and precise determination of trace amounts of mercury in natural water and industrial effluent samples. On the other hand, a calibration matrix constructed with β-correction spectrophotometric method has been successfully applied for the analysis of mercury (II) ions in real samples. The method requires no complex pretreatment of chromatographic separations and/or preconcentration of the analyte.

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