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Spectrophotometric Determination of Trace Amounts of Selenium Based on Catalytic Reduction of Toluidine Blue by Sulfide Ion

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A simple, rapid, and sensitive kinetic method for the determination of trace selenium (0.03—1.5 μg cm^{-3}) based on its catalytic effect on the reduction reaction of toluidine blue and sodium sulfide is reported. The reaction is monitored spectrophotometrically by measuring the decreasing absorbance of toluidine blue at 605 nm by the variable time method. The detection limit is 8 ng cm^{-3} and the relative standard deviation for 1 μg cm^{-3} selenium is 1.4%. The procedure was successfully applied to the determination of selenium in real samples.

Because of the increasing industrial use of selenium,[1,2] in one hand, and its serious toxicity and cumulative effect in body,[3,4] in the other, the separation and determination of the metal ion in trace levels is of special interest. Several extraction-spectrophotometric,[5,6] and spectrophotometric catalytic[7,8] methods for the determination of selenium have been reported recently. Despite the need for rigid control of experimental parameters in the catalytic methods, they have shown very promissing features for the determination of metal ion in ultratrace levels.

In this paper we wish to report a simple, rapid, and sensitive spectrophotometric method for the determination of Se(IV) based on its catalysis of the reduction of toluidine blue by sodium sulfide in neutral solutions.

Experimental

Reagents. All chemicals were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout.

Selenium (IV) stock standard solution (1000 μg cm^{-3}) was prepared by dissolving 3.3308 g of $Na_2SeO_3 \cdot 5H_2O$ (Merck) in water and diluting to 1 dm^3 in a volumetric flask. The solution was standardized iodometrically.[9] Working solutions were prepared by appropriate dilution of the stock solution with water.

Sodium sulfide solution (1000 μg cm^{-3}) was prepared by dissolving 1.8750 g of $Na_2S \cdot 9H_2O$ (Hopkin and Williams) in water and diluting to 250 cm^3 in a volumetric flask. This solution was prepared daily and standardized.[9]

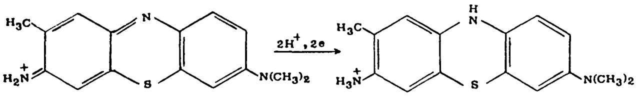
A 3.27×10^{-4} M (1 M=1 mol dm^{-3}) stock solution of toluidine blue (Merck) was prepared by dissolving the dyestuff in water.

Apparatus. Absorption spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer and the absorbance measurements were made on a Perkin-Elmer model 35 spectrophotometer. Measurements of pH was made using a corning 125 pH-meter. A Gallen Kamp BJH-400-010D thermostirrer in which the temperature could be fixed to ±0.1 °C was used.

Procedure. The catalyzed reaction was monitored spectrophotometrically by measuring the change in absorbance at 605 nm. An appropriate amount of sample solution containing 0.30 to 1.50 μg cm^{-3} of Se(IV) was transferred into a 10 cm^3 flask. Then 1 cm^3 of a 100 μg cm^{-3} solution of sodium sulfide and 0.3 cm^3 of 0.01 M HCl solution (to adjust pH between 6.5—7.5) and enough water for diluting the solution to ca. 8 cm^3 were added. The solution was kept in water bath at 25 °C for 20 min. Then, 2 cm^3 of 3.27×10^{-4} M solution of toluidine blue was added when diluted to the mark and time was measured from just after the addition of toluidine blue. A portion of solution was transferred into a glass cell immediately for the absorbance measurements. The time required for the absorbance to decrease to A=0.500 was then measured.

Results and Discussion

Catalytic Reduction of Toluidine Blue by Sulfide Ion. It was found that sulfide ion at neutral pH, where it is mostly in hydrogen sulfide form HS$^-$, reduces toluidine blue only slowly. The half-reaction for the reduction of the dyestuff is as follows:



blue colorless

Figure 1 shows the change in the absorption spectrum of toluidine blue in the presence of sulfide ion at pH=7. However, trace amounts of Se(IV) catalyzes the reaction so that it will proceed much faster.

The catalytic effect of selenium(IV) has been explained by the formation of SeS^{2-}, after the initial reduction of Se(IV) to its elemental state.[10] This compound can then reduce the dye molecule and reform Se(IV).

Effect of Variables on the Catalyzed Reaction. The rate of the reduction reaction both in the presence and absence of Se(IV) was found to increase by increasing temperature. A temperature of 25 °C was used as the most suitable.

The rate of the catalyzed reaction was investigated over the pH range of 4—12 and the results are shown in Fig. 2. It is seen that the largest difference between the

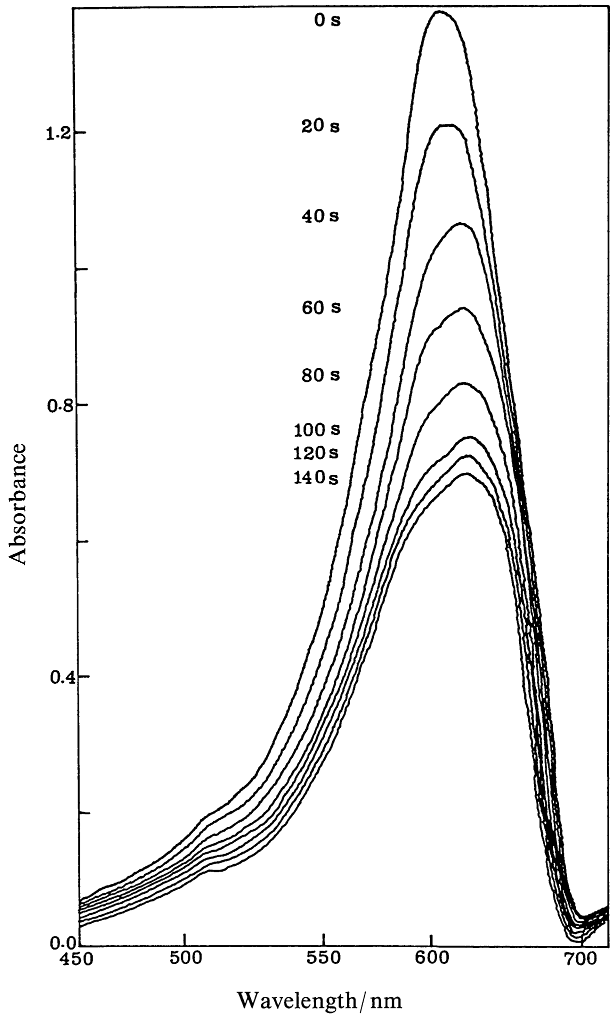


Fig. 1. Absorption spectra of 6.5×10^{-5} M toluidine blue in the presence of 3.1×10^{-4} M sodium sulfide at pH=7. Time intervals 20 s.

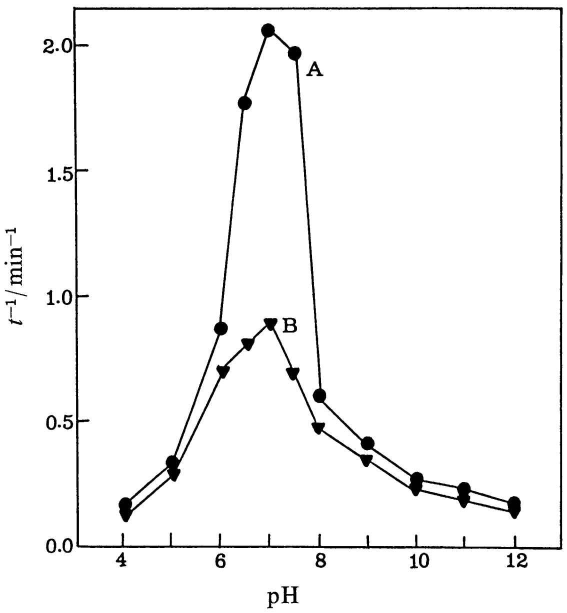


Fig. 2. Effect of pH on the reaction rate. A, sample; B, blank. Conditions: sodium sulfide, 3.13×10^{-4} M; Selenium (IV), 1 μg cm^{-3}; toluidine blue, 6.54×10^{-5} M. The letter t denotes the time required for absorbance to decrease to 0.500.

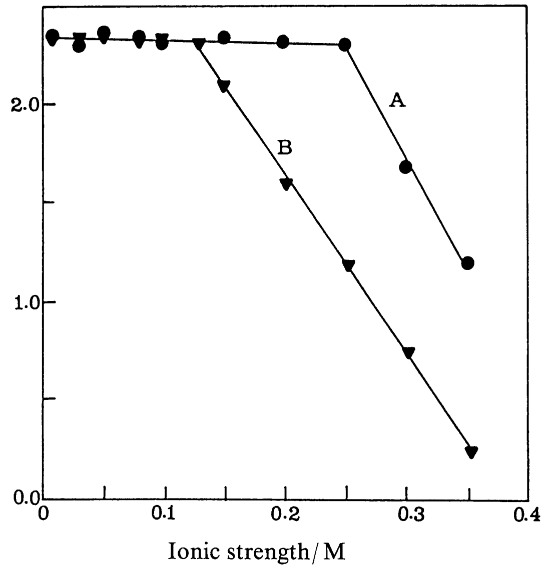


Fig. 3. Effect of ionic strength on the reaction rate. A, NaCl; B, NaClO$_4$. Conditions: Sodium sulfide, 3.13×10^{-4} M; Selenium (IV), 1 μg cm^{-3}; pH, 7; toluidine blue, 6.54×10^{-5} M.

reaction rate of the catalyzed reaction and blank occurs at pH 6.5—7.5.

Effect of ionic strength on the rate of catalyzed reaction was studied (Fig. 3). The ionic strength of solution varied from 0.01 to 0.35 M using NaCl and NaClO$_4$ solutions. As it is seen, change in the ionic strength of solution has no considerable effect on the reaction rate up to a value of about 0.15 M of NaClO$_4$ and 0.25 M NaCl. A further increase in the ionic strength would cause a drastic decrease in the reaction rate.

The influence of the concentration of sulfide ion and toluidine blue was also studied. The best results were obtained at about 3.13×10^{-4} M of sulfide ion and 6.45×10^{-5} M of the dyestuff.

Calibration. Under the optimum conditions described above, in the concentration range of 0.03—1.50 μg cm^{-3} the following regression equation is obtained:

$$1/t\ (\mathrm{min}^{-1}) = 0.9685 + 1.2045\ \ \mathrm{Se(IV)}$$
$$(r = 0.99968)$$

The limit of detection obtained from $Y_{\mathrm{DL}} = Y_{\mathrm{B}} + 3s_{\mathrm{B}}$[11] is 8 ng cm^{-3}, where Y_{B} is the average blank signal (0.9623 min^{-1} for ten replicate determinations) and s_{B} is the standard deviation of the blank signal (0.00520). The relative standard deviation of eight replicate determinations is 1.4% for a 1 μg cm^{-3} selenium(IV) solution.

Effect of Diverse Ions. In order to study the effect of various anions and cations on the determination of Se(IV), a fixed amount of selenium (1 μg cm^{-3}) was

Table 1. Tolerance Limits of Diverse Ions on the Determination of 1 μg cm^{-3} Selenium

Ion	Tolerated radio of foreign ion to Se(IV)
NO_3^-, Cl^-, Br^-, I^-, F^-, $C_2H_3O_2^-$, PO_4^{3-}, HPO_4^{2-}, SO_4^{2-}, HSO_4^-, NO_2^-, CO_3^{2-}, $S_2O_3^{2-}$, ClO_4^-, SO_3^{2-}, HSO_3^-, $S_2O_5^{2-}$, IO_3^-, EDTA	250
OCN^-, CN^-, SCN^-	20
Na(I), K(I), Li(I), Ca(II), Mg(II), Ba(II), Sr(II), Hf(IV), Zr(IV), Al(III), Ce(III), Cr(III)	500
Mo(VI), W(VI), V(V), As(V), Te(IV), Os(VIII)	250
Hg(II), Hg(I), Pb(II), Pd(II), Cu(II), Co(II), Bi(III), Mn(II), Cd(II), Zn(II), Fe(II), Ag(I)	Interfere

Table 2. Determination of Selenium in Kjeldal Tablets

Sample taken	Se/μg cm^{-3}		Recovery/%
cm^3	Contained	Found	
0.5	0.250	0.261	104.3
1.0	0.500	0.524	104.8
1.0	0.500	0.489	97.9
1.5	0.750	0.750	100.0
2.5	1.000	0.975	97.5

taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of 3% was considered tolarable. The results are summarized in Table 1. As it is seen, all the anions and a large number of cations used have no considerable effect on the determination of Se(IV). However, as it is expected, the presense of cations which can form insoluble precipitates with sulfide ion would interfere the selenium determination. These cations were successfully removed from the solution by passing it from a column containing a strongly acidic cation exchanger of H^+ form (Merck, R-SO_3^- type).

It is interesting to note that, by this method Se(IV) can be determined in the presence of Se(VI), which has no catalytic effect on the reduction reaction of toluidine blue by sulfide ion. However, determination of total selenium in different samples would also be possible by the recommended procedure after the conversion of Se(VI) fo Se(IV), which can easily be done by using hydrochloric acid. It is interesting to note that, Se(VI) showed no catalytic effect on the reduction reaction of toluidine blue and sulfide ion.

Application. In order to evaluate the applicability of the method to the real samples, it was applied to the determination of selenium in Kjeldal tablets. One tablet (1.1142 g) containing 0.05 g selenium was dissolved, using a suitable procedure[12] and diluted with water to 1 dm^3 in a volumetric flask. It should be noticed that the final stage of the dissolution process involves the boiling of sample in 4 M HCl, which completely converts Se(VI) to Se(IV).[13] Then 10 cm^3 of this solution was diluted to 100 cm^3 with water and selenium content in different portions of the resulting solution was determined by the recommended procedure. The results are given in Table 2.

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