# CATALYMETRIC 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 μM for iron(III) and 1.0 to 12.0 μM 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 catalymetrically. 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 catalymetric determination of molybdenum[1] and fluoride[2] by the potentiostatic method with an automatic buret using a platinum electrode as indicator electrode.

The uses of ion-selective electrode in some catalymetric investigations are reported. Efstathiou and Hadjiioannou determined chromium[3] and magnesium[4] by means of a periodate sensitive perchlorate ion-selective electrode using periodate as the oxidant. Rechnitz and co-worker[5] reported the enzymatic determination of cholesterol using a flow-through ion-selective electrode. We have also made catalytic micro determination of metal ions[6-10] 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:

$$H_2O_2 + 2\ I^- + 2\ H^+ \longrightarrow I_2 + 2\ H_2O \tag{1}$$
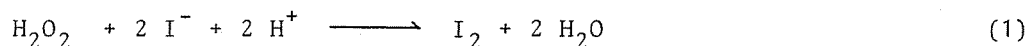
Yatsimirskii[11] suggested that the kinetic equation for iron(III) and zirconium(IV)
used as the catalyst have different forms: namely, one has for iron(III)[12]

$$-\frac{d[I^-]}{dt} = k \cdot C_k \cdot C_{H_2O_2} \cdot C_{I^-} \tag{2}$$

and for zirconium(IV)[13]

$$-\frac{d[I^-]}{dt} = k_1 \cdot C_k \cdot C_{I^-} \tag{3}$$

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 con-
centration 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,

$$-\frac{d[I^-]}{dt} = k_2 \cdot C_k \cdot C_{I^-} \tag{4}$$

where $k_2 = k \cdot C_{H_2O_2}$. 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.

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

where $k_3$ is the rate constant of uncatalyzed reaction including the concentra-
tion of hydrogen peroxide. Integration of eqn.(5) yields

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

where $[I^-]^*$ is the initial concentration of iodide ion.
  The potential of the iodide ion-selective electrode is shown by

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

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 056.  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 $dm^3$ 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 $dm^3$ 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 $FeCl_3 \cdot 6H_2O$ (Wako) into 250 ml of 2 M hydrochloric acid solution and dilute to 1 $dm^3$ with water.  The stock solution was standardized against 10.0 mM $Na_2H_2edta$ solution by using Cu-PAN metallochromic indicator at pH 3.0.
Zirconyl nitrate stock solution, $1.05_4$ mM.  Dissolve 0.2673 g of $ZrO(NO_3)_2 \cdot 2H_2O$ (Wako) to 143 ml of nitric acid and make up to 1 $dm^3$ with water.  The solution was standardized by the chelatometric back titration with 10.0 mM $Na_2H_2edta$ 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 $\mu$M of iron(III) or 10 $\mu$M 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)
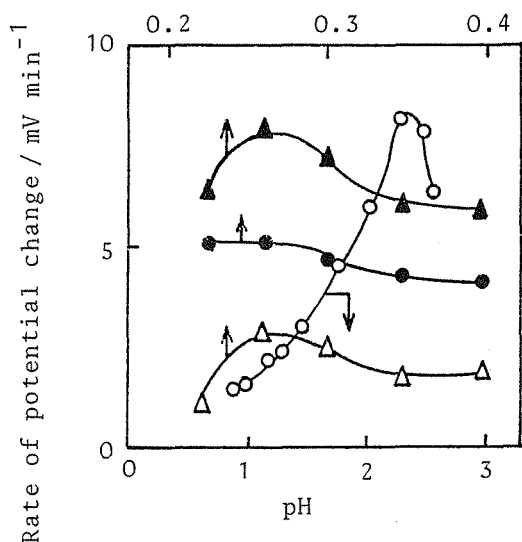catalyst, but all the iodide ion is oxidized



Fig. 1  Effect of pH

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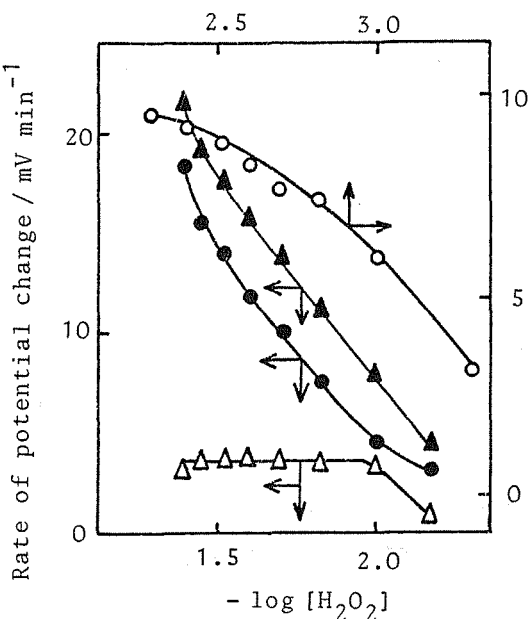


Fig. 2  Effect of the concentration
of hydrogen peroxide

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

within ten minuts 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 $\mu M$ and 1.0 - 12.0 $\mu M$, respectively. The blank value of the calibration curve for iron(III) is about 9.8 mV $min^{-1}$,

Fig. 3 Effect of the concentration of potassium iodide

—○— : [Zr(IV)] = 10 $\mu M$, $[H_2O_2]$ = 0.01 M, [HCl] = 4 mM, —▲— : [Fe(III)] = 100 $\mu M$, $[H_2O_2]$ = 0.01 M, [HCl] = 0.55 M, —●— : blank, —△— : Fe(III) − blank(net value).

Fig. 4 Calibration curve for Fe(III)

[KI] = 0.1 mM, [HCl] = 0.55 M, $[H_2O_2]$ = 0.02 M, Temp. 30°C. The calibration curve is expressed by y = (0.0396 ± 0.001)·$C_k$ + 9.766 ± 0.012, where y is rate of potential change in mV $min^{-1}$ and $C_k$ is the catalyst concentration in $\mu M$.
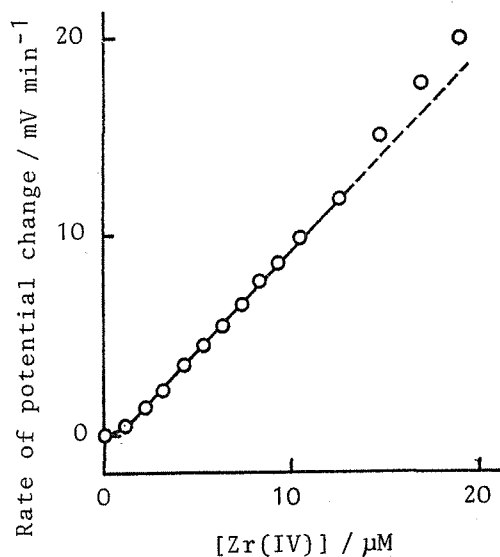
Fig. 5 Calibration curve for Zr(IV)
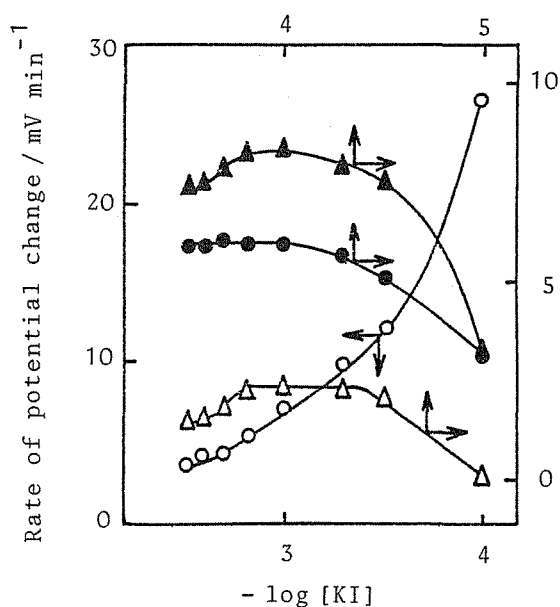
[KI] = 1 mM, [HCl] = 4 mM, $[H_2O_2]$ = 4 mM, Temp. 25°C. The curve is expressed by y = (1.049 ± 0.004)·$C_k$ - 0.792 ± 0.030, where y and $C_k$ are the same as in Fig. 4.

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 reac-
tion, 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) | $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ | 0.5 | +1.81 | 0.1 | +11.6 |
| V(IV) | $VOSO_4 \cdot 3H_2O$ | 0.5 | -2.43 | 1.0 | -6.14 |
| W(VI) | $(NH_4)_2WO_4$ | 0.5 | +1.28 | 1.0 | -6.13 |
| Mn(II) | $MnSO_4 \cdot 4H_2O$ | 5000 | -0.34 | 1.0 | -8.18 |
| Cu(II) | $CuSO_4 \cdot 5H_2O$ | 0.5 | +1.32 | 1.0 | -10.3 |
| Zn(II) | $ZnSO_4 \cdot 7H_2O$ | 5000 | -0.88 | 0.1 | -0.52 |
| Pb(II) | $Pb(NO_3)_2$ | 50 | -1.33 | 1000 | -4.56 |
| Fe(III) | $FeCl_3 \cdot 6H_2O$ | —— | —— | 10 | -9.43 |
| Zr(IV) | $ZrO(NO_3)_2 \cdot 2H_2O$ | 0.5 | +0.50 | —— | —— |

[Fe(III)] = 50 μM,   [Zr(IV)] = 10 μM

### References

1)  H. Weisz, D. Klockow, H. Ludwig : Talanta, 16, 928 (1969).
2)  D. Klockow, H. Ludwig, M. A. Giraucio : Anal. Chem., 42, 1682 (1970).
3)  C. E. Efstathiou, T. P. Hadjiioannou : Anal. Chem., 49, 414 (1977).
4)  C. E. Efstathiou, T. P. Hadjiioannou : Talanta, 24, 270 (1977).
5)  D. S. Papastathopoulos, G. A. Rechnitz : Anal. Chem., 47, 1792 (1975).
6)  M. Kataoka, T. Kambara : Bunseki Kiki, 10, 773 (1972).
7)  M. Kataoka, T. Kambara : Bunseki Kagaku, 23, 1157 (1974).
8)  M. Kataoka, T. Kambara : Denki Kagaku, 45, 674 (1977).
9)  M. Kataoka, M. Takahashi, T. Kambara : Bunseki Kagaku, 28, 169 (1979).
10)  M. Kataoka, S. Miyagata, T. Kambara : Nippon Kagaku Kaishi, 1980, 1520.
11)  K. B. Yatsimirskii : "Kinetic Methods of Analysis", (1966), (Pergamon Press,
     Oxford) p.87.
12)  K. B. Yatsimirskii, G. A. Karacheva : Zh. Neorg. Khim., 3, 352 (1958).
13)  K. B. Yatsimirskii, L. P. Raizman : Zh. Neorg. Khim., 5, 593 (1961).