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Kinetic Trace Determination of Molybdenum(VI), L-Ascorbic Acid, and Thiosulfate Using Landolt Reaction by the Aid of Fluorometry

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Trace amounts of molybdenum(VI) can be determined by the use of their catalytic effects on the peroxoborate-iodide redox reaction in acidic medium. The indicator reaction is transformed to a Landolt reaction by the addition of ascorbic acid into the reaction mixture, *i.e.*, the iodine produced by the reaction is immediately reduced by ascorbic acid. The end of the induction period of the Landolt process was fluorometrically detected by the aid of disappearence of fluorescence of Rhodamine B. Trace determination of molybdenum(VI) was carried out by employing the linear relationship between the reciprocal of induction period and catalyst concentration. The most suitable concentrations of sodium peroxoborate, potassium iodide, and hydrochloric acid in the reaction mixture were found to be 9 mM, 0.1 M, and 0.1 M, respectively. By this method, molybdenum(VI) can be determined from 80 nM to 10 mM (7.675 ng ml^{-1} to 95.95 mg ml^{-1}). The effect of foreign ions were studied and an equal amount of tungsten(VI), and 10-fold amounts of zirconium(IV), iron(II), iron(III), vanadium(IV), and copper(II) were found to show interference. Ascorbic acid and thiosulfate in micro mol l^{-1} levels were also determined by the present method employing the linear relationship between the induction period and the reductant concentration.

Kinetic methods of analysis by the aid of catalytic reactions are used in many fields of chemical analysis because of their extremely high sensitivity, and are summarized in books[1-4] and reviews[5-14]

The Landolt reaction is frequently applied to the micro-determination of various metal ions[15-23] and some reducing agents.[24] Svehla[14] reviewed the application of Landolt reaction in quantitative catalytic analysis.

The present authors had been reported kinetic micro-determinations of molybdenum(VI),[25] tungsten(VI), and vanadium(V)[26] which catalyse the redox reaction of peroxoborate-iodide system, using iodide ion-selective electrode as the tracer of reaction rate. In the present work, the indicator reaction is transformed to a Landolt reaction by the addition of L-ascorbic acid. The end of the induction period was monitored fluorophotometrically. Micro amounts of molybdenum(VI) can be determined by plotting the reciprocal of the induction period against its concentration. Also, L-ascorbic acid and thiosulfate in micro molar levels were determined by the use of the linear relationship between the induction period and their concentration.

Theory

The indicator reaction on which the present method is based proceeds as follows:

$$BO_3^- + 3\,I^- + 2\,H^+ \longrightarrow BO_2^- + I_3^- + H_2O. \quad (1)$$

In the presence of catalyst, this redox reaction proceeds with a considerable rate, but it proceeds very slowly without catalyst. In the presence of a reducing agent, *e.g.*, ascorbic acid, triiodide ions produced are immediataly reduced so that the iodide ion concentration is kept constant until all the L-ascorbic acid is oxidized.

$$C_6H_8O_6 + I_3^- \longrightarrow C_6H_6O_6 + 3\,I^- + 2\,H^+ \quad (2)$$

When ascorbic acid has been consumed completely, triiodide ions appear in the reaction mixture and the solution turns yellow. The time length necessary to elapse till the appearance of triiodide ions is called the induction period.

Concentration of hydrogen ion does not change during induction period because the oxidation of ascorbic acid releases the same number of hydrogen ions, as shown in Eq. 2. Thus, iodide and hydrogen ion concentrations remain constant so long as ascorbic acid is present. The reaction rate can be expressed as

$$-\frac{d[BO_3^-]}{dt} = (k \cdot C_k + k')[BO_3^-] \quad (3)$$

where k and k' are the products of rate constants of catalyzed and uncatalyzed reaction including the concentrations of hydrogen and iodide ion, and C_k is the catalyst concentration. Integration of Eq. 3 yields

$$\frac{1}{t} = \frac{k \cdot C_k + k'}{\ln \dfrac{[BO_3^-]_0}{[BO_3^-]_0 - [C_6H_8O_6]_0}}$$

where t is the induction period and $[BO_3^-]_0$ and $[C_6H_8O_6]_0$ are the initial concentrations of peroxoborate ion and ascorbic acid, respectively.

Hence plotting the reciprocal of induction period against catalyst concentration gives a linear calibration graph.

The end of the induction period, *i.e.*,the appearance of triiodide ion in the reaction mixture was fluorophotometrically detected by the aid of the following reaction:[27]

$$\underset{\text{(fluorescence)}}{\text{Bhodamine B}} + I_3^- \longrightarrow \underset{\text{(none-fluorescence)}}{\text{Product.}} \quad (5)$$

Here triiodide ion may act as a quenching ion.[28] Some reductants, *i.e.*, ascorbic acid and thiosulfate ion, can also be determined by utilizing the linear relationship between the induction period and their concentration.

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Experimental

Apparatus. All the fluorescence measurements were carried out with a Shimadzu spectrofluorophotometer, RF-510, connected with a Shimadzu recorder, U-125MU. The temperature of the fluorophotometric cell was kept constant to 25±0.5°C by the use of a Yanagimoto constant temperature bath, P8-PC. A Hitachi pH meter, F-5 was used for pH measurements.

Reagents. Molybdenum(VI) stock solution(0.01 M) was prepared by dissolving 1.7656 g of analytical reagent grade ammonium molybdate tetrahydrate obtained from Kishida Chemicals Co. into 1 dm^3 (dm^3=litre) of water. Concentration of the solution was standardized by an adding excess amount of 0.01 M Na_2H_2 edta and the solution was then back titrated with 0.01 M lead sulfate by the aid of XO metallochromic indicator at pH 5. Sodium peroxoborate solution (0.05 M) was prepared every week by dissolving 3.8465 g of sodium peroxoborate tetrahydrate obtained from Wako Pure Chemicals Co. into 0.5 dm^3 of water. It was stored in a dark bottle in a refrigerator. Potassium iodide solution (1 M) was prepared by dissolving about 166 g of reagent into 1 dm^3 of water. The stock solution was potentiometrically titrated against silver nitrate standard solution and stored in a dark bottle. Rhodamine B was obtained from Wako Pure Chemicals Co. as a chloride salt and 0.01 M stock solution was prepared by dissolving 0.4790 g of reagent into 100 ml of water. A stock solution was potentiometrically standardized with silver nitrate solution. L-Ascorbic acid was obtained from Wako Pure Chemicals Co. and a stock solution was prepared by dissolving 1.7613 g of reagent into 100 ml of water just before use. The chemicals used in this study were all of analytical reagent grade. All the water used was deionized and then twice distilled.

Procedure. The established procedure for the determination of 80 to 200 nM of molybdenum(VI) is as follows. To a 50 ml volumetric flask containing an appropriate amount of molybdenum(VI) sample solution were added 10 ml of 10 μM Rhodamine B solution and 18 ml of 50 mM sodium peroxoborate solution; the flask was filled up to the mark with water (solution A). To another 50-ml flask containing 10 ml of 1 M potassium iodide were added 3 ml of 0.1 M ascorbic acid solution and 10 ml of 1 M hydrochloric acid; this solution was diluted to the needed volume (solution B). Both solutions were thermostated at 25°C, and a 1-ml portion of solution A was transfered fluorometric cell (10×10×45 mm) in the spectrofluorophotometer. An equal amount of solution B was rapidly poured into the cell and the recorder switched on at the same time. The reaction solution in the cell was quickly mixed by using a small stirrer, and the fluorescence intensity was recorded at 555 nm of excitation and 573 nm of emission wave length. The amount of ascorbic acid added to the reaction mixture was changed according to the molybdenum(VI) ion concentration range.

Results and Discussion

Effect of pH. Effect of pH on the rate of the reaction was examined with fixed concentrations of sodium peroxoborate, potassium iodide and ascorbic acid. The pH of the reaction mixture was varied by the use of hydrochloric acid or acetate buffer. Calibration graphs for molybdenum(VI) in the concentration range from 2 to 10 μM with different pH values were obtained; the slopes of these graphs were plotted against pH. As shown in Fig. 1, the slope of the

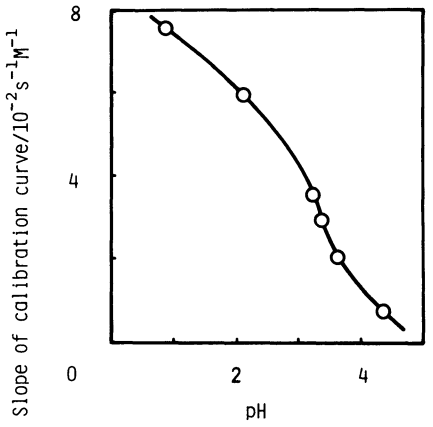

Fig. 1. Effect of pH on the slope of calibration curves. Composition of the reaction mixture: [$NaBO_3$]=2.5 mM, [KI]=1.0 mM, [Rh.B]=1.0 μM, [Asc.]=0.2 mM, temp=25±0.5°C, range of molybdenum(VI): 2 to 10 μM, pH of the reaction mixture was adjusted with HCl or acetate buffer.

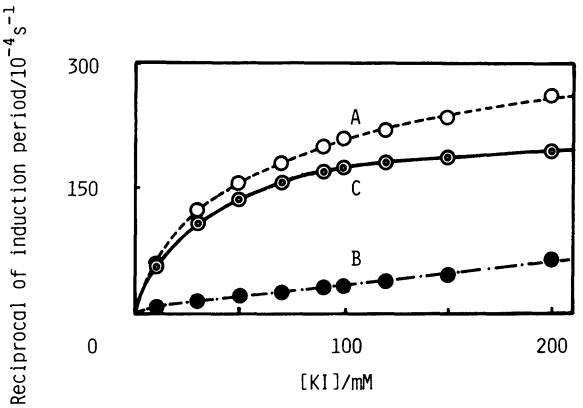

Fig. 2. Effect of potassium iodide concentration on the reciprocal of induction period.
Composition of the reaction mixture: [$NaBO_3$]=2.5 mM, [HCl]=0.1 M, [Rh.B]=1.0 μM, [Asc.]=1.0 mM, temp=25±0.5°C, A: [Mo(VI)]=6.0 μM, B: black, C: difference of reciprocal of induction period, (A−B).

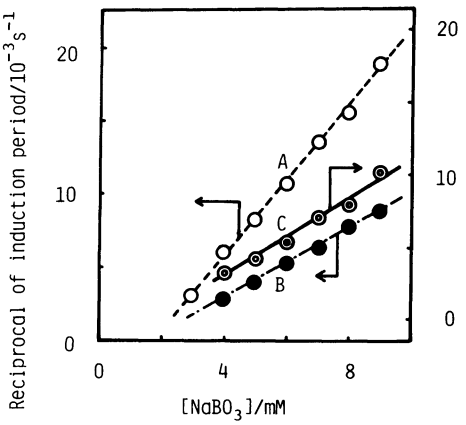

Fig. 3. Effect of potassium iodide concentration on the reciprocal of induction period.
Composition of the reaction mixture: [KI]=0.1 M, [HCl]=0.1 M, [Rh.B]=1.0 μM, [Asc.]=1.5 mM, temp=25±0.5°C, A; [Mo(VI)]=1.0 μM, B; black, C; difference of reciprocal of induction period, (A−B).

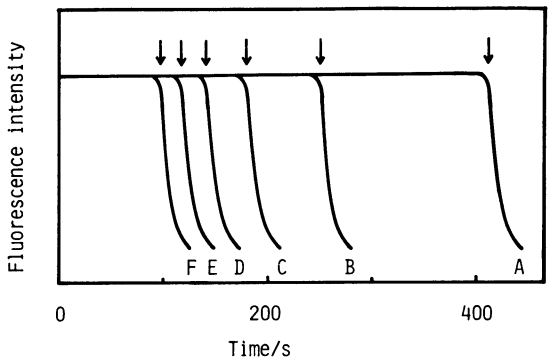

Fig. 4. Fluorescence intensity-time curve.
Composition of the reaction mixture: [KI]=0.1 M, [$NaBO_3$]=9 mM, [HCl]=0.1 M, [Rh.B]=1 μM, [Asc.]=5 mM, temp=25±0.5 °C, [Mo(VI)]: A; 0, B; 2, C; 4, D; 6, E; 8 F; 10 μM.

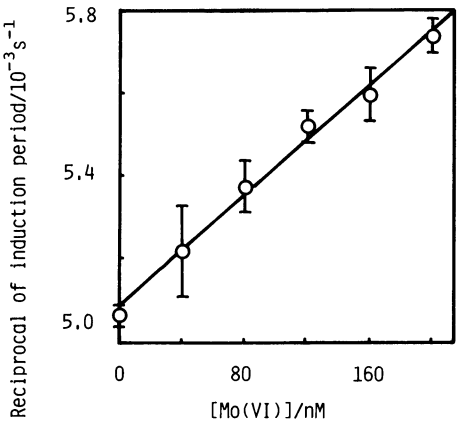

Fig. 5. Calibration curve for molybdenum(VI) (40—200 nM).
Composition of reaction mixture: [$NaBO_3$]=9.0 mM, [KI]=0.1 M, [HCl]=0.1 M, [Rh.B]=1.0 μM, [Asc.]=3 mM, temp=25±0.5 °C.

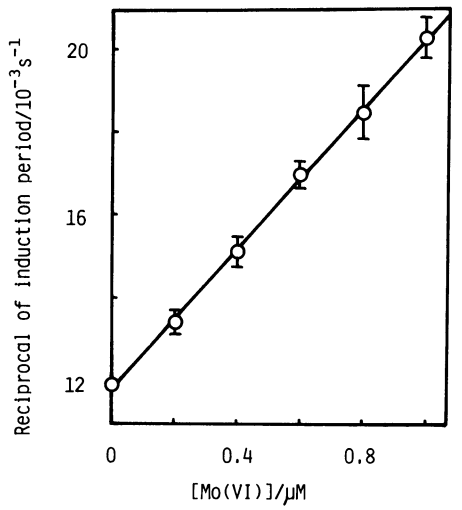

Fig. 6. Calibration curve for molybdenum(VI) (0.2—1.0 μM).
Composition of reaction mixture: [$NaBO_3$]=9 mM, [KI]=0.1 M, [HCl]=0.1 M, [Rh.B]=1.0 μM, [Asc.]=1.5 mM, temp=25±0.5 °C.

calibration curve increased with decreasing pH of the reaction mixture. The most suitable pH was found to be unity, because the rate of the blank reaction suddenly increased at pH values lower than unity.

Effect of Potassium Iodide Concentration. The dependence of iodide ion concentration on the reciprocal of induction period was investigated. The results are shown in Fig. 2. Various amounts of potassium iodide solution were added to the reaction mixture containing 6 μM of molybdenum(VI) (curve A). The blank reaction was also carried out (curve B). The differences of reciprocal of induction period are also shown in the figure (curve C). It was found that the net value (curve C) became almost constant at the iodide ion concentrations higher than 0.1 M. Thus, the concentration of potassium iodide was adjusted to 0.1 M.

Effect of Sodium Peroxoborate Concentration. The effect of peroxoborate ion concentration on the reciprocal of induction period was examined. The results are shown in Fig. 3. The net value of reciprocal of induction period increased with increasing the sodium peroxoborate concentration. However, a high peroxoborate ion concentration is not suitable because it decomposes itself by generating bubbles in the fluorometric cell. Thus, the peroxoborate ion concentration was adjusted to 9 mM.

Effect of Rhodamine B Concentration. Rhodamine B ion concentration lower than 0.1 μM is not suitable because of low fluorescence intensity. Rhodamine B ion concentration more than 0.1 mM is also not suitable because the reaction mixture becomes turbid. A concentration of 1.0 μM was adopted because the sharpness of the change in fluorescence intensity at the end of induction period is increased with decreasing its concentration.

Calibration Graph. The calibration graph for molybdenum(VI) was obtained according to the above procedure. Fluorescence intensity-time curves for various molybdenum(VI) concentrations in the range from 0 to 10 μM are shown in Fig. 4. Arrows in the figure show the end of induction period. As shown in Figs. 5 and 6, the calibration graphs of molybdenum(VI) are linear over the concentration range from 80 to 200 nM and 0.2 to 1.0 μM. The number of measurements at each molybdenum(VI) ion concentration levels are three and the graph is shown in mean and 95% confidence limit. Relative standard deviation at 8×10^{-8} and 2×10^{-7} M molybdenum(VI) concentrations are 0.47 and 0.24%, respectively.

Determination of Ascorbic Acid and Thiosulfate Ion. Since the induction period is linear to reductant concentration, micro-determination of a reducing agent such as ascorbic acid or thiosulfate is feasible. Concentration of potassium iodide, sodium peroxoborate, hydrochloric acid, Rhodamine B, and molybdenum(VI) were kept to 0.5 mM, 7.5 mM, 0.1 M, 1.0 μM, and 1.0 μM, respectively. A good calibration graph was obtained for the ascorbic acid concentration range from 1 to 10 μM. One can easily determine more concentrated ascorbic acid up to 10 mM by increasing the catalyst concentration. Thiosulfate ion in the concentration range from 2 to 10 μM was also determined by using

TABLE 1. EFFECT OF DIVERSE IONS

Diverse ion	Concentration of diverse ion			
	0.5 μM	5.0 μM	50 μM	500 μM
W^{VI}	+7.64	+49.73	—	—
Zr^{IV}	+1.48	+3.88	+113.3	—
Fe^{II}	+0.95	+4.88	+46.41	—
Fe^{III}	−0.31	+4.41	+44.63	—
Cr^{VI}	+2.44	+4.47	+13.28	—
V^{IV}	+3.18	+4.80	+11.63	+144.6
Mn^{II}	+1.27	−0.28	−3.51	−4.13
Zn^{II}	—	—	—	+0.23
Cr^{III}	—	+1.62	−8.39	−5.35
Cu^{II}	+0.58	−15.64	—	—

[$NaBO_3$]=9.0 mM, [KI]=0.1 M, [HCl]=0.1 M, [Rh.B]= 1.0 μM, [Asc.]=1.5 mM, temp=25±0.5 °C, [Mo(VI)]= 0.5 μM, Figures in the table show relative errors in percent.

the same composition of reaction solution. Relative standard deviations of 2μM ascorbic acid and 2μM thiosulfate ion concentration levels are 2.56 and 1.76%, respectively.

Interference. Interference by some diverse ions for the determination of molybdenum(VI) was evaluated; the results are shown in Table 1. The composition of the reaction solution is the same as that used for construction of the calibration graph and molybdenum(VI) concentration was kept to 0.5μM. The concentration of diverse ions were changed to 1 to 1000 times more than that of molybdenum(VI). Triplicate measurements were carried out in the presence and absence of interferent. Plus sign in the table implies acceleation of the rate of indicator reaction. Equal amounts of tungsten(VI), and tenfold amounts of zirconium(IV), iron(II), iron(III), vanadium(IV), copper(II), and chromium(VI) show interference.

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