CATALYTIC DETERMINATION OF IRON(III) AND ZIRCONIUM(IV) BY THEIR
EFFECTS ON THE HYDROGEN PEROXIDE-IODIDE REACTION WITH THE AID OF
IODIDE ION-SELECTIVE ELECTRODE

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Trace amount of iron(III) and zirconium(IV) can be determined by using their catalytic effects on the hydrogen peroxide-iodide reaction in the acidic environment. The reaction rate was followed by measuring the concentration of iodide ion by means of an iodide ion-selective electrode. The most suitable concentrations of hydrogen peroxide, potassium iodide, and hydrochloric acid for the determination of iron(III) and zirconium(IV) were found to be 0.02 M and 4 mM, 0.1 mM and 1.0 mM, 0.55 M and 4 mM, respectively. The calibration curves with good proportionality were obtained in the range of 5 to 160 μ M for iron(III) and 1.0 to 12.0 μ M for zirconium(IV).

1 Introduction

Many metal ions, which catalyze the oxidation of iodide ion to iodine by hydrogen peroxide in acidic medium, are determined catalytically. Almost all the methods are based on the formation of iodine, whose concentration is observed by photometric method by the addition of starch or Variamine Blue. On the other hand, consumption of iodide ion and/or formation of iodine can also be traced potentiometrically by the aid of a silver or platinum electrode as well as ion-selective electrode.

Klockow et al. described the catalytic determination of molybdenum¹⁾ and fluoride²⁾ by the potentiostatic method with an automatic buret using a platinum electrode as indicator electrode.

The uses of ion-selective electrode in some catalytic investigations are reported. Efstathiou and Hadjiioannou determined chromium³⁾ and magnesium⁴⁾ by means of a periodate sensitive perchlorate ion-selective electrode using periodate as the oxidant. Rechnitz and co-worker⁵⁾ reported the enzymatic determination of cholesterol using a flow-through ion-selective electrode. We have also made catalytic micro determination of metal ions⁶⁻¹⁰⁾ by the aid of an iodide ion-selective electrode.

In the present paper, determination of trace amount of iron(III) and zirconium(IV) was described by using iodide ion-selective electrode as the tracer of

consumption of iodide ion in the reaction mixture.

2 Theory

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

Yatsimirskii¹¹⁾ suggested that the kinetic equation for iron(III) and zirconium(IV) used as the catalyst have different forms: namely, one has for iron(III)¹²⁾

$$-\frac{d[\text{I}^-]}{dt} = k \cdot C_k \cdot C_{\text{H}_2\text{O}_2} \cdot C_{\text{I}^-} \quad (2)$$

and for zirconium(IV)¹³⁾

$$-\frac{d[\text{I}^-]}{dt} = k_1 \cdot C_k \cdot C_{\text{I}^-} \quad (3)$$

where k and k_1 are the rate constants, C_k and C_{I^-} are the concentration of the catalyst and iodide ion, respectively. If one chooses a much higher concentration of hydrogen peroxide than iodide ion, in the case of determining iron(III), the eqn.(2) is simplified into the same form as eqn.(3). Namely,

$$-\frac{d[\text{I}^-]}{dt} = k_2 \cdot C_k \cdot C_{\text{I}^-} \quad (4)$$

where $k_2 = k \cdot C_{\text{H}_2\text{O}_2}$. The present indicator reaction proceeds very slowly in the weakly acidic medium, but at the pH lower than unity, the reaction occurs without catalyst. The present investigation being carried out under such a condition, in the case of determining iron(III), the kinetic equation is shown as follows.

$$-\frac{d[\text{I}^-]}{dt} = (k_2 \cdot C_k + k_3) \cdot C_{\text{I}^-} \quad (5)$$

where k_3 is the rate constant of uncatalyzed reaction including the concentration of hydrogen peroxide. Integration of eqn.(5) yields

$$\log[\text{I}^-] = -(k_2 \cdot C_k + k_3) \cdot t + \log[\text{I}^-]^* \quad (6)$$

where $[\text{I}^-]^*$ is the initial concentration of iodide ion.

The potential of the iodide ion-selective electrode is shown by

$$E = E^\circ - \frac{2.303RT}{F} \log(a_{\text{I}^-} + \sum K_j \cdot a_j^{1/z_j}) \quad (7)$$

where K_j is the selectivity coefficient, a_j the activity of j -th ion, and z_j is the absolute value of charge on j -th ion. Combination of eqns.(6) and (7) indicates that the rate of potential change in unit time is proportional to the catalyst concentration.

3 Experimental

3.1 Apparatus Potential measurements were carried out with a Toa pH meter, type HM-7A, equipped with a Hitachi recorder O56. A Toa iodide ion-selective electrode, I-125, and a calomel electrode, HC-205C, were used throughout the study. Reaction mixture was thermostated at 25 or 30 °C with a Yanagimoto constant-temperature bath, P8-PC.

3.2 Reagents Hydrogen peroxide solution, 0.1 M. Dilute 11.34 g of 30% H_2O_2 solution (Wako Pure Chemicals Co.) into 1 dm³ with water. The solution was stored in a brown bottle in a refrigerator.

Potassium iodide stock solution, 0.1 M. Dissolve 16.6 g of analytical reagent grade KI (Wako) in 1 dm³ of water. It was stored in a brown bottle in a refrigerator.

The pH of the reaction mixture was adjusted with 2 M hydrochloric acid solution by using the pH meter equipped with a Toa glass electrode, HG-205, and the calomel electrode.

Ferric chloride stock solution, 0.990 mM. Dissolve 0.2703 g of analytical reagent grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako) into 250 ml of 2 M hydrochloric acid solution and dilute to 1 dm³ with water. The stock solution was standardized against 10.0 mM $\text{Na}_2\text{H}_2\text{edta}$ solution by using Cu-PAN metallochromic indicator at pH 3.0.

Zirconyl nitrate stock solution, 1.05₄ mM. Dissolve 0.2673 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Wako) to 143 ml of nitric acid and make up to 1 dm³ with water. The solution was standardized by the chelatometric back titration with 10.0 mM $\text{Na}_2\text{H}_2\text{edta}$ solution and CuSO_4 solution by the aid of PAN indicator.

All the water used in this study was once deionized and then twice distilled.

4 Results and Discussion

4.1 Procedure for the determination of zirconium(IV) To a sample solution containing 9.1 µg to 0.11 mg of zirconium(IV) in a 50-ml measuring flask were added 10 ml of 0.2 M hydrogen peroxide solution and then water was added to the mark (solution A). To another 50-ml measuring flask containing 10 ml of 1 mM potassium iodide solution were added 2 ml of 0.2 M hydrochloric acid and then water was added to the mark (solution B). After two solutions were thermostated at 25 °C, one transferred the solution B into a 100-ml beaker in the constant-temperature bath and then inserted the iodide ion-selective electrode and SCE. When the potential of the ion-selective electrode showed a stable value, the solution A was poured into the beaker and at the same time, one switched on the recorder. Potential change was recorded for 10 min.

4.2 Procedure for the determination of iron(III) To a sample solution containing 28 µg to 0.89 mg of iron(III) in a 50-ml measuring flask were added 10 ml of 0.2 M hydrogen peroxide solution and then water to the mark (solution A). To a solution containing 10 ml of 0.04 M potassium iodide were added 10 ml of 5.5 M hydrochloric acid solution and water was added to the mark (solution B). Then, one applies the same procedure as above.

4.3 Effect of pH Effect of pH on the rate of potential change was measured and the results are shown in Fig. 1. In the case of zirconium(IV) as the catalyst, the rate of potential change shows a maximum at pH 2.4, where the blank reaction is negligibly small. The rate of blank reaction at lower pH region increases with decreasing pH of the reaction mixture. Because ferric ion forms hydroxide in a mild acidic solution, pH of the reaction mixture must be less than unity. The most suitable pH was found to be 0.26 for the determination of iron(III).

4.4 Effect of the concentration of hydrogen peroxide The dependence of the net rate of potential change on the hydrogen peroxide concentration was observed and the results are shown in Fig. 2. Various amounts of hydrogen peroxide solution were added to the solution containing 100 μM of iron(III) or 10 μM of Zirconium(IV) and fixed concentrations of potassium iodide and hydrogen ion. It was found that the net rate of potential change showed a constant value for the concentration higher than 10^{-2} M of hydrogen peroxide, when iron(III) was used as a catalyst. In the case of zirconium(IV), the rate of potential change increased with increasing concentration of hydrogen peroxide, however, when the concentration exceeds 5 mM, blank reaction rate becomes remarkable. Thus, the concentration of the hydrogen peroxide was adjusted to 0.02 M for iron(III) and 4 mM for zirconium(IV).

4.5 Effect of iodide ion concentration Effect of iodide ion concentration on the rate of potential change was examined. As shown in Fig. 3, the rate of potential change increased with decreasing iodide ion concentration in the case of zirconium(IV) catalyst, but all the iodide ion is oxidized.

Fig. 1 Effect of pH

—○— : $[\text{Zr(IV)}] = 11.34 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 2.5 \text{ mM}$, $[\text{KI}] = 0.5 \text{ mM}$, —▲— : $[\text{Fe(III)}] = 100 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 0.01 \text{ M}$, $[\text{KI}] = 0.1 \text{ mM}$, —●— : blank, —△— : $\text{Fe(III)} - \text{blank}(\text{net value})$.

Fig. 2 Effect of the concentration of hydrogen peroxide

—○— : $[\text{Zr(IV)}] = 10 \mu\text{M}$, $[\text{KI}] = 1 \text{ mM}$, $[\text{HCl}] = 4 \text{ mM}$, —▲— : $[\text{Fe(III)}] = 100 \mu\text{M}$, $[\text{KI}] = 0.1 \text{ mM}$, $[\text{HCl}] = 0.55 \text{ M}$, —●— : blank, —△— : $\text{Fe(III)} - \text{blank}(\text{net value})$.

within ten minutes at the concentration lower than 0.5 mM. In the case of iron(III), the rate of potential change showed a constant value in the iodide ion concentration range from 0.05 to 0.15 mM. Namely, the most suitable iodide ion concentration was found to be 1.0 mM and 0.1 mM for zirconium(IV) and iron(III), respectively.

4.6 Calibration curve Calibration curves for iron(III) and zirconium(IV) were obtained according to the above established conditions, as shown in Figs. 4 and 5. The linear relationship between the net reaction rate and concentration of iron(III) and zirconium(IV) was observed in the range 5 - 160 μM and 1.0 - 12.0 μM , respectively. The blank value of the calibration curve for iron(III) is about 9.8 mV min^{-1} ,

Fig. 4 Calibration curve for Fe(III)
[KI] = 0.1 mM, [HCl] = 0.55 M, $[\text{H}_2\text{O}_2]$ = 0.02 M, Temp. 30°C. The calibration curve is expressed by $y = (0.0396 \pm 0.001) \cdot C_k + 9.766 \pm 0.012$, where y is rate of potential change in mV min^{-1} and C_k is the catalyst concentration in μM .

Fig. 3 Effect of the concentration of potassium iodide

—○— : $[\text{Zr(IV)}] = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 0.01 \text{ M}$, $[\text{HCl}] = 4 \text{ mM}$, —▲— : $[\text{Fe(III)}] = 100 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 0.01 \text{ M}$, $[\text{HCl}] = 0.55 \text{ M}$, —●— : blank, —△— : Fe(III) - blank (net value).

Fig. 5 Calibration curve for Zr(IV)
[KI] = 1 mM, [HCl] = 4 mM, $[\text{H}_2\text{O}_2] = 4 \text{ mM}$, Temp. 25°C. The curve is expressed by $y = (1.049 \pm 0.004) \cdot C_k - 0.792 \pm 0.030$, where y and C_k are the same as in Fig. 4.

while that of zirconium(IV) is almost zero. The difference is mainly due to the pH of reaction mixture, as mentioned before.

4.7 Interference Since some metal ions catalyze the present indicator reaction, the interference by some diverse ions was tested and summarized in Table 1. The composition of the reaction mixture is the same as above and the concentration of iron(III) and zirconium(IV) was 50 μM and 10 μM , respectively. As expected, molybdenum(VI), vanadium(IV), tungsten(VI), and copper(II) showed very strong interferences for the determination of both iron(III) and zirconium(IV).

Table 1 Effect of interfering ions

Ion	Added as	Fe(III)		Zr(IV)	
		Concn. (μM)	Error (%)	Concn. (μM)	Error (%)
Mo(VI)	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	0.5	+1.81	0.1	+11.6
V(IV)	$\text{VO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	0.5	-2.43	1.0	-6.14
W(VI)	$(\text{NH}_4)_2\text{WO}_4$	0.5	+1.28	1.0	-6.13
Mn(II)	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	5000	-0.34	1.0	-8.18
Cu(II)	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.5	+1.32	1.0	-10.3
Zn(II)	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	5000	-0.88	0.1	-0.52
Pb(II)	$\text{Pb}(\text{NO}_3)_2$	50	-1.33	1000	-4.56
Fe(III)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	—	—	10	-9.43
Zr(IV)	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.5	+0.50	—	—

[Fe(III)] = 50 μM , [Zr(IV)] = 10 μM

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