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

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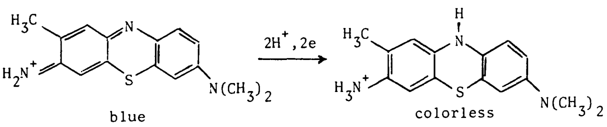
A simple, rapid, and sensitive method has been developed for the determination of trace sulfide (0.28—1.7 μg cm^{-3}) based on its catalytic reduction of Toluidine Blue in the presence of Se(IV). The reaction is monitored spectrophotometrically by measuring the decreasing absorbance of the dyestuff at 628 nm by the fixed time method. The limit of detection is 50 ng cm^{-3} and the relative standard deviation for 1 μg cm^{-3} sulfide is 2.4%. The method was applied to the determination of sulfide in spring water.

Since sulfide ion has a wide variety of industrial and biological effects even at low concentration,[1] its determination at μg cm^{-1} levels is of special importance. Many different methods are available for the determination of sulfide[2] including gravimetric, iodometric, spectrophotometric, and, in recent years, chemiluminescence[3,4] methods. Numerous direct, indirect and catalytic methods for the determination of sulfide by FIA have also been described.[5,6]

We have recently found that trace amounts of Se(IV) catalyzes the reduction reaction of Toluidine Blue by sulfide ion at neutral pH, where it is mostly in hydrogen sulfide form:[7]



(1)

In this paper we wish to report a simple, rapid, and sensitive kinetic-spectrophotometric method for the determination of sulfide in trace levels based on the above catalytic reduction reaction.

Experimental

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

Sulfide stock standard solution (1000 μg cm^{-3}) was prepared by dissolving 0.7500 g of $Na_2S \cdot 9H_2O$ (Hopkin and Williams) in water and diluting to 100 cm^3 in a calibrated volumetric flask. This solution was prepared daily and standardized.[8] Working solutions were prepared by appropriate dilution of the stock solution with water.

Toluidine Blue stock solution (500 μg cm^{-3}) was prepared by dissolving the dyestuff (Merck) in water.

Selenium (IV) stock solution (1000 μs cm^{-3}) was prepared by dissolving 0.1405 g of SeO_2 (Merck) in water and diluting to 100 cm^3 in a calibrated volumetric flask. The solution was standardized iodometrically.[8]

Apparatus. A Perkin Elmer Lambada 5 UV-vis. Spectrophotometer equipped with a thermostated cell holder was used for recording the absorption spectra and the absorbance measurements at fixed wavelengths. Measurements of pH was made using a corning 125 pH-meter. A Julabo-U3 thermostated water bath was used.

Procedure: The catalyzed reaction was monitored spectrophotometrically by measuring the change in absorbance at 628 nm. Into a 10-cm^3 volumetric flask was transferred 1 cm^3 of 10 μg cm^{-3} solution of Se(IV), 2 cm^3 of citrate buffer solution (pH=6.69), 1 cm^3 of 50 μg cm^{-3} Toluidine Blue and enough water for diluting the solution to ca. 9 cm^3. The solution was kept in water bath at 30 °C for 10 min. Then 1 cm^3 of the sulfide solution with appropriate concentration (2.8—17.0 μg cm^{-3}) was added and time was measured from just after the addition of sulfide solution. A portion of solution was transferred into a 1-cm glass cell within 30 s for the absorbance measurements. The decrease in absorbance during a time period of 1.4 min was then measured.

Results and Discussion

Toluidine Blue undergoes a reduction reaction with sulfide ion at neutral pH to form a colorless product. This reaction is slow, but is sharply increased by the addition of trace amounts of Se(IV).[7] At constant concentration of Se(IV), it has been found that the rate of reaction is proportional to the sulfide concentration. The λ_{max} value of Toluidine Blue is 628 nm and the oxidized form of the dye is colorless. In this study sulfide ion was determined using the fixed time method in which the change in absorbance of Toluidine Blue (ΔA) during a fixed period of time was measured for various amounts of sulfide. The calibration graph was constructed by plotting ΔA against sulfide concentration.

Effects of Variables. The rate of the oxidation reaction (1) both in the presence and absence of Se(IV) was found to increase by increasing temperature. A temperature of 30 °C was used as the most suitable.

The influence of pH on the rate of the catalyzed reaction was investigated in the range of 5.0—9.2 and the results are shown in Fig. 1. It is seen that the reaction possesses the largest rate at pH 6.7 (citrate buffer).

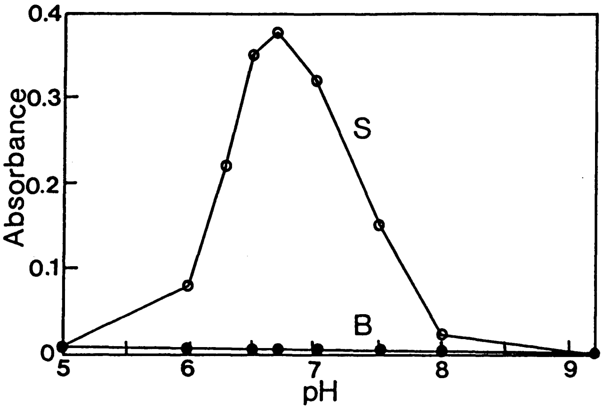


Fig. 1. Effect of pH on the reaction rate: (S) sample; (B) blank. Conditions: Sodium sulfide, 1.2 μg cm^{-3}; Selenium (IV), 1 μg cm^{-3}; Toludine Blue, 10 μg cm^{-3}.

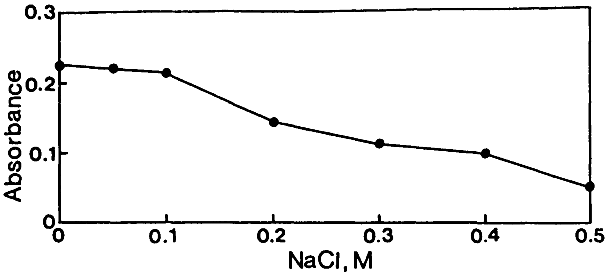


Fig. 2. Effect of ionic strength on the reaction rate. Conditions: Sodium sulfide, 1.2 μg cm^{-3}; Selenium (IV), 1 μg cm^{-3}; pH, 6.69; Toluidine Blue, 5 μg cm^{-3}.

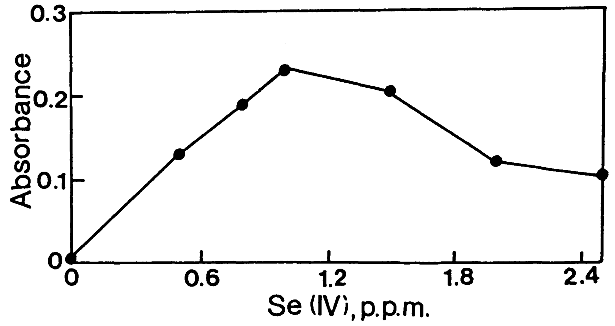


Fig. 3. Effect of selenium (IV) concentration on the reaction rate. Conditions: Sodium sulfide, 1.2 μg cm^{-3}; Selenium (IV), 1 μg cm^{-3}; Tomidine Blue, 10 μg cm^{-3}.

Table 1. Tolerance Limits of Diverse Ions on the Determination of 0.8 μg cm^{-3} Sulfide

Ion	Toleraled ratio of foreign ion to sulfide
Borate, Citrate, NO_3^-, Cl^-, PO_4^{3-}, HPO_4^{2-}, Li^+, Na^+, K^+, Ca^{2+}	850[a)]
Br^-, CH_3COO^-, Hf(IV)	350
HSO_4^-, NO_2^-, SO_4^{2-}, I^-	150
F^-	100
CO_3^{2-}, HCO_3^-, Zr(IV), Tl(I), Al(III)	50
SO_3^{2-}	50[b)]
SCN^-, $S_2O_3^-$, CN^-, OCN^-, EDTA	20
Bi(III), Ag(I), Pb(II), Pd(II)	Interfere

a) Above of which was not tested. b) The tolerated ratio of SO_3^{2-} ion was obtained in the presence of 3.0×10^{-4} M formaldehyde.

Effect of ionic strength on the reaction rate of catalyzed reaction was studied. The ionic strength of solution varied from 0.05 to 0.5 M (1 M=1 mol dm^{-3}) using NaCl solution (Fig. 2). It is seen that change in the ionic strength of solution has no consierable effect on the reaction rate up to a value of about 0.1 M. A further increase in the ionic strength caused a decrease in the reaction rate, probably due to a considerable change in the ratio of the activity coefficients of initial reactants and the corresponding activated complex.

The influence of the concentration of Se(IV) and Toluidine Blue on the reaction rate was also investigated. The best results obtained at about 5 μg cm^{-3} of the dyestuff and 1 μg cm^{-3} of selenium (Fig. 3).

Calibration. Under the optimum conditions described above, a linear calibration graph was obtained in the concentration range of 0.28—1.7 μg cm^{-3} with a correlation coefficient of 0.9985 and a regression equation of $A=-0.081+0.267C$. The detection limit (3X noise) was 50 ng cm^{-3}. The relative standard deviation of eleven replicate determinations is 2.4% for a 1 μg cm^{-3} sulfide solution.

Interferences. The effects of various anions and cations on the determination of 0.8 μg cm^{-3} sulfide ion were investigated and the results are summarized in Table 1. The tolerance limit was taken as the concentration of diverse ion causing less than a 3% relative error. As it is seen, almost all anions (with the exception of SO_3^{2-}) and many cations used have no considerable effect on the determination of sulfide. However, as it is expected, the presence of cations which can form insoluble precipitates with sulfide ion would interfere its determination. The interfering effect of sulfite ion was effectively removed using formaldehyde as a masking agent.[3)]

Application. To evaluate the analytical applicability of the method to the real samples, it was applied to the determination of sulfide in a sample of spring water. After proper dilution of the sample (100 folds), the proposed procedure was applied to determine its sulfide content. The sulfide concentration determined (58, 60 and 61 μg cm^{-3}) was found to be in satisfactory agreement with that obtained from iodometric titration (60, 61, and 63 μg cm^{-3}).

Conclusion. The method described provides a simple, fast and reliable means of determining trace amounts of sulfide. Although the sensitivity and selectivity of the proposed method is not much improved, compared with some previously reported methods,[3—6)] it could be considered superior in regard to the high blank stability and mild pH condition required.

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