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Kinetic-Catalytic-Spectrophotometric Determination of Trace Amounts of Tellurium(IV) by its Catalytic Effect on the Reduction of Brilliant Cresyl Blue with Sodium Sulfide in Cationic Micellar Medium

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A simple and sensitive kinetic-spectrophotometric method is proposed for the determination of ultra trace amounts of tellurium(IV). It is based on the catalytic effect of Te(IV) on the reduction of brilliant cresyl blue by sodium sulfide in presence of cetyl trimethylammonium bromide as a micellar media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of brilliant cresyl blue at 635 nm for 0.5–2.0 min from initiation of the reaction. Calibration curve is linear over the concentration range of 0.004–0.200 and 0.20–1.00 μg/mL of Te(IV) with a detection limit of 0.6 ng/mL. The relative standard deviation for ten replicates determination of 0.040 and 0.100 μg/mL Te(IV) was 0.8 and 1.2%, respectively. The method was applied for the determination of tellurium in synthetic samples.

Key Words: Tellurium(IV), Brilliant cresyl blue, Micellar media.

INTRODUCTION

In most inorganic materials and in biological samples, tellurium is found in very low concentration. Tellurium is used extensively in the electronics industry, and in metallurgy as an additive to steel and copper to provide mach inability[1, 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. Hence a sensitive, simple and fast method is required for monitoring tellurium concentration. 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 kinetic methods for the determination of Te(IV) are quite spare[13–15]. However, none of the above methods have a good selectivity for tellurium determination and a relatively large number of ions interfere with the determination of tellurium and/or these methods are not sensitive to determine less than 50

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ng/mL of Te(IV). The present method is based on the catalytic effect of Te(IV) on the reduction of brilliant cresyl blue by sulfide in the presence of cetyl trimethylammonium bromide (CTAB) as a micellar medium. The reaction was monitored spectrophotometrically at 635 nm by measuring the decrease in absorbance of the reaction mixture for the first 0.5–2.0 min from initiation of the reaction.

EXPERIMENTAL

All chemicals used were of analytical reagents 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 trimethylammonium bromide stock solution (0.013 M) was prepared by dissolving 1.197 g of CTAB (BDH) in a 250 mL volumetric flask. Brilliant cresyl blue stock solution, 1.56×10^{-3} M, was prepared by dissolving 0.052 g of brilliant cresyl blue (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 a 100 mL volumetric flask and standardized[16]. Working solutions were prepared by appropriate dilution with water.

The absorption spectra were recorded with a Shimadzu, Model UV-210 spectrophotometer with 1.0 cm quartz cells. A model UV-120-01 spectrophotometer (Shimadzu) with a 1.0 cm glass cuvette was used to measure the absorbance changes at 635 run. A thermostat water batch (Fateh Electronic) was used to keep the reaction temperature at 30°C.

Recommended procedure: All solutions were kept in a thermostat bath at 30°C for 30 min before initiation of the experiment. The reaction was monitored spectrophotometrically at 635 nm for the first 0.5–2 min from initiation of the reaction. Into a 10 mL volumetric flask an appropriate amount of sample was transferred. Then 2.0 mL of buffer (pH = 6.8 Briton Rabinson buffer), 2.0 mL 0.013 M CTAB and 1.0 mL of 1.56×10^{-3} M brilliant cresyl blue solution was added. Then the solution was diluted to *ca.* 8 mL with water and 1.0 mL of 0.020 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 a cell and the decrease in absorbance was measured from 0.5 to 2.0 min from addition of last drop of sodium sulfide solution. This signal was labelled as ΔA_S. The same procedure was repeated without addition of Te(IV) solution to get the blank signal, and the signal was labelled as ΔA_b. The calibration graph was constructed by plotting $\Delta A_S - \Delta A_b$ *vs.* Te(IV) concentration.

For determination of higher concentration of tellurium (0.20–1.00 μg/mL), the above procedure was repeated with brilliant cresyl blue and sulfide final concentration of 3.1×10^{-4} M and 1.2×10^{-3} M, respectively.

RESULTS AND DISCUSSION

Brilliant cresyl blue undergoes a reduction reaction with sulfide ion to form a colourless product at slow rate. It is noted that this reaction rate is sharply increased by addition of trace amount of Te(IV), especially in the presence of CTAB as a micellar medium. The rate equation of the catalyzed reaction is:

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

where k is the rate constant. Because $[S^{-2}] > [BCB]$, $[S^{-2}]$ 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 as:

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

where t is the reaction time. There are many methods, such as fixed-time, initial rate method and variable time method, for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simple, involving the measurement of ΔA at 635 nm. 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 brilliant cresyl blue at 635 nm (Fig. 1). In many reactions, suitable

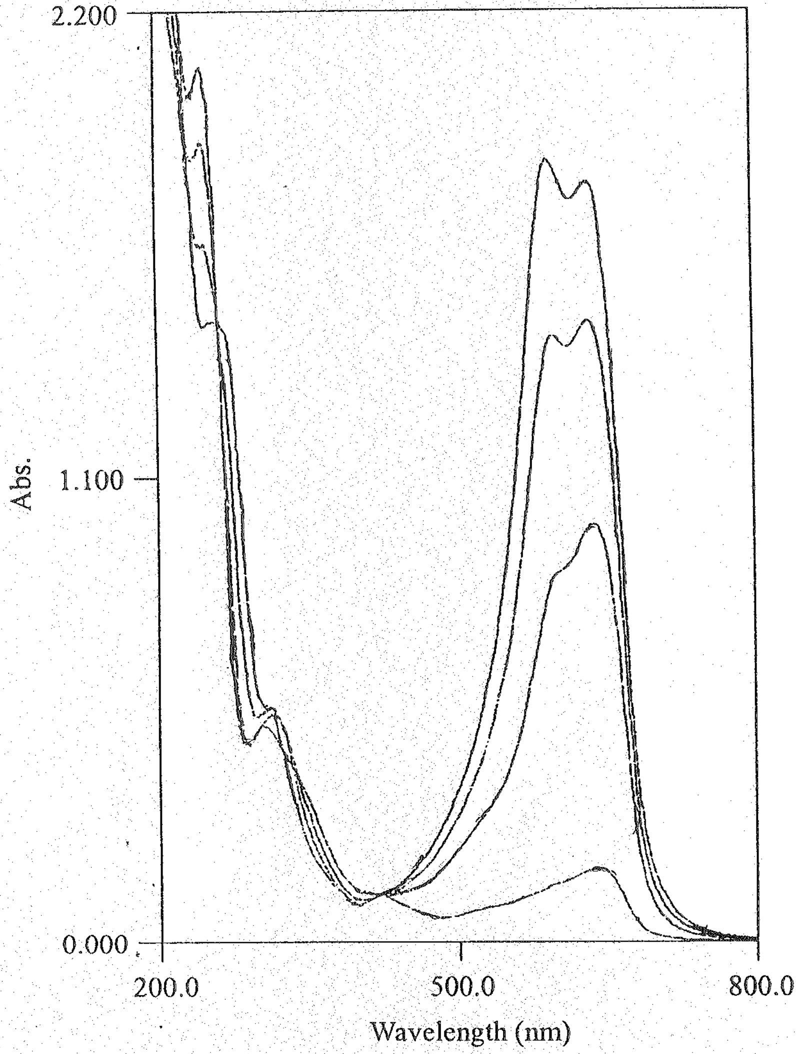

Fig. 1. Variation of the system brilliant cresyl blue-S^{2}–Te(IV) with time (condition: 0.20 µg/mL Te(IV), 2.0×10^{-3} M sulfide ion, pH 6.8, BCB 1.56×10^{-4} M, 2.6×10^{-3} M CTAB at 30°C, interval time for each scan 90 s from initiation of the reaction

micelles can affect the rate of reaction[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 that reaction which has charge species, these micelles can affect the rate of reaction by increasing the effective collisions. In order to choose an appropriate micelle system to enhance the sensitivity, one must take into account the type of charge of the reactants, because the accelerating effect of micelles arises essentially from electrostatic and hydrophobic interactions between the reactants and micellar surface[17]. It seems logically to consider that the cationic micelles can enhance the rate of BCB-S^{2-}-Te(IV) reaction. For this purpose, non-ionic micelles (such as Triton X-100), anionic micelle (such as sodium dodecyl sulfate, SDS) and cationic micelle (such as CTAB and cetyl pyridinium chloride (CPC)) were tested at concentrations above their critical micelle concentration (CMC). Tellurium and sulfide are negatively charged and brilliant cresyl blue is positively charged. Therefore, it seems logical to consider that the cationic micelles can enhance the rate of BCB-S^{2-}-Te(IV) reaction. Nonionic micelles (such as Triton X-100), anionic micelle (sodium dodecyl sulfate, SDS), cationic micelle (CTAB) and cetyl pyridinium chloride (CPC) were tested at concentrations above their critical micelle concentration (CMC). The results obtained (Table-1) confirmed the presented assumption. Therefore, from cationic micelles, CTAB was selected for practical purposes.

TABLE-1
SURFACTANT TESTED AS POTENTIAL MICELLAR CATALYSTS FOR THE ENHANCED RATE OF BCB-S^{-2}-Te(IV) REACTION

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

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

Influence of variables on sensitivity: The influence of pH on sensitivity was studied in the pH range of 4.0–8.0 with 0.20 μg/mL Te(IV), 0.0026 M CTAB, 3.1×10^{-3} M BCB and 2.0×10^{-3} M sulfide at 30°C. Fig. 1 shows that the net reaction rate increases with increasing pH up to 6.8, whereas higher pH values cause decrease in sensitivity. This is due to the fact that by increasing pH values (pH6.8) the blank reaction rate (without Te(IV)) goes to a greater extent than the catalyzed reaction. Therefore, a pH of 6.8 was selected for the study.

The effect of sulfide concentration on the sensitivity was studied in the concentration range of 4.0×10^{-4}–3.2×10^{-3} M in the presence of 0.20 μg/mL Te(IV), 2.6×10^{-3} CTAB, pH 6.8 and 9.4×10^{-5} M brilliant cresyl blue at 30°C (Fig. 2). The results showed that by increasing sulfide concentration to

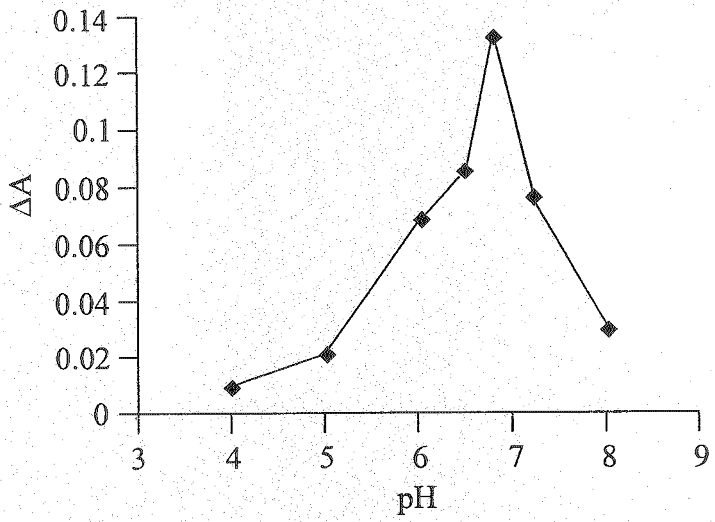

Fig. 2. Influence of pH on the sensitivity; Conditions: 0.20 μg/mL Te(IV); 2.6×10^{-3} M CTAB, 9.36×10^{-5} M brilliant cresyl blue and 2.0×10^{-3} M sulfide at 30°C

2.0×10^{-3} M, the net reaction rate increases, whereas greater amounts of sulfide concentration decrease the sensitivity. This is due to the fact that the unanalyzed reaction rate increases with sulfide concentration to a greater extent than the catalyzed reaction in higher sulfide concentrations ($> 2.0 \times 10^{-3}$ M). Therefore, 2.0×10^{-3} M sulfide was selected as the best sulfide concentration.

Fig. 3 shows the influence of brilliant cresyl blue concentration on the sensitivity for the range of 3.1×10^{-5}–2.5×10^{-4} M, in the presence of 0.20 μg/mL Te(IV), 2.0×10^{-3} M sulfide ion, pH of 6.8 and 2.6×10^{-3} M CTAB at 30°C. The results show that by increasing Brilliant cresyl blue concentration up to 1.56×10^{-4} M, the net reaction rate (sensitivity) increases, whereas greater

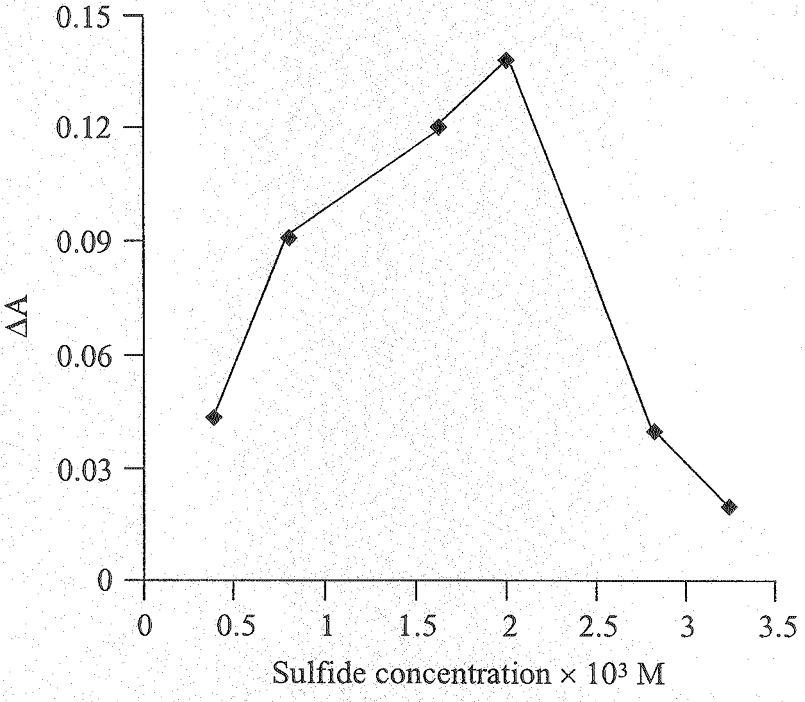

Fig. 3. Effect of sulfide concentration on the sensitivity; Conditions: 0.20 μg/mL Te(IV); 2.6×10^{-3} M CTAB, pH, 6.8 and 9.36×10^{-5} M brilliant cresyl blue at 30°C.

amount of the dye causes decrease in the sensitivity. This is due to the aggregation of the dye in higher concentration.

The influence of CTAB concentration on the reaction rate was studied in the range of 1.3×10^{-3}–3.9×10^{-3} M with the optimum reagents concentration pH of 6.8 and in the presence of 0.20 µg/mL Te(IV) at 30°C. The results showed that the sensitivity increased by increasing the CTAB concentration up to 2.6×10^{-3} M and decreased at higher concentration values (Fig. 4). Therefore a final concentration of 26×10^{-3} M was selected as the optimum CTAB concentration.

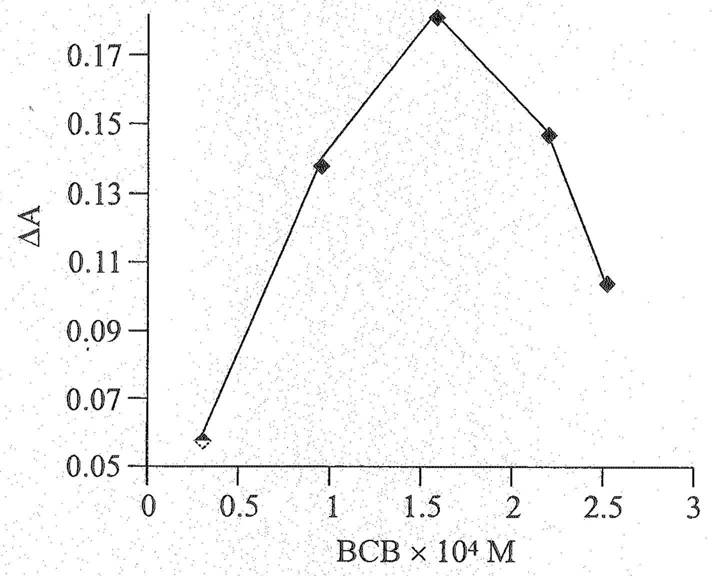

Fig. 4. Influence of brilliant cresyl blue concentration on the sensitivity; Conditions: 0.20 µg/mL Te(IV); 2×10^{-3} M sulfide ion; pH 6.8; and 2.6×10^{-3} M CTAB at 30°C

The effect of temperature on the sensitivity was studied in the range of 15–45°C with the optimum reagents concentrations and pH 6.8. The results show that by increasing temperature up to 30°C the net reaction rate increases, whereas

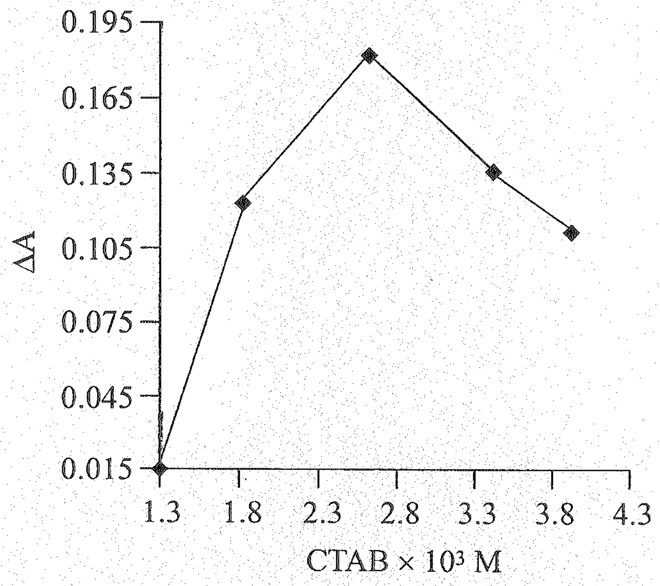

Fig. 5. Influence of CTAB concentration on the sensitivity; Conditions: 0.20 µg/mL Te(IV), 2.0×10^{-3} M sulfide ion; pH 6.8; BCB, 1.56×10^{-4} M at 30°C

higher temperature values cause decreasing the net reaction. This means that at higher temperature values, the unanalyzed reaction rate goes to a faster rate than the catalyzed reaction. Therefore, 35°C was selected for further study.

Analytical parameters: Under the optimum conditions described above the fixed-time method was applied to measure the change in absorbance over an interval time of 0.5–2.0 min from initiation of the reaction, because of its sensitivity and reproducibility. The calibration graph was linear for Te(IV) concentration in the range of 0.004–0.200 μg/mL with the regression equation: $\Delta A = 0.659 + 0.819C_{Te(iv)}$ with $r = 0.9998$ ($n = 10$) and in the range 0.20–1.00 μg/mL Te(IV) with regression equation of $\Delta A = 0.600 + 0.774C_{Te(IV)}$ with $r = 0.9996$, where ΔA is the change in absorbance for the sample reaction for 0.5–2.0 min from initiation of the reaction (catalytic reaction) and C is Te(IV) concentration in μg/mL.

The limit of detection (equal to the average blank signal plus three times of its standard deviation) is equal to 0.6 ng/mL Te(IV).

The relative standard deviation for ten replicates determinations of 0.040 and 0.10 μg/mL Te(IV) is 0.8 and 1.2%, respectively.

Interference study: In order to assess the application of the proposed method, the influence of different ions on the determination of 0.20 μg/mL Te(IV) was studied. The tolerance limit was defined as the concentration of added ions causing a relative error less than 3%. The results are summarized in Table-2, showing that many ions did not interfere even present in 100–1000 fold excess over tellurium concentration. The results showed that the method is relatively selective for tellurium determination.

TABLE-2
EFFECT OF FOREIGN IONS ON THE DETERMINATION
OF 0.20 μg/mL Te^{4+}

Species	Tolerance limit (μg/mL)
Na^+, K^+, Rb^+, Li^+, NH_4^+, Ba^{2+}, Br^-, Cl^-, CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, CH_3COO^-, Tartarate	1000
$S_2O_3^{2-}$, Mg^{2+}, Ca^{2+}	500
Mn^{2+}, Ti^{3+}, Al^{3+}, Mo^{6+}	100
CN^-, Cr^{3+}	50
SO_3^{2-}, Ce^{3+}	20
$S_2O_8^{2-}$, Fe^{3+}	5
Ag^+, Hg^{2+}, Pb^{2+}, Se^{4-}	1

Sample Analysis: In order to evaluate the applicability of the proposed method, real samples such as river water, tap water and well water were analyzed to determine Te^{4+}. The results are given in Table-3. The results showed good recovery and accuracy of the method.

TABLE-3
DETERMINATION OF Te^{4+} ADDED TO WATER SAMPLES

Sample	Te^{4+} added (ng/mL)	Te^{4+} found (ng/mL)	Recovery (%)
Well water	—	< detection limit	—
Well water	20.0	20.2	101.0
Well water	30.0	29.6	98.6
River water*	—	< detection limit	—
River water	30.0	29.3	97.6
River water	40.0	39.6	99.0
Tap water	—	< detection limit	—
Tap water	20.0	19.8	99.0
Tap water	40.0	41.0	102.5

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Conclusion

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

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