

CATALYTIC SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF TELLURIUM(IV)

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ABSTRACT : *A simple, rapid and sensitive method has been developed for determination of traces of tellurium(VI) (0.096–1.250 µg/mL) based on its catalytic effect on the reduction reaction of toluidine blue by sulfide ion at pH 4. The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of the dyestuff at 628 nm by the fixed time method. The detection limit is 80 ng/mL and the relative standard deviation for 1 µg/mL tellurium is 2.2%.*

KEY WORDS : *Tellurium(IV), Determination, Catalytic effect, Toluidine blue, Spectrophotometry.*

INTRODUCTION :

Because of the increasing use of tellurium in electronic industries and semiconductor technology [1,2], its determination in trace levels is of special interest. Furthermore, since tellurium and selenium have similar chemical and analytical properties and usually occur together, determination of tellurium in the presence of selenium is also an important task [3]. Although numerous methods have been developed for the spectrophotometric determination of tellurium(IV) in the literature [3-14] the reported kinetic methods for this purpose are quite sparse [15]. Despite the need for rigid control of experimental parameters in

the kinetic catalytic methods, they have shown very promising features for the determination of metal ions in ultratrace levels [16]. These methods have the advantage of high sensitivity combined with the simplicity of procedure and, consequently, low cost.

We have recently reported a spectrophotometric method for the determination of trace amounts of selenium(IV) based on catalytic reduction of toluidine blue by sulfide ion in neutral solutions [17]. In this paper we report a simple, rapid and sensitive method for the spectrophotometric determination of traces of tellurium(IV) based on its catalysis of the

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reduction reaction of toluidine blue by sulfide at pH 4 and 25°C.

EXPERIMENTAL :

Reagents

All chemicals used were of analytical reagent grade and used without further purification except for vacuum drying over P_2O_5 . Triply distilled deionized water was used throughout this work.

Tellurium(IV) stock standard solution (1000 μ g/mL) was prepared by dissolving 0.1246g TeO_2 (Merck) in 3M HCl and diluting it to 100mL in a volumetric flask and standardized [18]. Working solutions were prepared by appropriate dilution with water.

Sodium sulfide stock solution (1000 μ g/mL) was prepared by dissolving 0.7500g $Na_2S \cdot 9H_2O$ (Hopkin and Williams) in water and diluting it to 100mL in a volumetric flask. This solution was prepared daily and standardized iodometrically [18].

Toluidine blue stock solution (500 μ g/mL) was prepared by dissolving the dyestuff (Merck, Darmstadt, Germany) in water.

Apparatus

A Perkin Elmer Lambda 5 UV-Vis spectrophotometer equipped with a thermostated cell holder was used for recording spectra and absorbance measurements. Measurement of pH was made using a Corning 125 pH-meter. A Julabo-U3 thermostated water bath was used. The glassware used was scrupulously cleaned to eliminate any traces of ions from the glass surface. The cells were cleaned after use by immersion in nitric acid for 10 min to remove traces of ions adsorbed on their walls.

Procedure

The catalysed reaction was monitored spectrophotometrically by measuring the change in absorbance at 628 nm. An appropriate amount of sample containing 0.96 to 12.5 μ g of tellurium(IV) was transferred into a 10mL flask. Then 1mL of 50 μ g/mL sulfide, 2mL of citrate

buffer solution (pH 4) and enough water for diluting the solution to ca. 9mL were added. The solution was kept in water bath at 25°C for 10 min. Then 1mL of 50 μ g/mL toluidine blue at the same temperature was added and time was measured just after addition of the dyestuff. A portion of solution was transferred into a 1mL glass cell within 30 seconds for the absorbance measurements. The decrease in absorbance during a time period of 3 min was then measured.

RESULTS AND DISCUSSION :

Toluidine blue undergoes a reduction reaction with sulfide ion to form a colorless product [17]. Preliminary experiments showed that this reaction is very slow in acidic solutions, but is sharply increased by addition of trace amounts of tellurium (Fig. 1). At constant concentration of toluidine blue and sulfide, it was found that the rate of reaction is proportional to the tellurium(IV) concentration. Maximum absorbance of the dyestuff occurs at 628nm and its

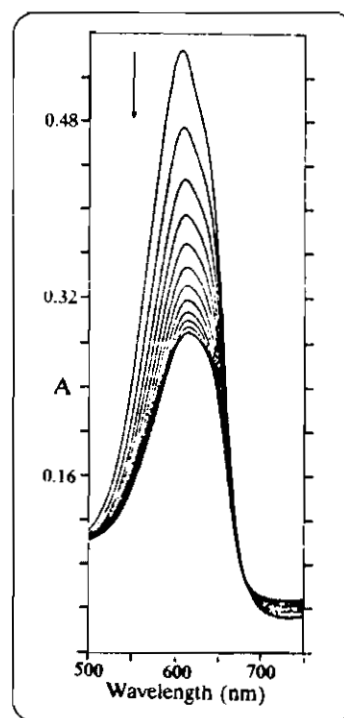


Fig. 1: Absorption spectra of 10 μ g/mL toluidine blue in the presence of 5 μ g/mL sulfide and 1 μ g/mL tellurium(IV) at pH 4. Time intervals, 55s.

reduced form is colorless. In this study, tellurium(IV) was determined using the fixed time method in which the decrease in absorbance of toluidine blue, ΔA , during a fixed period of time was measured for various amounts of tellurium. The calibration graph was constructed by plotting ΔA against tellurium(IV) concentration.

Effect of Variables

The rate of both catalysed and uncatalysed reactions was found to increase by increasing temperature (in the range of 15-40°C). A temperature of 25°C was used as the most suitable.

As pointed out elsewhere [17], in neutral solutions selenium(IV) has a pronounced catalytic effect on the reduction reaction of toluidine blue by sulfide, while tellurium(IV) can not catalyze the reaction at all. However, in acidic solution we noticed an opposite catalytic behavior; the presence of tellurium(IV) enhances the rate of the reduction reaction, while selenium(IV) is not a suitable catalyst for the reaction any more (Fig. 2). Thus, the variation of reaction rate with pH was studied over the range 1.1-6.7. Fig. 3 shows the results obtained in the presence and absence of tellurium. The maximum range of catalysed reaction does not depend on pH in the range 4.0-5.2. A pH of 4 (maintained by citrate buffer) was chosen because it leads to the largest difference between the sample and blank solutions.

The influence of several buffer solutions at

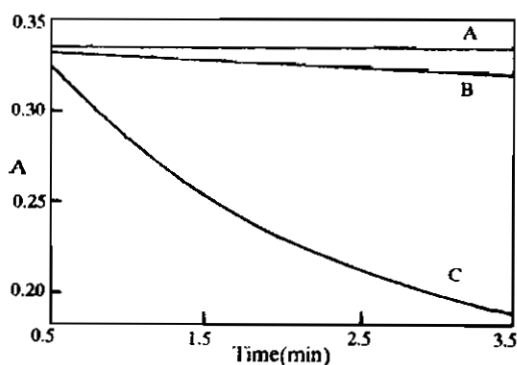


Fig. 2: Absorbance vs. time, 5 µg/mL toluidine blue-sulfide system in the absence and presence of 1 µg/mL catalyst at pH 4; A, uncatalysed; B, selenium(IV) as catalyst; C, tellurium(IV) as catalyst.

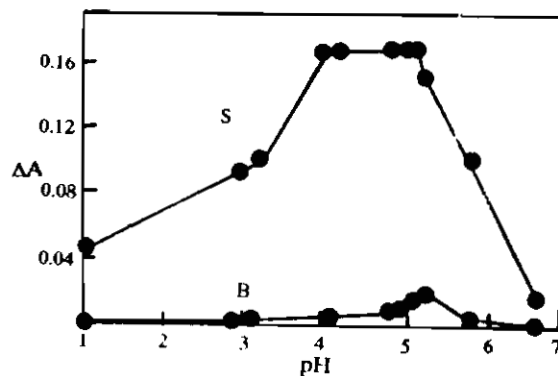


Fig. 3: Effect of pH on the reaction rate: S, sample; B, blank. Conditions: toluidine blue, 10 µg/mL; sulfide, 5 µg/mL; tellurium(IV), 1 µg/mL.

pH 4 was examined. The best results were obtained with a 0.1M citrate buffer.

The effect of ionic strength on the rate of catalysed reaction was investigated. The ionic strength of solution varied from 0.02 to 0.50M using NaNO₃ solution. It was found that the change in the ionic strength of solution has no considerable effect on the reaction rate up to a value of 0.10M. A further increase in the ionic strength caused a decrease in the reaction rate.

The influence of the concentration of toluidine blue and sulfide ion on the rate of catalysed reaction was also studied. The best results were obtained at 5.0-10.0 µg/mL of the dyestuff and 2.0-5.0 µg/mL of sulfide (Figs. 4 and 5).

Thus, the optimum conditions selected were pH 4, temperature 25°C, toluidine blue and sulfide concentrations 5.0 µg/mL and measuring time 3 min.

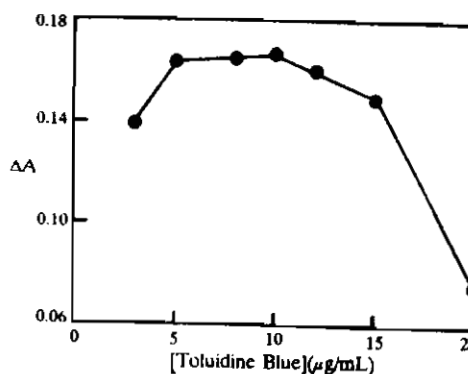


Fig. 4: Effect of toluidine blue concentration on the reaction rate. Conditions: sulfide, 5 µg/mL; tellurium(IV), 1 µg/mL; pH, 4.0.

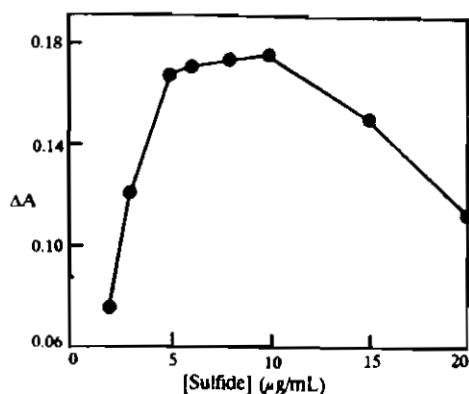


Fig. 5: Effect of sodium sulfide concentration on the reaction rate. Conditions: toluidine blue, 10 μg/mL; tellurium(IV), 1 μg/mL; pH, 4.

Calibration

Under the optimum conditions described above, a linear calibration graph was obtained in the tellurium(IV) concentration range of 0.096–1.250 μg/mL with the regression equation $\Delta A = -0.023 + 0.198C_{Te}$ and a correlation coefficient of 0.9978. The experimental limit of detection ($3 \times$ noise) was 80 ng/mL and the relative standard deviation of ten replicate determinations was 2.2% for a 1 μg/mL tellurium(IV) solution.

Effect of Various Anions and Cations

In order to investigate the interference effect of various cations and anions on the determination of tellurium(IV), a fixed concentration of tellurium (1 μg/mL) was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of 3% was considered tolerable. The results are summarized in Table 1. As it is seen, all the anions and many of cations used have no considerable effect on the determination of tellurium(IV). However, as it is predicted, the presence of cations which form insoluble precipitates with sulfide ion would interfere the tellurium(IV) determination. These cations can be successfully removed from the solution by passing it from a column containing a cation exchanger of H⁺ form (Merck, R-SO₃⁻ type).

It is interesting to note that, by the proposed method, tellurium(IV) can be determined in the

presence of tellurium(VI), which has no catalytic effect on the reduction reaction of toluidine blue by sulfide ion. However, determination of total tellurium in the sample solution would also be possible by the recommended procedure after the complete conversion of tellurium(VI) to tellurium(IV) using hydrochloric acid [19].

Table 1: Tolerance limits of diverse ions on determination of 1 μg/mL tellurium(IV).

Ion	Tolerated ratio of foreign ion to tellurium(IV)
Citrate, Tartrate, Glycine, NO ₃ ⁻ , Li(I), Na(I), K(I)	1000*
ClO ₄ ⁻ , H ₂ PO ₄ ⁻ , HSO ₄ ⁻ , S ₂ O ₃ ²⁻ , OCN ⁻ , F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , Te(VI), As(V), Co(II), Mn(II)	100*
BrO ₃ ⁻ , HCO ₃ ⁻ , Mo(VI), Cr(III), Ce(III), Al(III)	80
SCN ⁻ , Acetate	50
SO ₃ ²⁻	30
Hg(I), Hg(II), Ag(I), Cu(II), Pb(II), Cd(II), Pd(II), Bi(III)	Interfere

* Above of which was not tested.

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