Catalytic Analysis. XVII : Microdetermination of Iron by the Reaction between p-Phenylendiamine and Hydrogen Peroxide

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Microdetermination of Iron by the Reaction between p-Phenylendiamine and Hydrogen Peroxide*

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Synopsis

Applying the catalytic action of iron to the reaction between p-phenylendiamine and hydrogen peroxide, the relation between the time required for the development of the brown color and the amount of iron added was studied with Duboscq's colorimeter, which rendered it possible to determine 0.5~5γ of iron by the time measurement under the same condition. The condition of the solution and influences of some diverse ions on the determination were studied.

I. Introduction

Applying the catalytic action of osmium to the reaction between p-phenylen-diamine and hydrogen peroxide, the microdetermination of osmium was investigated[1], as reported in the preceding paper, by measuring the time required for the development of the brown color in a certain concentration with Pulfrich's photometer. It has already been found that iron also has the catalytic action on the same reaction. Using Duboscq's colorimeter, the microamount of iron was determined by the similar method.

II. Experiments and results

1. Apparatus and reagents

An usual lamp was used as the light source of the Duboscq's colorimeter.

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(1) T. Shiokawa, Sci. Rep. RITU, A **2** (1950), 293,

Para-phenylendiamine solution was prepared by dissolving the reagent in redistilled water every day.

Hydrogen peroxide solution was standardized with 0.1 N potassium permanganate solution every day, and its concentration was adjusted at about 0.5%. A standard ferric solution was prepared by dissolving ferric chloride in redistilled water and its stock solution contained about 1 mg Fe/ml, which was determined by the liquid amalgam method.

2. Experimental procedure

A definite amount of redistilled water was taken in a small Erlenmeyer flask in which the final volume of the solution became 8 ml, and then the reagents were added in it. It was shaken and transferred to the cell which was fixed at the position of 20 on the scale. The cell of a standard color solution was kept at the position of 25 on the scale. When the coloration of the sample solution became just the same color, the time measurement with a stop watch was started. The cell of the standard solution was transferred rapidly to the position of 60 on the scale.

By measuring the time required until the brown color of the sample solution became deep and then matched with the color of the standard, some relations were found between the time measured and the amount of iron which might be applicable to the determination of microamounts of iron. Experiments were carried out at room temperature, $5°{\sim}10°C$, with the exception of specially mentioned cases.

3. Standard color solution

The standard color solution was prepared by mixing 0.3 ml of potassium dichromate 10 mg/ml solution, 3 ml of chromium nitrate 8.4 mg/ml solution with 10 ml of water, and 8 ml of it was used in every measurement.
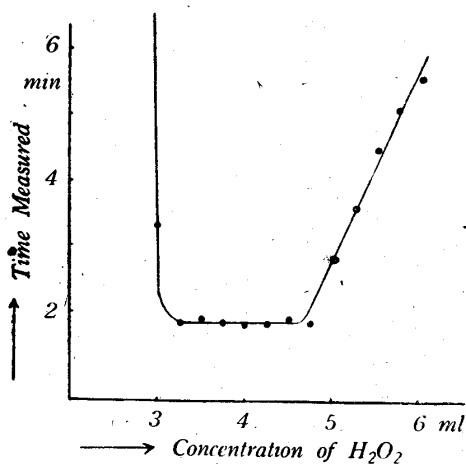
4. Concentration of hydrogen peroxide

↑ Time Measured

——→ Concentration of H_2O_2

Fig. 1

Various volumes of 0.5% hydrogen peroxide solution were used against 2.5 ml of 0.2% p-phenylendiamine, water and 5 γ of iron in 8 ml of the total solution, and the time was measured. As shown in Fig. 1, the reaction velocity was not affected by varying 0.5% hydrogen peroxide contents from 3.2 up to 4.75 ml. Therefore, 4.0 ml of 0.5% hydrogen peroxide was used hereafter.

5. Concentration of p-phenylendiamine

Experiments were made by adding various volumes of p-phenylendiamine

under the condition in which the total volume of the solution was 8 ml containing 4 ml of 0.5% hydrogen peroxide and 5 γ of iron. As shown in Fig. 2, the reaction velocity was not affected by varying 0.2% *p*-phenylendiamine contents from 0.25 up to 3.00 ml and this constant velocity was the largest. Hence, 2.7 ml of 0.2% *p*-phenylendiamine was used in the following experiment.
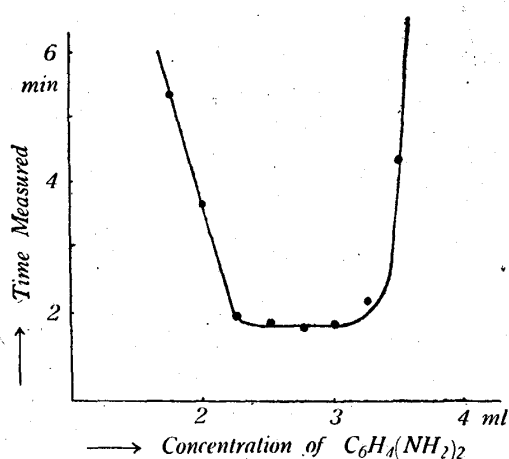

Fig. 2

6. Effect of pH

The experiments were made on the influence of pH, keeping the other conditions constant. Results obtained at several values of pH from 4.2 up to 5.2, which were adjusted by acetic acid-sodium acetate buffer solution, are shown in Table 1. pH was further changed from 5.8 up to 7.2 by the potassium dihydrogenphosphate-disodium hydrogen phosphate buffer solution, and from 7.0 up to 9.0 by the borax-boric acid buffer solution but the reaction velocity was very slow in all cases and so it could not be applied to the determination of iron. Therefore, any buffer solution was not used in the determination of iron.

Talbe 1.

CH_3COOH 0.5N (ml)	CH_3COONa 5% (ml)	pH	Fe 5γ	Time measured (mean of twice) (min)
0	0	4.2	none	about 70
"	"	"	added	1.65
1.75	0.25	4.0	none	10.69
"	"	"	added	0.68
1.00	1.00	4.6	none	9.55
"	"	"	added	0.66
0.50	1.50	5.2	none	6.43
"	"	"	added	0.79

7. Relations between amount of iron and reaction velocity

Under the most suitable condition found in the preliminary experiments, in which 4.0 ml of 0.5% hydrogen peroxide and 2.7 ml of 0.2% *p*-phenylendiamine were contained in 8 ml of the total solution, the time measurements were made with various amounts of iron at 10°C.

As shown in Fig. 3, the relations between the reciprocals of the time and the amounts of iron were linear. This linear relation was represented by the following
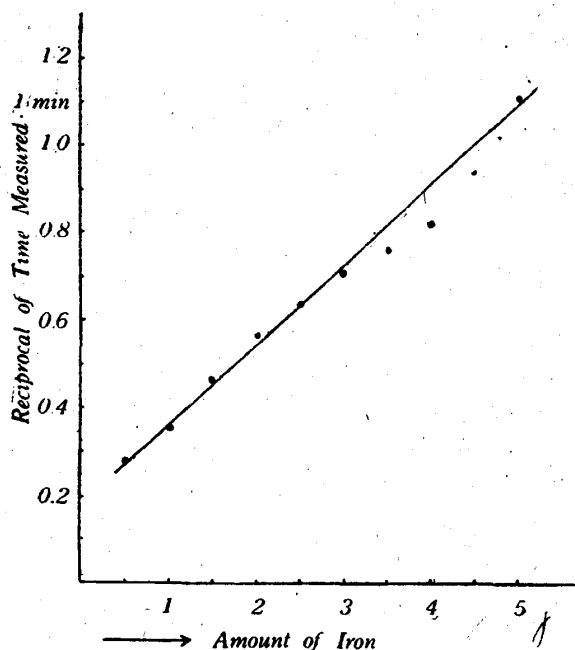
Fig. 3

equation :

$$Q = 6/T - 1.2$$

Q : amount of iron (γ) ; T : time measured (min). Therefore, by measuring the time under the same conditions, the unknown amount of iron can be determined from this graph or equation.

8. Effects of other substances

Effects of organic acid and other ions were studied with the following reagents : formic, tartaric, acetic and citric acids, sulfates of aluminium, chromium and zinc, nitrates of nickel, cobalt and cadmium, acetate of lead, chloride of mercury and manganese, and potassium salts of sulfate, nitrate and chloride and the results are shown in Table 2, 3, 4, 5, 6 and 7. The experiments were made by adding respectively various amounts of these compounds in the presence of 5 γ of iron, keeping the other in the suitable conditions. The

Table 2.

Organic substances used (ml)	Time measured (mean of twice) (min)	
	Alcohol	Aceton
0	1.62	1.62
0.1	1.68	1.60
0.5	1.66	1.54
1.0	1.56	1.71

Table 3.

Organic acids used (ml)	Time measured (mean of twice) (min)			
	Formic acid 0.2N	pH	Acetic acid 1N	pH
0	1.56	4.2	1.75	4.2
0.1	1.63	3.6	—	—
0.3	2.05	2.6	—	—
0.5	—	—	1.71	3.2
1.0	5.01	1.6	1.77	3.0
1.5	—	—	1.86	2.8
2.0	—	—	1.79	2.6

Table 4.

Organic acids used (mg)	Time measured (mean of twice) (min)			
	Tartaric acid	pH	Citric acid	pH
0	1.56	4.2	1.67	4.2
0.05	—	—	12.96	4.2
0.1	3.16	4.0	—	—
0.5	3.50	3.8	—	—
1.0	3.96	3.6	—	—

Table 5.

Ions used (mg)	Time measured (mean of twice) (min)			
	Al^{+++}	Pb^{++}	Cr^{+++}	Mn^{++}
0	1.27	1.18	1.20	1.46
0.1	1.28	0.99	1.20	—
0.2	—	0.71	—	—
0.5	1.25	—	1.14	1.30
1.0	1.17	—	1.10	1.09
2.0	0.77	—	—	—
3.0	—	—	1.20	0.75

Table 6.

Ions used (mg)	Time measured (mean of twice) (min)			
	Hg^{++}	Zn^{++}	Ni^{++}	Co^{++}
0	1.24	1.21	1.26	1.26
0.1	1.12	1.14	1.27	1.08
0.5	0.97	0.93	1.18	0.66
1.0	0.82	0.74	1.15	—

Table 7.

Ions used (mg)	Time measured (mean of twice) (min)			
	Cd^{++}	Cl^-	SO_4^{--}	NO_3^-
0	1.20	1.20	1.16	1.23
0.5	1.16	1.20	1.20	—
1.0	1.20	1.19	1.14	1.21
5.0	1.19	1.07	1.01	1.19
10.0	1.17	0.87	0.72	0.88

reaction velocity was not affected by the addition of 1 ml of alcohol or acetone and 2 ml of 2 N acetic acid, but it became slow by the addition of formic, tartaric and citric acids, especially the effect of citric acid was remarkable.

The reaction velocity was not affected by the addition of other metallic ions in the range from several tenfold to several thousand times, but Co^{++} and Pb^{++} had a considerable influence.

Summary

(1) Applying the catalytic action of iron to the reaction between p-phenylendiamine and hydrogen peroxide, the microamounts of iron were determined using Duboscq's colorimeter.

(2) By measuring the time required until the brown coloration of the sample solution changed from a certain color concentration to the another, some relations between the time measured and the amount of iron were found, which were applicable to the determination of microamounts of iron.

(3) The standard color solution was prepared by mixing potassium dichromate with chromium nitrate solution.

(4) The suitable concentration of the reagents and the suitable condition were discussed.

(5) Influences of some diverse ions on the determination were examined.