Kinetic-Spectrophotometric Determination of Tellurium (IV) by Its Catalytic Effect on the Reduction of Thionine by Sodium Sulfide in Cationic Micellar Medium

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KINETIC-SPECTROPHOTOMETRIC DETERMINATION OF TELLURIUM (IV) BY ITS CATALYTIC EFFECT ON THE REDUCTION OF THIONINE BY SODIUM SULFIDE IN CATIONIC MICELLAR MEDIUM

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A simple and highly sensitive method is proposed for the determination of Te(IV) by its catalytic effect on the reduction of thionine by sodium sulfide in the presence of cetyl trimethyl ammonium bromide as a micelle media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of thionine at 600 nm with a fixed time of 0.5–2.5 min from initiation of the reaction. Tellurium can be measured in the concentration range of 0.6–500.0 ng/mL, with a limit of detection of 0.3 ng/mL Te(IV). The influence of more than thirty potential interfering ions was studied on the determination of tellurium. The relative standard deviation for ten replicate measurements of 0.020 and 50.0 ng/mL Te(IV) was 2.1 and 1.9%, respectively. The method was applied for the determination of tellurium in synthetic samples.

Keywords: Tellurium; Catalytic; Sulfide-thionine; Spectrophotometry

INTRODUCTION

Tellurium is widely distributed in small amounts in the Earth's crust with the average abundance in crystal rocks of tellurium being reported as 0.001 µg/mL by weight. Tellurium used extensively in the electronics industry, and in metallurgy as an additive to steel and copper to provide mach inability [1]. In most inorganic materials and in biological samples, tellurium is found in very low concentrations [2]. Tellurium is less toxic than selenium, but tellurium compounds, such as hydrogen tellurides, are very toxic. Therefore, it is a potentially toxic environmental pollutant [3]. Hence sensitive, simple, and fast methods are required for monitoring tellurium concentrations. Although different methods have been used for the determination of tellurium, including spectrophotometric methods [4–8], hydride generation atomic fluorescence spectrometry [9,10], and stripping voltammetry [11,12]. The reported catalytic

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kinetic methods for the determination of Te(IV) are quite spare [13–15]. These kinetic methods have high limit of detection (> 50 ng/mL) and/or suffer from many interfering substances.

The proposed method is based on the catalytic effect of Te(IV) on the reduction of thionine by sulfide in the presence of cetyl trimethyl ammonium bromide (CTAB) as a micellar media. The reaction was monitored spectrophotometrically at 600 nm, The method is highly sensitive and rapid for Te(IV) determination.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade and used without further purification and doubly distilled water was used throughout.

Sodium sulfide stock solution (0.10 M) was prepared by dissolving 2.402 g $Na_2S \cdot 9H_2O$ (Merck) in water and diluted in a 100-mL volumetric flask. This solution was prepared daily and standardized iodometrically [16].

Cetyl trimethyl ammonium bromide stock solution, 0.013 M was prepared by dissolving 1.197 g CTAB (BDH) in water and diluted in a 250-mL volumetric flask.

Thionine stock solution, 1.0×10^{-3} M, was prepared by dissolving 0.0287 g thionine (Merck) in water and diluted in a 100-mL volumetric flask.

Tellurium (IV) stock solution, 1000 μg/mL, was prepared by dissolving 0.1246 g TeO_2 (Merck) in 0.10 M NaOH solution in a100-mL volumetric flask and standardized [16]. Working solutions were prepared by appropriate dilution with water.

Apparatus

The absorption spectra were recorded with a Shimadzu Model UV-210-spectrophotometer with a 1.0 cm quartz cell. A Model UV-120-01 spectrophotometer (Shimadzu) with 1.0 cm glass cuvettes was used to measure the absorbance at 600 nm. A thermostat water bath (Gallen Kamp, Griffin, BGL 240 V) was used to keep the reaction temperature at 35°C.

Recommended Procedure

All solutions were kept in a thermostat bath at 35°C for 30 min before initiation of the experiments. The reaction monitored spectrophotometrically at 600 nm for the first 0.5–2.5 min from initiation of the reaction. Into a 10-mL volumetric flask an appropriate amount of sample (containing up to 1000 ng of Te(IV)) was transferred. Then 1.0 mL of buffer (acetate, 0.10 M, pH = 4.0), 2.0 mL 0.013 M CTAB and 2.0 mL 1.0×10^{-1} M thionine solution was added. Then the solution was diluted to *ca.* 8 mL with water and 1.0 mL 2.5×10^{-3} M sodium sulfide was added to the mixture of the reaction. The solution was diluted to the mark with water and mixed well. A portion of the solution was transferred into the 1.0 cm glass cell and the decrease in absorbance was measured from 0.5 to 2.5 min from addition of last drop of sodium sulfide solution. This signal was labeled as ΔAs. The same procedure was repeated without addition of

Te(IV) solution to get the blank signal, and the signal was labeled as ΔAb. The calibration graph was constructed by plotting $\Delta As-\Delta Ab$ vs Te(IV) concentration.

RESULTS AND DISCUSSION

Thionine (TN) undergoes a reduction reaction with sulfide ion to form a colorless product at slow rate as the following reaction.
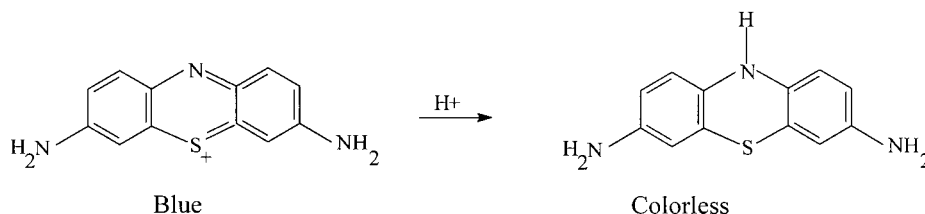
We found that this reaction rate is sharply increased by addition of trace amount of Te(IV) according to the following reaction, especially in the presence of CTAB as a micellar medium. The rate equation of the catalyzed reaction is:

$$\text{Rate} = -d\,[\text{TN}]/dt$$
$$= k[\text{Te(IV)}][\text{TN}]^m[\text{S}^{2-}]^n \tag{1}$$

where k is the rate constant. Because $[\text{S}^{2-}] > [\text{TN}]$, $[\text{S}^{2-}]$ can be considered to be constant and m was found to be 1. By integration of Eq. (1) and by incorporating Beer's law, we obtain the final expression:

$$\Delta A = k'[\text{Te(IV)}]t \tag{2}$$

where t is the reaction time.

There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 600 nm. Figure 1 shows the relationship between A and reaction time. It was found that the rate of reaction is proportional to the Te(IV) concentration. The reaction rate was monitored spectrophotometrically by measuring the decrease in absorbance of the characteristic band of thionine at 600 nm (Fig. 1). In many reactions, suitable micelles can affect the rate of reactions [17–19]. A micelle usually can be formed by aggregation of charged organic molecules. These micelles have the same charge at the outer sphere. For those reactions which have charge species, this micelles can affect the rate of reaction by increasing the effective collisions. In order to choose an appropriate micelle system to enhance the sensitivity (rate of reaction rate), one must take into account the type of charge of the reactants, because the accelerating effect of micelles arises essentially from electrostatic and hydrophobic interaction between the reactants and micellar surface [17]. Tellurium and sulfide are negatively charged, and thionine is
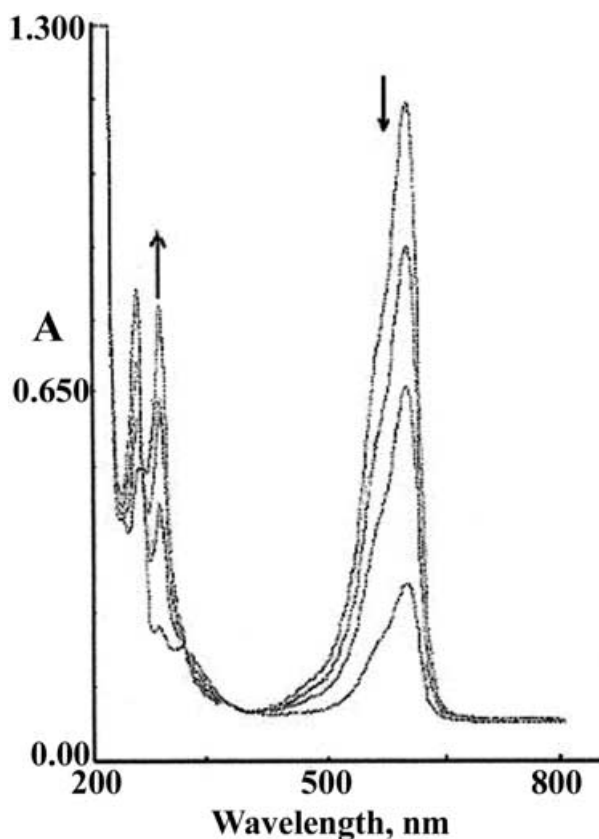
FIGURE 1   Variation of the thionine–S^{2-}–Te(IV) system with time. Conditions: pH, 4.0; thionine, 2.0×10^{-5} M; S^{2-}, 2.0×10^{-5} M; Te(IV), 100.0 ng/mL; CTAB, 0.0026 M; temperature, 30°C; interval time for each scan, 60 sec from initiation of the reaction.

TABLE I   Surfactant tested as potential micellar catalysts for the enhanced rate of Thionine–S^{2-}–Te(IV) reaction

Surfactant	Type	c.m.c. (M)	Micellar catalysis
Triton X-100	Nonionic	3.0×10^{-4}	Positive
SDS	Anionic	8.1×10^{-3}	Negative
CTAB	Cationic	1.3×10^{-3}	Positive
CPC	Cationic	1.2×10^{-4}	Positive

positively charged. Therefore, it seems logical to consider that the cationic micelles can enhance the rate of thionine–S^{2-}–Te(IV) reaction. Nonionic micelles (such as Triton X-100), anionic micelle (sodium dodecyl sulfate, SDS) and cationic micelle (CTAB), and cetyl pyridinium chloride (CPC)) were tested at concentration above their critical micelle concentrations (c.m.c.). The results obtained (Table I) confirmed that the presented assumption. Therefore, from cationic micelles, CTAB was selected for practical purposes.
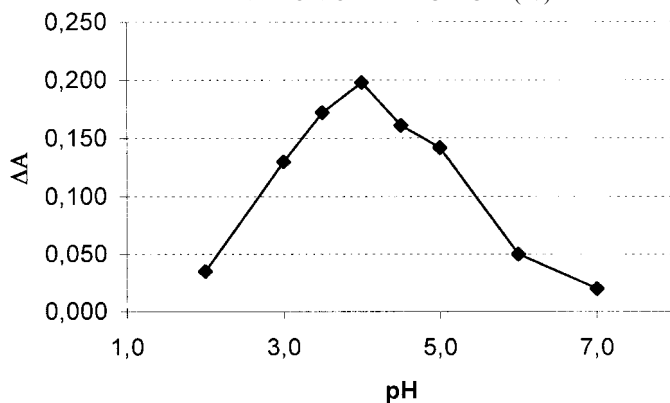
FIGURE 2 Influence of pH on the sensitivity. Conditions: $0.2\,\mu g/mL$ Te(IV), $0.0026\,M$ CTAB, $1.6 \times 10^{-5}\,M$ thionine and $4.0 \times 10^{-4}\,M$ sulfide at $30°C$.
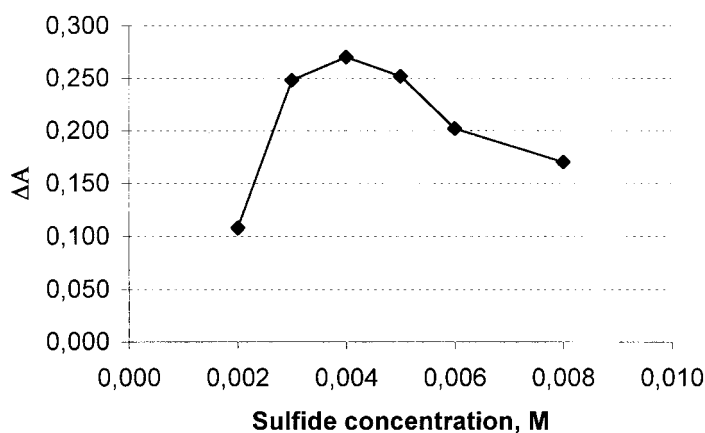

FIGURE 3 Effect of sulfide concentration on the sensitivity. Conditions: $0.2\,\mu g/mL$ Te(IV), $0.0026\,M$ CTAB, pH 4.0 and $1.6 \times 10^{-5}\,M$ thionine at $30°C$.

Influence of Variables

In order to optimize the reaction to get the best sensitivity the variables affect the sensitivity such as pH, thionine concentration, sulfide concentration, type of surfactants and their concentration and temperature on the rate of catalyzed reaction (with Te(IV) and unanalyzed reaction (without Te(IV)) was studied.

The influence of pH on the sensitivity was studied in the pH range of 2.0–7.0 with $0.2\,\mu g/mL$ Te(IV), $0.0026\,M$ CTAB, $1.6 \times 10^{-5}\,M$ thionine and $4.0 \times 10^{-4}\,M$ sulfide at $30°C$. Figure 2 shows that the net reaction rate increases with pH up to pH 4.0, whereas higher pH values cause decrease in the sensitivity. This is due to the fact that by increasing pH values (pH > 4.0) the blank reaction rate (without Te(IV)) goes to a greater extent than the catalyzed reaction. Therefore, pH of 4.0 (acetate, 0.1 M) was selected for the study.

The effect of sulfide concentration on the sensitivity was studied in the concentration range of 1.3×10^{-4} to $5.2 \times 10^{-4}\,M$ in the presence of $0.2\,\mu g/mL$ Te(IV), $0.0026\,M$ CTAB, pH 4.0 and $1.6 \times 10^{-5}\,M$ thionine at $30°C$ (Fig. 3). The results show that by
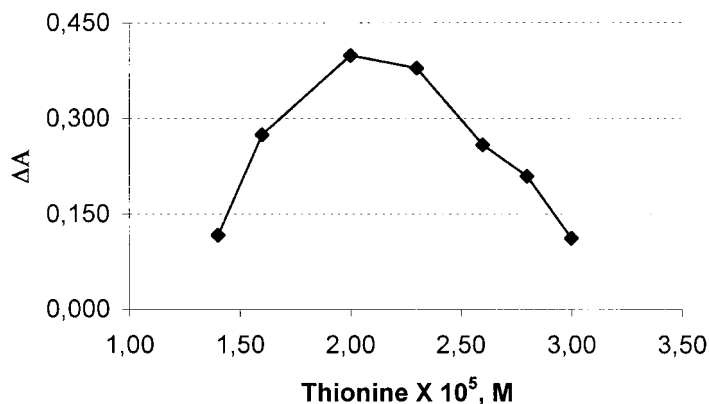
FIGURE 4   Influence of thionine concentration on the sensitivity. Conditions: $0.20\,\mu g/mL$ Te(IV), $2.5 \times 10^{-4}\,M$ sulfide ion pH 4.0 and 0.0026 M CTAB at 30°C.
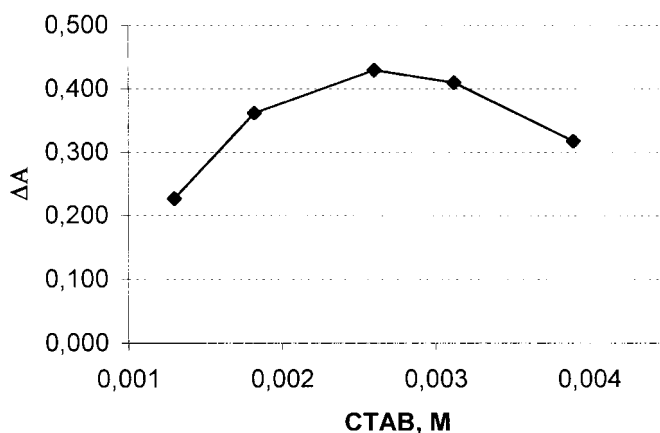

FIGURE 5   Influence of CTAB concentration on the reaction rate. Conditions: with the optimum reagents concentration and pH at 30°C.

increasing sulfide concentration to $2.5 \times 10^{-4}\,M$, the net reaction rate increases whereas, greater amounts of sulfide concentration decreased the sensitivity. This is due to the fact that the uncatalyzed reaction rate increases with sulfide concentration to a greater extent than the catalyzed reaction in higher sulfide concentration ($> 2.5 \times 10^{-4}\,M$). Therefore, $2.5 \times 10^{-4}\,M$ sulfide was selected as the best sulfide concentration.

Figure 4 shows the influence of thionine concentration on the sensitivity, for the range of 1.4×10^{-5} to $3.0 \times 10^{-5}\,M$, in the presence of $0.20\,\mu g/mL$ Te(IV), $2.5 \times 10^{-4}\,M$ sulfide ion, pH 4.0, and 0.0026 M CTAB at 30°C. The results show that by increasing thionine concentration up to $2.0 \times 10^{-5}\,M$, the net reaction rate (sensitivity) increases whereas, greater amount of the dye cause decreasing sensitivity. This is due to the aggregation of the dye in higher concentrations.

The influence of CTAB concentration on the reaction rate was studied in the range of 1.3×10^{-3} to $3.9 \times 10^{-3}\,M$ with the optimum reagents concentration and pH = 4.0 at 30°C. The sensitivity increased by increasing the CTAB concentration up to $2.6 \times 10^{-3}\,M$ and decreased at higher concentration values (Fig. 5). Therefore a find concentration of $2.6 \times 10^{-3}\,M$ was selected as the optimum CTAB concentration.

The effect of temperature on the sensitivity was studied in the range of 15–45°C with the optimum reagents concentrations and pH 4.0. The results showed that by increasing temperature up to 35°C, the net reaction rate increases, whereas higher temperature values because decreasing the net reaction. This means that at higher temperature values, the uncatalyzed reaction rate goes to faster rate. Therefore, 35°C was selected for further study.

Calibration Graph, Precision and Limit of Detection

Under the optimum conditions described above, with a fixed time of 0.5–2.5 min from initiation of the reaction, a linear calibration graph was obtained for Te(IV) in the concentration range of 0.6–0.100 µg/mL with the regression equation of $\Delta A = 0.105 + 3.015 C_{Te(IV)}$ with a correlation coefficient of 0.9999, where $C_{Te(IV)}$ is the concentration of Te(IV) in µg/mL, and ΔA is the change in absorbance for the catalyzed reaction.

The limit of detection, defined as $signal_{LOD} = \Delta A + 3s$ (where ΔA is average of the absorbance change for the blank solution for ten replicate determinations and s is its standard deviation), was equal to 0.3 ng/mL Te(IV).

The relative standard deviation of 0.02, 0.05 and 0.10 µg/mL of Te(IV) was 2.1, 1.9 and 1.4%, respectively.

Interference Study

In order to assess the application of the proposed method to synthetic samples, the influence of various ions on the determination of 0.10 µg/mL Te(IV) were studied. The tolerance limit was defined as the concentration of added ion causing a relative error less than 3%. The results are summarized in Table II. Many ions did not interfere, even when present in 100–1000-fold excess over tellurium. The results show that the method is relatively selective for tellurium determination.

Sample Analysis

In order to evaluate the applicability of the proposed method, synthetic samples were analyzed to determine Te(IV). The results are presented in Table III. The good recoveries with a precision of the results showing good reproducibility and accuracy of the method.

TABLE II   Effect of foreign ions on the determinations of 0.10 µg/mL Te(IV)

Species	Tolerance limit $(W_{ion}/W_{Te(IV)})$
Tartarate, SO_4^{2-}, Cl^-, $H_2PO_4^-$, Na^+, K^+, Li^+, Rb^+, NH_4^+	1000
ClO_3^-, SO_3^{2-}, Br^-, Mg^{2+}, Ca^{2+}, Co(II)	500
$S_2O_3^{2-}$	200
BrO_3^-, CH_3COO^-, Ba^{2+}, Mn(II)	100
I^-, Ce(III), Zn(II), Al(III), Ti(III), Mo(VI)	50
IO_3^-	10
$S_2O_8^{2-}$, Mg(II), Cu(II), Hg(I), Se(IV)	5

TABLE III   Determination of Te(IV) added to water samples

Sample	Te(IV) added (ng/mL)	Te(IV) found (ng/mL)	Recovery %
Well water	–	Not determined	–
	20.0	19.1 ± 1.3	95.5
	40.0	40.8 ± 1.7	102.0
Zayandeh Roud river water	–	Not determined	–
	10.0	9.7 ± 0.5	97.0
	20.0	20.5 ± 1.2	102.5
Tap water	–	Not determined	–
	10.0	10.2 ± 0.8	102.0
	20.0	19.7 ± 1.1	98.5

CONCLUSION

The kinetic–spectrophotometric method developed for tellurium(IV) in environmental samples such as river and tap water is inexpensive and readily available and allows rapid determination at low operating costs and shows simplicity, adequate selectivity, low limit of detection and very good precision and accuracy, relation to the other kinetic procedures.

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