# Catalymetric Trace Determination of Molybdenum(VI) Based on a Landolt Type Peroxoborate-Iodide Reaction Using an Ion-Selective Electrode

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### Katalymetrische Bestimmung von Molybdän(VI)spuren durch die Landoltsche Peroxoborat-Iodid-Reaktion mit Hilfe der Iodid-Elektrode

**Zusammenfassung.** Das Verfahren beruht auf der katalytischen Wirkung des Molybdäns auf die Peroxoborat-Iodid-Reaktion. Durch Zugabe einer definierten Menge von Ascorbinsäure, die das zunächst entstehende Iod sofort reduziert, wird eine Landolt-Reaktion aufgebaut. Der Endpunkt (Verminderung an Iodid) wird potentiometrisch mit der Iodid-Elektrode indiziert. Zwischen der Zeitdauer bis zum Endpunkt (*t* in Sekunden) und der Molybdänkonzentration besteht die Beziehung $1/t$ = 4,79 [Mo(VI)] + 0,598 im Bereich von 0,5–5,0 μM Mo(VI). Wolfram(VI) stört. Molybdän kann nach diesem Verfahren in Meerwasser nach Konzentration am Chelationenaustauscher Chelax-100 bestimmt werden (Standardabweichung 0,52 μg/l für 8,62 μg Mo/l).

**Summary.** Trace amounts of molybdenum(VI) have been determined by means of its catalytic effect on the peroxoborate-iodide reaction in acidic medium. The indicator reaction is transformed to a Landolt reaction by the addition of L-ascorbic acid which reduces iodine to iodide. The end-point of the reaction (decrease of iodide) is potentiometrically monitored by the aid of an iodide ion-selective electrode. The relationship between the time required to reach the end-point (*t* in seconds) and the concentration of molybdenum(VI) was found to be $1/t$ = 4.79 [Mo(VI)] + 0.598 in the range of 0.5–5.0 μM Mo(VI). Tungsten(VI) interferes. The method has been applied to the determination of molybdenum(VI) in sea water after its concentration by the chelating resin Chelex-100 (standard deviation 0.52 μg/l for 8.62 μg Mo/l).

## Introduction

Kinetic methods of analysis by means of catalytic reactions are useful in many fields of chemical analysis because of their extremely high sensitivity and selectivity and are described in many books [12, 13, 17, 20] and reviews [1, 14–17, 20]. It is reported that some metal ions catalyze the oxidation of iodide ion to iodine and the majority of the methods are based on the observation of the reaction rate by tracing the iodine concentration spectrophotometrically.

The present authors had reported the determination of trace metal ions which catalyze the oxidation of iodide ion by oxidizing agents such as hydrogen peroxide, peroxoborate and chlorate by means of an iodide ion-selective electrode [3–9] and a spectrofluorophotometer [10]. These indicator reaction can be transformed to a Landolt reaction by the addition of L-ascorbic acid and the present authors have reported the determination of molybdenum(VI) [8, 10] and tungsten(VI) [9].

The present paper describes the application of the Landolt reaction to the trace determination of molybdenum(VI) on the basis of its catalytic effect on the peroxoborate-iodide indicator reaction by using an iodide ion-selective electrode. The proposed method is successfully applied to the determination of molybdate ion in sea water.

## Theoretical Consideration

The indicator reaction on which the present method is based proceeds according to the following stoichiometry:

$$BO_3^- + 3\,I^- + 2\,H^+ \xrightarrow{Mo(VI)} BO_2^- + I_3^- + H_2O\,. \qquad (1)$$

In the presence of a catalyst, this redox reaction proceeds with a considerable rate, but it is very slow without catalyst. The reaction is transformed to a Landolt reaction by the addition of L-ascorbic acid. The triiodide ions produced are then reduced immediately so that the iodide ion concentration is kept constant to the initial concentration until all the L-ascorbic acid is oxidized:

$$C_6H_8O_6 + I_3^- \rightarrow C_6H_6O_6 + 3\,I^- + 2\,H^+\,. \qquad (2)$$

The time necessary to elapse till the appearance of triiodide ions is called the induction period. As the oxidation of L-ascorbic acid releases the same number of hydrogen ions, the concentration of hydrogen ion does not change during the induction period. Thus, iodide and hydrogen ion concentrations remain constant as long as L-ascorbic acid is present in the reaction mixture.

The reaction rate can be expressed as

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

where $C_k$ is the catalyst concentration, $k$ and $k'$ are the products of the rate constants of the catalyzed and

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uncatalyzed reaction including the concentrations of iodide and hydrogen ion, respectively. Integration of Eq. (3) yields

$$\frac{1}{t} = \frac{k \cdot C_k + k'}{\ln \dfrac{[BO_3^-]_0}{[BO_3^-]_0 - [C_6H_8O_6]_0}} \tag{4}$$

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

A linear calibration curve can be obtained by plotting the reciprocal of the induction period against the catalyst concentration.

The concentration of iodide ion begins to decrease when all the L-ascorbic acid has been consumed. The time required for the complete consumption of L-ascorbic acid is measured by recording the potential of the iodide ion-selective electrode against time.

## Experimental

### *A. Apparatus*

Potential measurements were carried out with a Corning Digital 110 pH-meter equipped with a Hitachi recorder, 056. A Toa iodide ion-selective electrode, I-125 and calomel electrode, HC-205C, were used throughout the study. The temperature of the reaction mixture was kept constant to 25 ± 0.5°C by the use of a Yanagimoto constant temperature bath, P8-PC.

### *B. Reagents*

Molybdenum(VI) stock solution (0.01 M) was prepared by dissolving 3.0899 g of $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ in 250 ml of water. The concentration of the solution was standardized by a adding an excess amount of 0.01 M $Na_2H_2$EDTA and the solution was then back-titrated with standard 0.01 M lead sulfate at pH 5 by the aid of XO metallochromic indicator.

Sodium peroxoborate solution (0.1 M) was prepared every week by dissolving 15.3860 g of $NaBO_3 \cdot 4\,H_2O$ in 1 l of water. It was stored in a dark bottle in a refrigerator.

Potassium iodide stock solution (0.1 M) was prepared by dissolving about 16.6 g of reagent in 1 l of water. The stock solution was potentiometrically titrated against silver nitrate standard solution by the aid of an iodide ion-selective electrode and stored in a dark bottle in a refrigerator. L-Ascorbic acid solution (0.1 M) was prepared by dissolving 1.7613 g of reagent in 100 ml of water just before use. The chemicals used in this study were all of analytical reagent grade and all the water used was deionized and then twice distilled.

Chelex-100 resin (100–200 mesh) was obtained from Bio-Rad Laboratories. The resin was digested by 2 M nitric acid and was filled in a 12-mm diameter ion-exchange column to make a 5-cm resin bed. The resin was rinsed with water until pH 5–6 of the effluent.

Dowex 50W-X8 resin (100–200 mesh) was filled in a 12-mm diameter ion-exchange column to make a 5-cm resin bed. This was rinsed first with 5 M hydrochloric acid, then with water, and the resin was transformed to the Na-form by 2 M sodium chloride and then rinsed thoroughly with water.

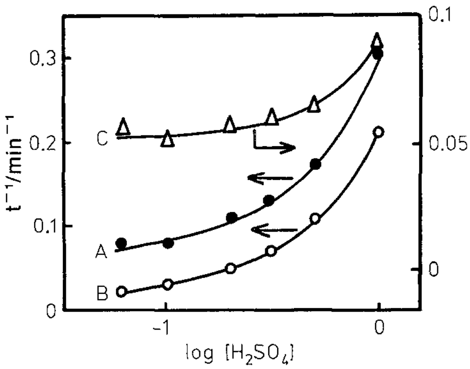

**Fig. 1.** Effect of sulfuric acid concentration on the reciprocal of induction period. *A* Observed with [Mo(VI)] = 14 µM, *B* blank value, *C* net value, (*A*–*B*). Composition of reaction mixture: [KI] = 5 mM, $[NaBO_3]$ = 62.5 mM, [L-ascorbic acid] = 10 mM, temp. = 25 ± 0.5°C

### *C. Procedure*

The established procedure for the determination of 0.5 to 5.0 µM of molybdenum(VI) is as follows: To a 25-ml volumetric flask containing an appropriate amount of molybdenum(VI) sample solution were added 5 ml of 0.1 M potassium iodide, 1 ml of 5 M sulfuric acid and 5 ml of 0.01 M L-ascorbic acid, and the flask was filled up to the mark with water (solution A). Another 25-ml flask was filled with 30 mM sodium peroxoborate solution (solution B). Bring both solutions to 25°C in a thermostat, then transfer solution B to a 200-ml beaker in the thermostat and insert the iodide ion-selective electrode and the SCE. When the e.m.f. of the electrodes is stable, rapidly pour solution A into the beaker and at the same time switch on the recorder. The e.m.f. remains almost constant until all the L-ascorbic acid is consumed, and shifts to a more positive value when the concentration of the iodide ions begins to decrease.

## Results and Discussion

### *a) Effect of Sulfuric Acid Concentration*

The effect of sulfuric acid concentration on the reciprocal of the induction period was investigated with fixed concentrations of sodium peroxoborate, potassium iodide, L-ascorbic acid and molybdenum(VI). The results are shown in Fig. 1. Various amounts of sulfuric acid solutions were added to the reaction mixture containing 14 µM of molybdenum(VI) (curve A). Blank reactions with the same sulfuric acid concentrations were also carried out (curve B). The difference of the reciprocal of the induction period are also shown in the figure (curve C). It was found that the reciprocal of the induction period of both catalyzed and uncatalyzed reaction increased with increasing sulfuric acid concentration in the reaction mixture. Net values of the reciprocal of the induction period remain almost constant at these concentration ranges while the blank reaction increased with increasing sulfuric acid concentration. Thus, the most suitable concentration was found to be $10^{-1}$ M.

### *b) Effect of Sodium Peroxoborate Concentration*

The effect of sodium peroxoborate concentration on the reciprocal of the induction period was examined. As shown

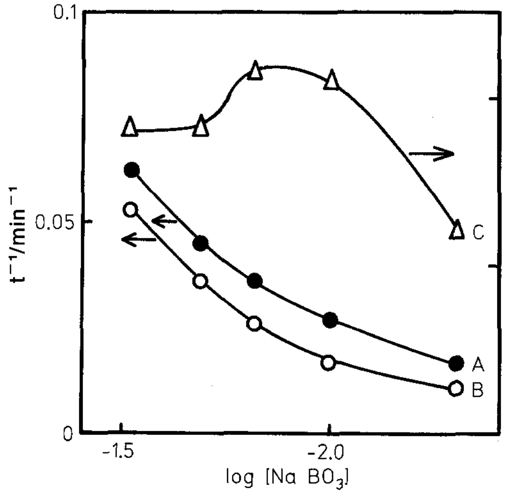

**Fig. 2.** Effect of sodium peroxoborate concentration on the reciprocal of induction period. A Observed with [Mo(VI)] = 1.4 μM, *B* blank value, *C* net value, (*A*−*B*). Composition of reaction mixture: [KI] = 10 mM, $[H_2SO_4]$ = 0.1 M, [L-ascorbic acid] = 10 mM, temp. = 25 ± 0.5°C

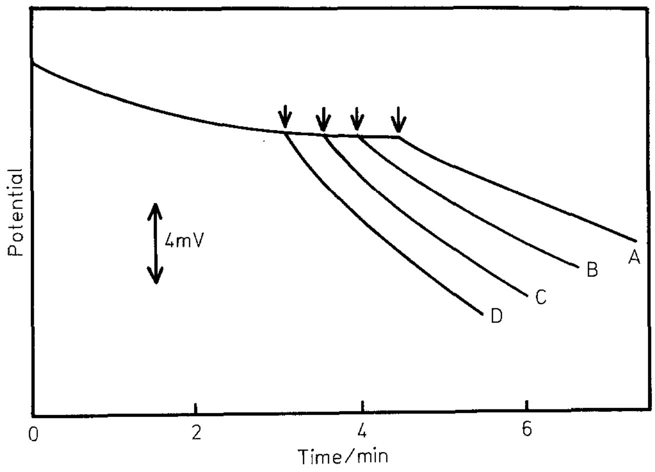

**Fig. 4.** Potential change of iodide ion-selective electrode. Composition of reaction mixture: [KI] = 10 mM, $[NaBO_3]$ = 15 mM, $[H_2SO_4]$ = 0.1 M, [L-ascorbic acid] = 1.0 M, [Mo(VI)]: *A* 0, *B* 0.5, *C* 1.0, *D* 2.0 μM, temp. 25 ± 0.5°C. Arrow indicates the appearance of triiodide ion

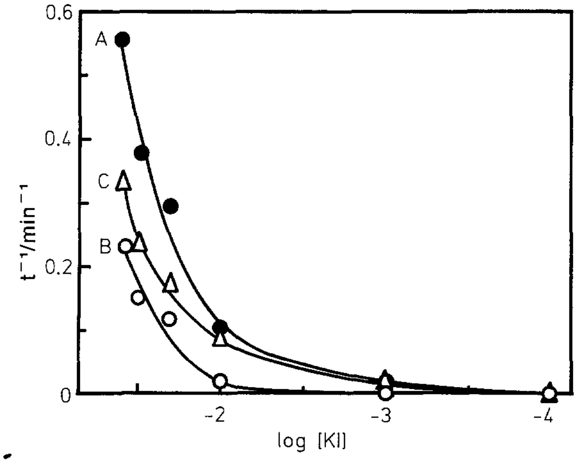

**Fig. 3.** Effect of potassium iodide concentration on the reciprocal of induction period. *A* Observed with [Mo(VI)] = 14 μM, *B* blank value, *C* net value, (*A*−*B*). Composition of reaction mixture: $[NaBO_3]$ = 15 mM, $[H_2SO_4]$ = 0.1 M, [L-ascorbic acid] = 10 mM, temp. 25 ± 0.5°C

**Table 1.** Effect of diverse ions

| Ion | Added as | Conc. (μM) | Error of [Mo(VI)] found (%) |
|---|---|---|---|
| Mg(II) | $MgCl_2$ | 2,000 | +3.21 |
| Ca(II) | $CaCl_2$ | 2,000 | +3.17 |
| Zn(II) | $Zn(CH_3COO)_2$ | 2,000 | +2.11 |
| Ni(II) | $NiCl_2$ | 200 | −1.74 |
| Cd(II) | $CdCl_2$ | 200 | −1.18 |
| Zr(IV) | $ZrOCl_2$ | 40 | −3.24 |
| Mn(II) | $MnCl_2$ | 2 | +2.45 |
| Mn(II)[a] | $MnCl_2$ | 200 | −2.53 |
| V(IV) | $VOSO_4$ | 2 | +3.74 |
| V(IV)[a] | $VOSO_4$ | 200 | −1.48 |
| Cu(II) | $CuCl_2$ | 2 | −4.23 |
| Cu(II)[a] | $CuCl_2$ | 200 | −4.43 |
| Fe(II) | $FeSO_4$ | 2 | +5.38 |
| Fe(II)[a] | $FeSO_4$ | 200 | +5.15 |
| Fe(III) | $FeCl_3$ | 2 | −4.52 |
| Fe(III)[a] | $FeCl_3$ | 200 | −8.56 |
| Mixture[b] | – | 1,000[c] | −7.00 |
| W(VI) | $Na_2WO_4$ | 2 | +56.67 |
| W(VI) | $Na_2WO_4$ | 0.2 | +0.52 |

[Mo(VI)] = 2 μM, [KI] = 10 mM, $[NaBO_3]$ = 15 mM, $[H_2SO_4]$ = 0.1 M, [L-ascorbic acid] = 1.0 mM, temp. = 25 ± 0.5°C

[a] Treated with Dowex 50W-X8 column (Na-form)

[b] Concentration of Mn(II), V(IV), Cu(II), Fe(II) and Fe(III) each 200 μM

[c] Total concentration

in Fig. 2, the net value became maximum at a sodium peroxoborate concentration of about 15 mM.

### *c) Effect of Potassium Iodide Concentration*

The dependence of the iodide ion concentration on the reciprocal of the induction period was investigated. As shown in Fig. 3, the blank value increases rapidly when the concentration of the iodide ions is higher than 10 mM, and this was chosen as the most suitable concentration.

### *d) Calibration Curve*

The calibration curve for molybdenum(VI) was obtained according to the above procedure. Potential-time curves for various molybdenum(VI) concentrations in the range from 0 to 2.0 μM are shown in Fig. 4. Arrows in the figure mark the end of the induction period. The calibration curve was obtained by plotting the reciprocal of the induction period vs. the molybdenum(VI) concentration. The linear range was found to be 0.5 to 5.0 μM and 5.0 to 50.0 μM. The regression equations (and the 95% confidence limits) are as follows:

*0.5−5.0 μM:* $1/t = [(4.79 \pm 0.0244)\,[\mathrm{Mo(VI)}] + (0.598 \pm 0.0703)] \times 10^{-2}$, where *t* in s and [Mo(VI)] in μM.

*5.0−50.0 μM:* $1/t = [(0.681 \pm 0.0023)\,[\mathrm{Mo(VI)}] + (0.718 \pm 0.0644)] \times 10^{-2}$.

**Table 2.** Determination of molybdate ion in sea water

| | Location of sampling | | Mo found ($\mu g \cdot l^{-1}$) |
|---|---|---|---|
| Present method[a] | Japan Sea, Zenibako | | 7.90 |
| | | | 8.70 |
| | | | 8.73 |
| | | | 9.14 |
| | | Av. | 8.62 |
| | | St. Dev. | 0.52 |
| Kuroda and Tarui [11] | Tokyo Bay, Chiba Harbour | | 12.0[b] |
| Ternero and Gracia [20] | Atlantic Ocean, Huelva | | 7.5 |
| | | | 7.2 |

[a] Sampling: Feb. 26, 1984

[b] Average of eight determinations

### *e) Interference*

The interference by some diverse ions for the determination of molybdenum(VI) was examined; the results are compiled in Table 1. The composition of the reaction mixture is the same as that used for the construction of the calibration curve. The molybdenum(VI) concentration was kept to 2.0 μM. The concentrations of diverse ions were changed from 0.1 to 1,000 times more than that of molybdenum(VI). Triplicate measurements were carried out in the presence and absence of interferent. A plus sign in the table implies acceleration of the rate of indicator reaction. Equal amounts of maganese(II), vanadium(IV), copper(II), iron(II) and iron(III) caused slight interferences. However, as shown in the table, the interference by these metal ions can easily be reduced by treating the sample solution containing both molybdenum(VI) and the foreign ions with a Dowex 50W-X8 column.

### *f) Determination of Molybdate Ion in Sea Water*

The proposed method was successfully applied to the determination of trace amounts of molybdate ion in sea water. Sea water was sampled from the Japan Sea at Zenibako beach. The samples were filtered by the use of Toyo No. 5C filter paper and stored in polyethylene bottles. The pH of the sample solutions (1.5 l) was adjusted to 5.5 by the addition of 75 ml of 2 M acetate buffer. Then the sample solution was passed through the Chelex-100 column at a rate of less than 5 ml · $min^{-1}$. The resin was rinsed with 200 ml of 0.1 M acetate buffer solution (pH 5.5), then the molybdate was eluted with 40 ml of 4 M ammonia solution and the solution was evaporated to about 10 ml by the use of a hot plate. The concentration of molybdate was determined by the above procedure. Results are compiled in Table 2. They show good agreement with the reported value of 10 $\mu g \cdot l^{-1}$ [2, 10, 20].

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