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A Facile Catalytic- Kinetic Method for The Determination of Selenium (IV)

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**ABSTRACT**

A catalytic-kinetic method for the determination of selenium is proposed. Alizarin navy blue is reduced by sodium sulfide to form a colorless product. The reaction is accelerated by trace amounts of Se (IV), and can be followed by measuring the decrease in absorbance of the dye at 620nm and 30 ° C by the fixed time method. Selenium can be determined in the range of 0.004 – 0.12  $\mu\text{g}\cdot\text{ml}^{-1}$ . The detection limit is 0.03  $\text{ng}\cdot\text{ml}^{-1}$  Se (IV). The relative standard deviation for 0.08, and 0.1  $\mu\text{g}\cdot\text{ml}^{-1}$ : Se (IV) was 2.2%, and 1.8%, respectively. The method is free from most interferences and it was applied to determination of selenium in water real samples.

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## INTRODUCTION

Selenium is widely distributed in nature in relatively small concentrations in rocks, plants, coal and other fossil fuels. Selenium compounds are extensively used in paints, dyes, glass, electrical, rubber and insecticides [1]. The determination of selenium is of considerable interest because of its contrasting biological effects; selenium is a toxic as well as a trace element for animals and humans [2]. Its deficiency causes pulmonary edema, hair loss and fatigue in humans [3], which have been frequently reported in China [4]. It also plays a major role in life cycle of plants [2]. Selenium is also reported to be present in cigarette paper, tobacco [5] and various cosmetic samples [6]. There are many methods for determination of selenium [7-10]. The kinetic catalytic methods have shown very promising features for determination of metal ions in ultra-trace levels [11]. These methods have proved to be a cheaper and more reliable alternative to the instrumental analyses for trace determinations [12, 13]. Catalytic Kinetic methods are attractive alternatives for the determination of selenium [14,19]. A method for the determination of Se (IV) with methylene blue [14] has a high detection limit ( $50 \text{ ng. ml}^{-1}$ ). Other methods are based on the oxidation of p-hydrazino benzenesulphonic acid [15] with a limit of detection of  $7.8 \text{ } \mu\text{g.ml}^{-1}$ , on the reduction of resazurin [17] and bromate [18] with limits of detection  $1 \text{ ng. ml}^{-1}$  and on oxidation of Variamine Blue with potassium iodide with limit of detection  $0.003 \text{ } \mu\text{g.ml}^{-1}$  [19]. Most of these methods lack sufficient sensitivity for determination of selenium at  $\mu\text{g.ml}^{-1}$  levels. Therefore, more sensitive and selective methods are required.

In this paper we wish to report a simple, rapid and sensitive method for determination of Se (IV) based on its

catalytic effects on the reduction reaction of alizarin navy blue (ANB) with sodium sulfide in  $\text{pH}=7$ .

## EXPERIMENTAL

### Reagents

Double distilled water and analytical reagent grade chemicals were used. Standard (1000ppm) selenite solution was prepared by dissolving  $0.2211 \text{ g Na}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$  (Merck) in water and diluting to 100 ml in a volumetric flask.

A solution  $5.94 \times 10^{-4} \text{ M ANB}$  was prepared by dissolving  $0.0210 \text{ g}$  (Aldrich) in 10 ml ethanol, 1.5ml NaOH (0.1M) and diluting to 100 ml in a 100-ml volumetric flask with water.

Sodium sulfide solution (0.010 M) was prepared by dissolving  $0.2402 \text{ g}$  of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  (Merck) in water and diluting to 100 ml in a volumetric flask. This solution must be prepared daily.

### Apparatus

Absorption spectra were recorded on a Shimadzu Model 160-A UV-Vis-Spectrophotometer with a 1-cm glass cell and it was used for absorbance measurements at a fixed wavelength. A thermostat bath (Gallenkamp) was used to keep the reaction temperature at  $30 \pm 0.1^\circ \text{C}$ . A stopwatch was used for recording the reaction time.

### Recommended Procedure

The reaction was followed spectrophotometrically by monitoring the change in absorbance of the reaction mixture at 620 nm by a fixed time method for the first 0.5-4.0 min from initiation of the reaction.

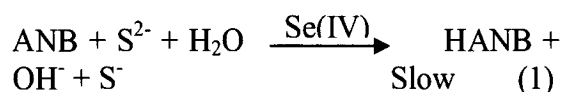
An aliquot sample containing up to  $1.2 \text{ } \mu\text{g}$  of Se (IV) was added to a 10-ml volumetric flask. Then 3.0 ml of buffer solution ( $\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$  0.4 M,

pH=7.0) and 2.5 ml  $5.94 \times 10^{-4}$  M ANB was added. The solution was diluted to ca. 8 ml with water. Then 0.6 ml of 0.01 M  $\text{Na}_2\text{S}$  was added and the solution was diluted to the mark with water and mixed well. The mixture was transferred into a 1.0cm glass cell within 30 sec from initiation of the reaction. The decrease in absorbance was measured during the first 0.5-0.4 min from initiation of the reaction ( $\Delta A_s$ ). Time was measured from just after the addition of the last drop of sodium sulfide. The measurement in the absence of selenium (IV) was prepared to obtain the values for the uncatalyzed reaction ( $\Delta A_b$ ). The net reaction rate was calculated from the difference in the absorbance changes at a fixed time ( $\Delta A_s - \Delta A_b$ ). All the solution were preheated to working temperature of  $30 \pm 0.1^\circ \text{C}$  in a thermostat bath.

## RESULTS AND DISCUSSION

ANB can be reduced by sulfide ion at a very slow rate at room temperature. In the presence of trace amounts of Se (IV) as a catalyst, the reaction is fast.

The accelerating effect of selenium has been explained by the fact in the presence of selenium ion,  $[\text{SeS}]^{+2}$  ions are formed, which react much faster than sulfide ions. The selenium liberated again reacts with sulfide ion [20]. The reaction can be monitored spectrophotometrically by measuring the decrease in the absorbance at 620 nm (decrease in concentration of ANB) with time. Figure 1(a) shows the absorption spectra for ANB- $\text{S}^{2-}$ -Se (IV) system and 1(b) shows ANB- $\text{S}^{2-}$  system. Under the chosen conditions, the uncatalyzed reaction occurs simultaneously. This reaction between ANB and sulfide ion occurs according to the equations 1 and 2:



The rate equation for the overall reaction is shown in equation 3:

$$\text{rate} = -d[\text{ANB}]/dt = \frac{k_c [\text{ANB}] [\text{S}^{2-}] [\text{Se(IV)}]}{K_{un} + [\text{ANB}] [\text{S}^{2-}]} \quad (3)$$

Where  $k_c$  and  $K_{un}$  are the rate constants for the catalyzed and uncatalyzed reaction respectively. Because the  $K_{un} \ll K_c$  and concentrations of  $\text{S}^{2-}$  and ANB are greater than Se (IV), it is presumed that the reaction is pseudo first-order with respect to Se (IV).

$$\text{rate} = -d[\text{ANB}]/dt = K' [\text{Se(IV)}] \quad (4)$$

By integration of the equation 4 and by incorporation Beer's law ( $A = \epsilon bC$ ), we obtain final expression as:

$$\Delta A_s - \Delta A_b = \Delta \Delta A = K' [\text{Se(IV)}] t \quad (5)$$

Where  $\Delta A_s$  is the changes of absorption in catalyzed reaction ( $A_{s(t=30s)} - A_{s(t)}$ ),  $\Delta A_b$  is the changes of absorption in uncatalyzed reaction ( $A_{b(t=30s)} - A_{b(t)}$ ) and  $t$  is the reaction time.

### Effect of Variables on The Reaction Rate

The effect of pH, reagent concentration, time of the reaction and temperature on the reaction were studied with  $0.10 \mu\text{g.ml}^{-1}$  Se(IV) concentration. A fixed time method of 4.0 min from initiation of the reaction was chosen for use, giving a good comparison between sensitivity and short analysis time.

#### Effect of pH

The effect of pH on the catalyzed and uncatalyzed reaction was studied with  $1.18 \times 10^{-4}$  M ANB, and 0.001 M  $\text{S}^{2-}$  at  $30^\circ \text{C}$  with the pH range of 6.0-9.0(Fig. 2). The results showed that the reaction rate increases for the catalyzed and uncatalyzed reaction up to pH 7.0, but the rate of

increment for the catalyzed reaction is faster. In greater pH value, the sensitivity decreases. This effect is due to the fact that the reduction of ANB occurs in neutral solution as indicated before. Therefore, pH 7.0 (phosphate buffer) was selected for the study.

#### *Effect of Sulfide Concentration*

The effect of sulfide concentration on the rate of reaction was studied with pH 7.0 and ANB concentration of  $1.18 \times 10^{-4}$  M at  $30^\circ\text{C}$ . Fig. 3 shows that the net reaction rate increases by increasing sulfide concentration up to  $6.0 \times 10^{-4}$  M. Higher concentrations of the reagent cause a decrease in sensitivity. This effect is due to the fact that at high concentration of sulfide ions, the reduction of ANB for the uncatalyzed reaction is too fast to accurately detect the catalytic effect of Se (IV). Thus, a sulfide concentration of  $6.0 \times 10^{-4}$  M was used for further studies.

#### *Effect of ANB Concentration*

The effect of ANB concentration on the rate of reaction was studied with pH 7.0 and  $6.0 \times 10^{-4}$  M  $\text{S}^{2-}$  at  $30^\circ\text{C}$  (Fig. 4). Results show that the both of reactions (catalyzed and uncatalyzed) rate increase with increasing ANB concentration. Therefore,  $1.78 \times 10^{-4}$  M ANB concentration was selected. Higher concentration of dye cannot be used due to its molar absorptivity coefficient.

#### *Effect of Temperature*

The influence of temperature on the reaction rate was studied in the range of  $10\text{-}60^\circ\text{C}$  in the presence of optimum pH and reagent concentration. Both reaction rates increased with increasing temperature. A temperature of  $30^\circ\text{C}$  was selected due to its simplicity for this study.

#### *Effect of Time*

The reaction rate was studied in the range of 0.5-7.5 min in the presence of optimum conditions (fig. 5). Sensitivity increases up

to 5.5 min, but at 4.0 min the reaction has good sensitivity and 4.0 min was selected.

#### *Effect of Ionic Strength*

The effect of ionic strength on the reaction rates for both the catalyzed and uncatalyzed reactions was investigated, the salt concentration being from 0.00 to 0.75 M using 3.0 M  $\text{KNO}_3$  solution. The results (table1) indicate that, with increase in  $\text{KNO}_3$  concentration, the rates of both catalyzed and uncatalyzed reactions decrease.

#### *Calibration Graph*

The calibration graph was obtained under the optimum working condition and 620 nm with the fixed-time method. Measurements were for 4.0 min from initiation of the reaction; because it provided the best regression and sensitivity and reaction time. Under the optimum conditions described above, Se (IV) can be determined in the concentration range of 0.04-12.0  $\mu\text{g.ml}^{-1}$ : the following regression equation was obtained with Excel program;  $\Delta A = 0.020 + 0.0147C$  ( $R = 0.9945$ ,  $n = 12$ , and  $S_r = 7.3 \times 10^{-4}$ ), The relative standard deviation for ten replicate determinations of 0.05, 0.08, and  $0.1 \mu\text{g.ml}^{-1}$ : Se (IV) was 2.5%, 2.2%, and 1.8%, respectively. The experimental limit of detection is  $0.03 \text{ ng.ml}^{-1}$  Se (IV).

#### *Interference Study*

The influence of foreign ions on the system was examined with  $0.1 \mu\text{g.ml}^{-1}$ : Se(IV). The tolerated limits for the ions assayed are shown in Table 2 (with relative errors less than 7%). As can be seen, most ions used have no considerable effect on the determination of Se (IV), even when present in 100-1000-fold excess over selenium. The results show that the method is relatively selective for tellurium determination.

### CONCLUSION

A kinetic-spectrophotometric method is proposed for ultra-trace amounts of selenium. The method is simple, highly sensitive, inexpensive and rapid. Selenium can be determined in the range of 0.004 –

0.12  $\mu\text{g.ml}^{-1}$ . The detection limit is 0.03  $\text{ng.ml}^{-1}$  Se (IV).

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Table 1. Effect of ionic strength on the reaction rates

[NaNO <sub>3</sub> ] M	$\Delta A_s$	$\Delta A_b$	$\Delta\Delta A$
0.00	0.814	0.18	0.634
0.15	0.801	0.279	0.522
0.30	0.762	0.54	0.22
0.45	0.739	0.545	0.194
0.6	0.674	0.569	0.105

Table 2. Effect of foreign ions on the determination of Se(IV)

Species	(ppm <sub>i</sub> /ppm <sub>Se</sub> )
Br <sup>-</sup> -I <sup>-</sup> -SO <sub>3</sub> <sup>2-</sup> -Cl <sup>-</sup> -SCN <sup>-</sup> -NO <sub>3</sub> <sup>-</sup> -ClO <sub>3</sub> <sup>-</sup> -NO <sub>2</sub> <sup>-</sup> CO <sub>3</sub> <sup>2-</sup>	>1000
Na <sup>+</sup> -K <sup>+</sup> -Mg(II)-Ba(II)-Al(III)	>1000
Cr(III)-Fe(II)-Fe(III)-Co(II)-	100
Cd(II)-Cu(II)-Ag(I)-Mn(II)-Pb(II)	Interfere

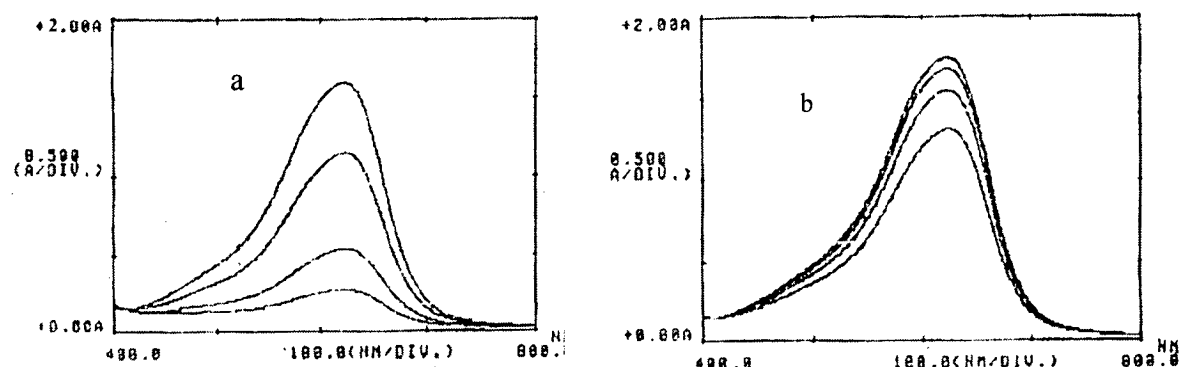
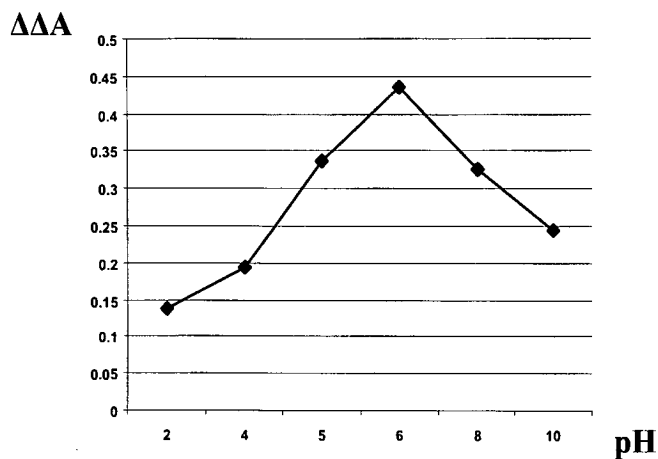
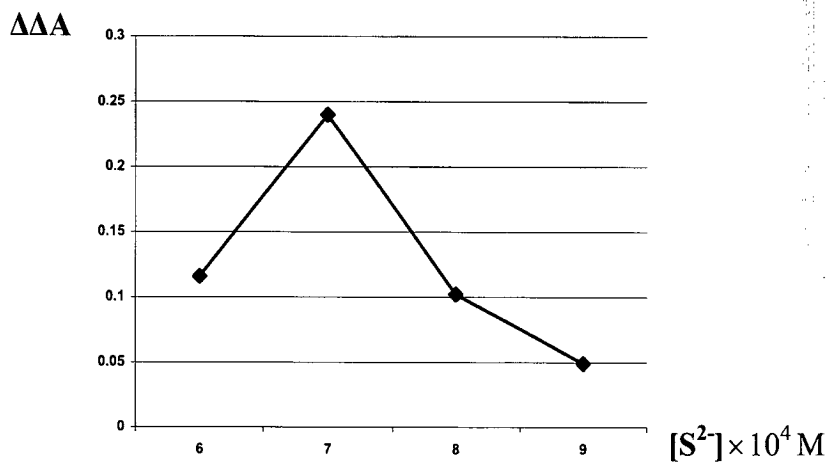


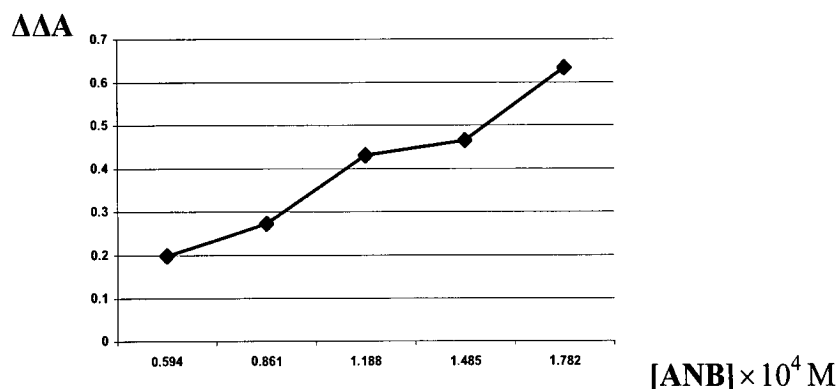
Fig1. a: Variation of the Alizarin navy blue -S<sup>2-</sup> Se (IV)with time. b: without Se(IV). Conditions: pH, 7.0, Alizarin navy blue  $1.78 \times 10^{-4}$  M, Sulfide  $6.0 \times 10^{-4}$  (a: 100 ng/ml Se(IV), at 30° C.



**Fig2:** Effect of pH on sensitivity. Conditions: Alizarin navy blue  $1.18 \times 10^{-4}$  M,  $0.001$  M  $S^{2-}$ ,  $100$  ng/ml Se(IV), at  $30^\circ$  C and  $t=240$ sec



**Fig3:** Effect of sulfide concentration. Conditions: pH= 7, Alizarin navy blue  $1.18 \times 10^{-4}$  M,  $100$  ng/ml Se(IV), at  $30^\circ$  C and  $t=240$ sec



**Fig4:** Effect Alizarin navy blue concentration on reaction. Conditions: pH= 7.0, Sulfide  $6.0 \times 10^{-4}$  M , 100 ng/ml Se(IV) at 30 ° C and  $t=240$ sec

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