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ARTICLES

Spectrophotometric Determination of Tin(II) by Redox Reaction Using 3,3',5,5'-Tetramethylbenzidine Dihydrochloride and N-Bromosuccinimide[1]

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Abstract—A rapid, straightforward spectrophotometric method based on the redox reaction of tin(II) with a mixture of N-bromosuccinimide (**NBS**) and 3,3',5,5'-tetramethylbenzidine dihydrochloride (**TMB**) was developed for determining low concentrations of tin(II). The redox method improved sensitivity by 2.3-fold relative to the existing spectrophotometric methods by titrating tin(II) into an equimolar solution of colorimetric reagent TMB and oxidant NBS buffered with acetate to pH between 4.0 and 4.4 at 25°C. The spectral absorption at 452 nm was linear with respect to tin(II) concentration between the limit of quantitation (**LOQ,** 10σ) of 0.05 and 0.34 μg/mL over which a response curve was generated ($R^2 = 0.9981$, $n = 7$). The limit of detection (**LOD**) was calculated (3σ) at 0.01 μg/mL. Deviation between actual and measured concentrations varied from 0.014 μg/mL near the LOQ to 0.042 at 0.255 μg/mL.

Keywords: tin(II) quantification, spectrophotometric method, TMB, NBS, redox

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Tin(II) compounds are important in ^{99m}Tc radiopharmaceutical kits as stabilizing agents [1], in dental gels and food as preservatives [2–4], and in electroless plating as electrochemical catalysts [5–8]. Common methods to determine tin(II) are limited by some combination of the range and/or limit of detection, ease of application, reproducibility, and inability to distinguish tin(II) from tin(IV). A need to rapidly quantitate tin(II) concentration in an electroless plating sensitization solution at concentrations less than 0.3 μg/mL to evaluate its effectiveness motivated the development of the present colorimetric approach. A spectrophotometric approach was selected which complements the existing spectrophotometric methods for quantification of boron [9], vanadium(IV) [10], and mercury(II) [11].

Common methods for determining tin(II) concentration are summarized in Table 1. These methods are: electrochemistry [1–4, 12–19], membrane sensor [18], inductively coupled plasma–optical emission spectrometry (**ICP–OES**) [19], flame atomic absorption spectrometry (**FAAS**) [20], fluorescence [21], and spectrophotometry [22–29]. The electrochemical method, which includes anodic stripping voltammetry (**ASV**) [1–4, 12] and differential pulse polarography (**DPP**) [13–17], has been widely used because of selective determination of tin(II) in the presence of tin(IV). The ASV method has a low LOD. For example, a LOD equal to 0.00026 μg/mL was achieved by Hutton et al. by using the ASV method with a bismuth film electrode [3]. However, the limitation of the ASV method is that it requires either formation of a tin(II) complex such as a tin(II)–oxine [1] or a tin(II)–tropolone [2], or use of a modified electrode such as an epoxy-carbon electrode or the BiFE [3, 4, 12]. The DPP method does not require a tin(II) complex or a modified electrode but it is limited by the detection range and the LOD. Decristoforo et al. [14] reported a DPP method with a LOD of 0.005 μg/mL but the concentration range was from 10 to 15 μg/mL. Similarly, using the DPP method, Sebastian et al. [15] quantified tin(II) within the concentration range 0 to 10 μg/mL but the LOD was 0.5 μg/mL.

Recently published methods based on membrane sensor, ICP, FAAS, and fluorescence quenching improved the detection concentration range and the LOD, but the constraints in the methods limit their usage. The tin(II) selective potentiometric membrane sensor method was reported to have a concentration range of 0.013 to 1190 μg/mL and a low LOD of 0.0025 μg/mL, but preparation of the membrane electrode was work-intensive [18]. ICP–OES was used to

[1] The article is published in the original.

Table 1. Methods for determining tin(II)

Method	Principle	Concentration range, μg/mL	LOD, μg/mL	Conditions	Reference
Anodic stripping voltammetry	Tin(II)–8-hydroxyquinoline (oxine) complex	0.03–2.38[a]	0.012[a]	Acetate buffer, 0.01 M, pH 6	[1]
	Tin(II)–tropolone complex	0.03–2.38[a]	0.012[a]	Acetate buffer, 0.05 M, pH 5.5	[2]
	Bismuth film electrode (**BiFE**)	0.001–0.1	0.00026	Acetate buffer, 0.1 M, pH 4.5	[3]
	BiFE	0.01–0.15	0.00026	HCl and NH_4Cl, pH ~ 1.4	[4]
	Epoxy-carbon powder composite–8-hydroxyquinoline composite electrode	0.0006–0.119[b]	5.5×10^{-5} [b]	Acetate buffer, 0.1 M, pH 5.8	[9]
Differential pulse polarography	Static mercury drop electrode (**SMDE**)	10–15[c]	0.005[c]	Methanol and perchloric acid	[10]
	Dropping mercury electrode (**DME**)	0–5		0.7 M NaF, 0.1 M $NaNO_3$, and 0.1 M HEPES[e], pH 8.0	[11]
	Hanging mercury drop electrode	0–10[c]	0.5[c]	3 M H_2SO_4 and 3 M HCl	[12]
	SMDE	2.0–6.0	0.21	3 M H_2SO_4 and 3 M HCl	[13]
	DME	>0.1309[b]	0.06545[b]	0.1 M NaOH and 0.1 M KNO_3	[14]
Potentiometric membrane sensor	Polyvinyl chloride membrane electrode	0.013–1190[b]	0.002[b]	HCl and NaOH, pH 2.0–8.5	[15]
Inductively coupled plasma–optical emission spectrometry	Combine ICP–OES and solid phase extraction	0.0–0.200	0.0007	HCl, pH 2.0	[16]
Flame atomic absorption spectrometry	Combine FAAS and cloud point extraction	0.01–1.3	0.00286	NH_3/NH_4Cl buffer, pH 8.0	[17]
Quenching fluorescence	Tin(II) quenches fluorescence of carbon nano-dots	0–476[d]	0.043[d]	Water and pH 8 buffer	[18]
Spectrophotometry, iodine, 520 nm	Reduce iodine monochloride, ICl, to iodine	8–80		6 M HCl and carbon tetrachloride	[19]
Spectrophotometry, molybdenum-thiocyanate complex, 460 nm	Reduce molybdenum(VI) to molybdenum(V) and molybdenum(III)	0.5–5.0		3 M HCl	[20]
Spectrophotometry, iron(II)–ferrozine complex, 562 nm	Reduce iron(III) to iron(II)	0.2–3.2		1–1.5 M HCl	[21]
Spectrophotometry, triiodide ion (I_3^-), 350 nm	Reduce sodium periodate to iodine	0.91–3.33[f]	0.20[c]	Sodium acetate and glacial acetic acid, pH 2.2–4.7	[22]
Spectrophotometry, palladium(II)–tin(II) complex, 410 nm	Complex with palladium chloride	3.33–150		1.5 M HCl	[23]
Spectrophotometry, rhenium(IV)–SCN^- complex, 353 nm	Reduce rhenium(VII) to rhenium(IV)	1.6–6.4	0.2	3 M HCl	[24]
Spectrophotometry, tin(II)–DMPHBH complex, 430 nm	Complex with diacetylmonoxime *p*-hydroxybenzoylhydrazone (**DMPHBH**)	0.25–2.76	0.242	Ascobic acid, HCl and cetylpyridinium chloride	[25]
Spectrophotometry, pyrocatechol violet (**PCV**), 550 nm	Rate of complex reaction of tin(II) with PCV	0.10–1.80	0.03	Acetic acid-acetate buffer, 1.0 M, pH 4.0	[26]

[a] 1 μmol/L equals 0.119 μg/mL; [b] 1.00×10^{-6} M equals 0.119 μg/mL; [c] 1 ppm equals 1 μg/mL; [d] 1 mM equals 119 μg/mL; [e]HEPES represents N-2-hydroxyethylpiperazine-N'-2-ethane sulphonic acid; [f] the conversion is based on the total amount tin(II) added to the acetate buffer.

quantify trace amounts of tin(II) by separating tin(II) from tin(IV) with a biosorbent. However, recovery of tin(II) in solution was less than 90% [19]. Cloud point extraction (**CPE**) followed by FAAS is another method that can quantify tin(II and IV) in a low concentration range (0.01–1.3 μg/mL), but the CPE procedure is complicated (including pH and temperature adjustment, centrifugation, and cooling in an ice bath) [20]. Quenching the fluorescence of carbon nano-dots (C-dots) by tin(II) was found to enable detection of tin(II) concentrations between 0 to 476 μg/mL. However, synthesis of the C-dots with a specific size distribution was difficult to repeat [21].

Spectrophotometry is widely employed for the determination of tin(II) (Table 1). Linear correlation is observed between absorbance and concentration (Beer–Lambert law) [22–29]. However, existing spectrophotometric methods are limited by various constraints. Reducing iodine monochloride [21] or sodium periodate [25] to iodine and extracting iodine with chloroform is a toxic, insensitive (LOD = 0.20 μg/mL) method. Using complexes of molybdenum [23], ferrozine [24], palladium [26], and rhenium [27] is expensive, and these chemicals did not improve the LOD. Synthesized chemical diacetylmonoxime *p*-hydroxybenzoylhydrazone was reported to determine tin(II) concentration from 0.25 to 2.76 μg/mL, but synthesizing DMPHBH was time consuming and the LOD was high (0.24 μg/mL) [28]. A spectrophotometric method that showed improvement in both the concentration range and the LOD using the mean centering of ratio kinetic profiles was reported by Madrakian et al. [29]. This method was operated at a concentration range of 0.10 to 1.80 μg/mL and a LOD of 0.03 μg/mL. However, the detection concentration range and the LOD must be lowered in order to provide sensitivity competitive with the other methods.

The present work introduces a spectrophotometric method using TMB as a color indicator for quantitative measurement of tin(II) in aqueous solution. This approach follows a recent report by Jang and Roper [30] regarding a simple, rapid and accurate method for determining Au(I) using TMB. In that work, the absorption coefficient of the reagent was reported at 2.75×10^5 L/mol cm [30], 3 times higher than iron–ferrozine complex (5.56×10^4 L/(mol cm)) [24]. Reduction of the fully oxidized TMB (diimine) by tin herein resulted in a measurable, proportional decrease in absorption at 452 nm under selected conditions. A linear correlation between absorption and tin(II) concentration was generated in concentration range of 0.049 (LOQ) to 0.340 μg/mL. The LOD (which represented the sensitivity of the method) was calculated at 0.013 μg/mL (3σ) [1–3]. This new method allowed quantification of tin(II) without use of complexation agent, at a lower LOD and concentration range when compared with the other spectrophotometric methods. To date, the lowest published tin(II) LOD and concentration range with spectrophotometric methods had been 0.03 μg/mL and 0.10 to 1.80 μg/mL, respectively [29]. Sensitivity of the method introduced herein is comparable to the ASV method using tin(II) complexes as indicators, which reported an LOD at 0.012 μg/mL [1, 2]. Moreover, this new method is more sensitive than the novel quenching fluorescent of C-dots method, which reported an LOD at 0.043 μg/mL [21]. This method could be applied to quantify tin(II) concentration in a solution with tin(II) as the only reducing agent to reduce the diimine form of TMB.

EXPERIMENTAL

Apparatus. The light source was purchased from Avantes with a deuterium lamp (215–500 nm) and a halogen lamp (500–2500 nm) (Avalight-DH-S-BAL, Broomfield, CO, USA). The absorption across the spectral ranges 300 to 750 nm was measured using an USB4000-UV-vis from Ocean Optics (Detector range 200–1100 nm) (Dunedin, FL, USA). A pH meter (Orion model 920A, Manufacturer's reported pH measurement range: –2.00 to 19.99) with a tip (Orion 9156 BNWP, Thermo Scientific) was used to measure pH. A Branson Sonifier 250 from VWR scientific was used to dissolve TMB and NBS in deionized water.

Reagents. Sodium hydroxide (NaOH) (99.9%) was purchased from Mallinckrodt. Acetic acid (99.7%) was purchased from VWR. 3,3',5,5'-Tetramethylbenzidine dihydrochloride (TMB) (98.0%) was purchased from Electron Microscopy Sciences. N-bromosuccinimide (NBS) (99.0%) was purchased from Alfa Aesar. Anhydrous tin(II) chloride ($SnCl_2$) (99.99%) was purchased from Sigma-Aldrich. The NBS was recrystallized in 95°C water before it was used. The other chemicals were used as obtained.

Procedure. The spectrum of 1.9 mL acetate buffer (0.2 M, pH 4.3–4.5) in a 1 cm polystyrene cuvette was measured as a reference. A dark background was subtracted by blocking the light source. To the sample cuvette with 1.9 mL acetate buffer, 0.05 mL TMB (0.3 mM), 0.05 mL NBS (0.3 mM) and 0.09 mL of degassed, distilled, deionized water were added one by one in the order listed. The solution was mixed using a pipette to draw and release it. Finally, 0.01 mL of tin(II) 0.3 mM solution (0.170 μg/mL, in total volume of 2.1 mL) was added into the cuvette and the solution was mixed again using the pipette. Error could be introduced in making the standard 0.3 mM tin(II) solution by air oxidation of the in stored tin(II) chloride and the inaccuracy in the scale (about ±2.5%). The light source was blocked for 3 min by switching it off before the absorption data was recorded (TMB and NBS are sensitive to light). A detecting concentration range of 0.049 (the LOQ) to 0.340 μg/mL was achieved by adding a different amount of 0.3 mM tin(II) into a constant volume (2.1 mL) of the assay. The standard correlation curve was generated by repeating 7 individual

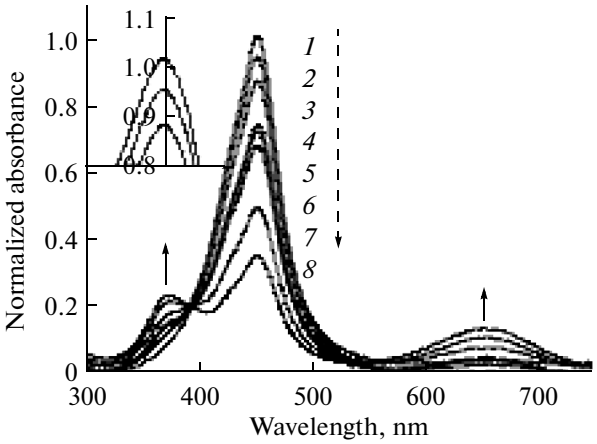

Fig. 1. Spectra change with increasing tin(II) concentration. Recorded 3 min after TMB and NBS were added to pH 4.4 acetate buffer, 25°C. The dashed arrow indicates the diimine absorption peak at 452 nm decreased. The solid arrows show the charge-transfer complex absorption peaks at 370 and 652 nm increased. Tin(II) concentration, μg/mL: *1* – 0, *2* – 0.034, *3* – 0.068, *4* – 0.102, *5* – 0.136, *6* – 0.17, *7* – 0.255, *8* – 0.34.

tests ($n = 7$). In each individual test, 7 different results (because of signal noise) were recorded by computer in 7 s. The error bar on the curve was calculated as the standard deviation from at least 49 data points. Measured absorption at 452 nm for each sample was normalized to the absorption value at 452 nm in 0 μg/mL tin(II) in each individual test. For example, Fig. 1 shows the absorption spectra of different tin(II) concentration in one standard test. The absorption unit (A.U.) in Fig. 1 was normalized to the highest absorption at 452 nm in 0 μg/mL (1.0 A.U.). Detailed procedures to make the standard correlation curve and to justify the method are described in Supporting Information. The normalized absorption was used in this experiment because it facilitated comparison between replicates with different baselines and supported evaluation of reproducibility.

RESULTS AND DISCUSSION

Mechanism. Using equal molar amounts of NBS and TMB to fully oxidize TMB to the two-electron oxidation product (diimine) yielded a yellow-brown solution with an absorption maximum of 452 nm (Fig. 2). The absorption at 452 nm decreased when the concentration of tin(II) increased, because the diimine was reduced to the blue charge transfer complex (Fig. 2). Based on the difference in redox potentials, NBS (>+1.83 V vs. normal hydrogen electrode, **NHE**) oxidized TMB (+0.22–0.7 V, NHE) to diimine [30] and tin(II) (+0.15 V vs. NHE) reduced the diimine to the charge transfer complex (Fig. 2, part A). The yellow color of equimolar TMB and NBS product (diimine) changed into the blue color of the charge transfer complex, when the tin(II) solution was added [30, 31]. Meanwhile the tin(II) was oxidized to tin(IV). Figure 2 (part B) shows the absorption spectra changed from the initial TMB spectra (peak at 285 nm) to the diimine spectra (peak at 452 nm), after the TMB was fully oxidized by NBS. By adding tin(II) to the diimine, a mixture spectra of the charge transfer complex (two new peaks at 370 and 652 nm) and the

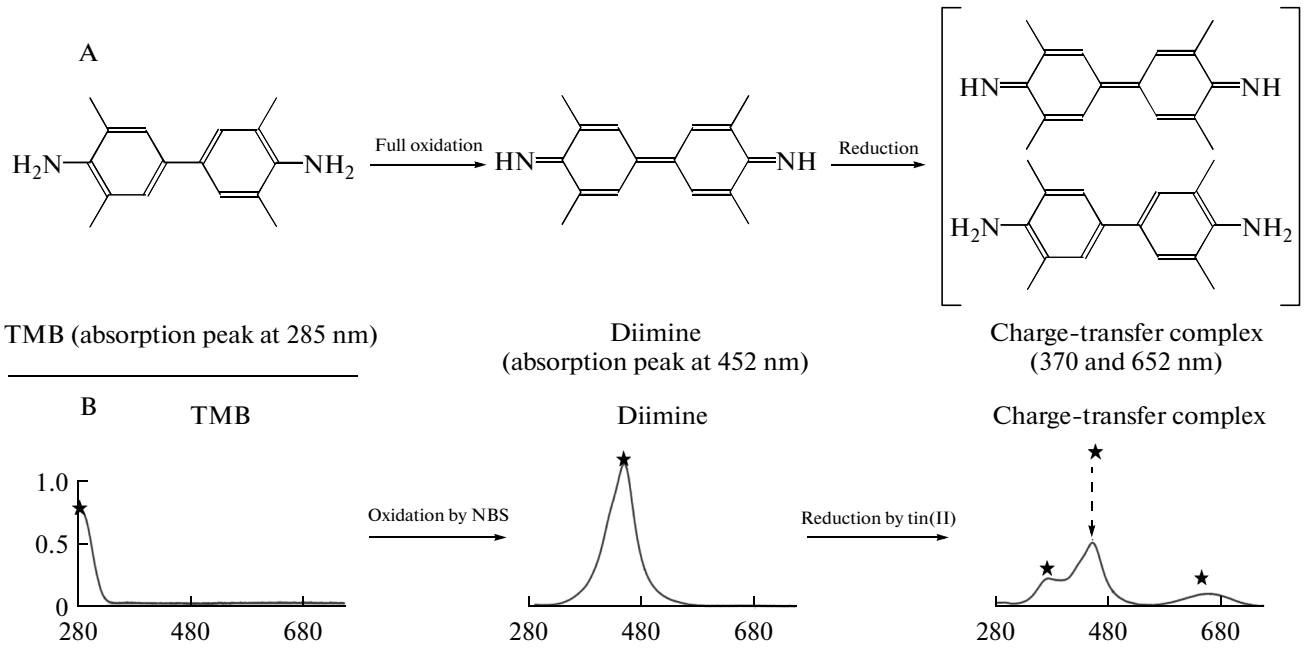

Fig. 2. TMB reactions. Tin(II) reduces diimine to charge-transfer complex.

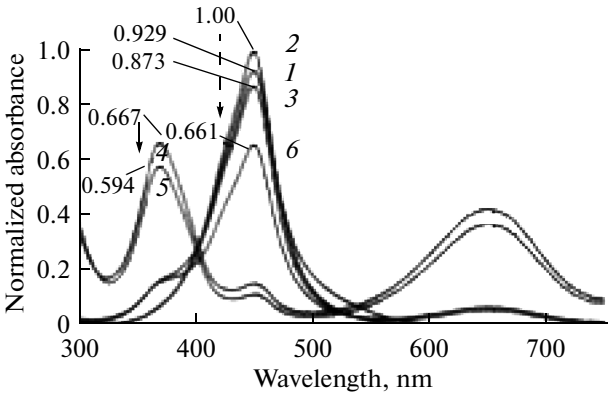

Fig. 3. TMB : NBS ratio and indicator peak selection. Recorded 3 min after the reagents were mixed in pH 4.4 acetate buffer, 25°C. TMB : NBS ratios (v/v, μL): *1* – 50 : 60, *2* – 50 : 50, *3* – 60 : 50, *4* – 150 : 50. Spectra after the addition of 10 μL 0.3 mM tin(II) (0.170 μg/mL in total volume) in TMB : NBS ratios of 150 : 50 (*5*) and 50 : 50 (*6*) were compared.

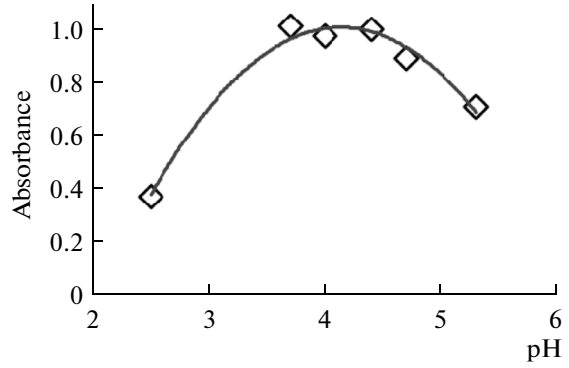

Fig. 4. Effect of acetate buffer pH on absorption. The absorbance at 452 nm was recorded 3 min after mixing equal moles of TMB and NBS at 25°C.

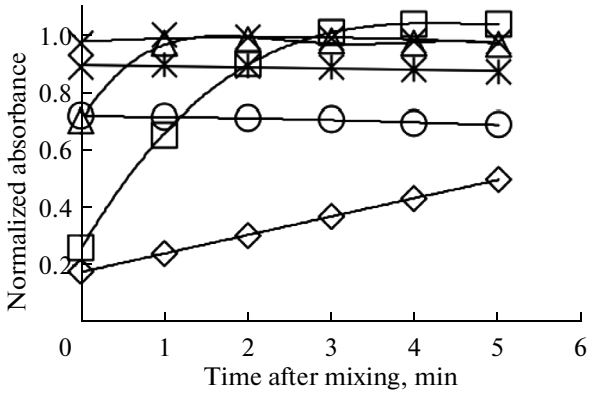

Fig. 5. Dynamics of absorbance change at 452 nm in acetate buffer with different pH at 25°C. Equal moles of TMB and NBS were used. pH: 2.5 (◇), 3.7 (□), 4.0 (△), 4.4 (×), 4.7 (✳), 5.3 (○).

diimine residue (peak at 452 nm) appeared. The absorption peak at 452 nm (diimine) decreased with tin(II) concentration, implying that the diimine was reduced by tin(II). On the other hand, the absorption peaks at 370 and 652 nm (the charge transfer complex form) increased with increasing tin(II) concentration, confirming that the diimine was reduced to the charge-transfer complex [31].

The optimum detection condition. *Selection of TMB/NBS ratio.* An equimolar mixture of TMB and NBS displayed the maximum absorption peak height at 452 nm. Either increasing or decreasing the relative amount of NBS or TMB decreased the corresponding maximum absorption. The spectra in Fig. 3 show that increasing NBS concentration broadened the peak at the bottom (500 nm), indicating degradation of the diimine. Increasing the TMB concentration led to two side peaks appearing at 370 and 652 nm, indicating the formation of the charge-transfer complex form from the diimine and the extra TMB. Increasing both the NBS and TMB concentrations could improve the upper limit of the concentration range beyond 0.34 μg/mL.

Selection of indicator peak. It was found that the absorption peak at 452 nm (diimine) was 3 times more sensitive to tin(II) than the absorption peak at 370 nm (charge-transfer complex). From Fig. 3, the absorption decrease at 452 nm (0.34 ± 0.04) was 3 times higher than at 370 nm (0.08). This indicated that the absorption peak at 452 nm was 3 times more sensitive than the peak at 370 nm.

Specification of pH using acetate buffer. An acetate buffer (0.2 M) with pH between 3.7 and 4.4 at 25°C generated the optimum absorption at 452 nm (0.976–1.013) after 3 min of mixing time. The error in the pH of the buffers was estimated at ±0.1 in this work. The reaction of NBS oxidizing TMB was sensitive to the solution pH value [30, 32, 33]. Figure 4 shows that the absorption was maximized between pH 3.7 and 4.4. At higher pH the diimine degraded, so the absorption at 452 nm decreased.

Mixing time selection. A stable absorption value at 452 nm was obtained by controlling the reaction time for 3 min in pH 4.4 ± 0.1 (acetate buffer, 25°C). Figure 5 illustrates the effect of reaction time on TMB redox reaction at different pH. The TMB redox reaction rate was increased when buffer's pH value increased. In a buffer with a higher pH than the TMB oxidation product, H^+ is readily scavenged in the buffer, which drives the reaction to the diimine side [31, 32]. Figure 5 shows that when the buffer pH was higher than 4.0 (pH 4.4, 4.7 and 5.3), the redox reaction finished immediately after mixing. The absorption-time response was not influenced by the addition of tin(II).

Standard calibration curve and error evaluation. Under the optimized conditions (equal moles of TMB and NBS, pH 4.4 ± 0.1, acetate buffer, absorption measurement at 452 nm after 3 min reaction), a standard calibration curve was generated (A = 1.9008 ×

Table 2. Method test with different amounts of tin(II)

Tin(II) concentration, μg/mL	Found, μg/mL		Deviation from the real value, μg/mL (the highest of the two tests)
	test 1	test 2	
0.017	0.015	0.031	0.014
0.085	0.081	0.103	0.018
0.153	0.160	0.190	0.037
0.187	0.184	0.208	0.021
0.255	0.275	0.293	0.038
0.323	0.318	0.342	0.019

tin(II) concentration + 0.9954, $R^2 = 0.9981$, $n = 7$). A decrease in the diimine absorption peak (452 nm) was used to measure the tin(II) concentration, because it proved 3 times more sensitive than the charge-transfer complex absorption peaks. The error evaluation on the *y*-axis was based on the 7 repetitions and 7 continuously monitored data points in each test. This included the method error, the operating error, and the system noise. The error evaluation on the *x*-axis was estimated from the weighing error and tin(II) oxidation in air. The last digit of the scale (0.1 mg) had a difference of ±0.05 mg. In experiments, typically 2.0 ± 0.05 mg tin(II) chloride was weighed. Three of the 7 tests used 20–23 mg tin(II) chloride to make a concentrated solution, and were diluted twice to make the standard 0.3 mM tin(II) solution. The 0 μg/mL tin(II) point absorption was repeated at least twice in each test. The standard deviation (σ) at 0 μg/mL tin(II) was determined at 0.0098 (A.U.), and the corresponding LOD was calculated (3σ) to be 0.013 μg/mL. The LOQ was calculated (10σ) to be 0.05 μg/mL.

Evaluation of method. This method was evaluated in duplicate by spiking different amounts of 0.3 mM $SnCl_2$ solution (1, 5, 9, 11, 15 and 19 μL) into 1.9 mL of pH 4.4 acetate buffer (25°C) with equimolar mixture of TMB and NBS (0.3 mM). Table 2 lists all the tested concentration results of the two tests and the actual tin(II) concentrations injected. The maximum deviations of the tested results from the actual concentrations were calculated. The maximum deviation was 0.038 μg/mL at tin(II) concentration of 0.255 μg/mL and the minimum deviation was 0.014 μg/mL at 0.017 μg/mL. The deviation was hypothesized to come from the standard tin(II) concentration difference and measurement method used.

* * *

A linear correlation curve of tin(II) concentration and absorption ($R^2 = 0.9981$, $n = 7$) in concentration range from 0.049 (LOQ) to 0.340 μg/mL was obtained by using TMB and NBS mixture as a spectra indicator. The detection conditions were optimized to obtain intensive, fast, and stable absorption at 452 nm. An equimolar mixture of TMB and NBS at 0.3 mM exhibited the maximum absorption at 452 nm. The 452 nm peak (diimine) was selected for detection because it was 3 times more intense than the peaks at 370 or 652 nm (charge-transfer complex). The pH of the acetate buffer and the reaction time were optimized to pH 4.4 at 25°C and 3 min, respectively. A lower LOQ (0.049 μg/mL) and more sensitive detection range (to 0.340 μg/mL) was obtained in this method when compared with the other spectrophotometric methods [22–29] (Table 1). Meanwhile the LOD was improved to 0.013 μg/mL relative to a recently published spectrophotometric value of 0.03 μg/mL [29]. The simplicity and sensitivity of this spectrophotometric method make it preferable to other published methods.

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