Ultraviolet Spectrophotometric Determination of Iron(III) as Chloro-complex

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In order to establish a series of methods for ultraviolet spectrophotometric determination of iron(III), especially of the method based on differential absorptiometry, we have already reported the two following methods. One of them¹⁾ is based on measurement of absorbance at 300 mμ due to the formation of ferric sulfato-complex using sulfuric acid as reagent, but in the other²⁾ the absorbance was measured at an isosbestic point (271 mμ) which is attributed to the equilibrium between ferric aquo ion and ferric hydroxo ion in the dilute perchloric acid solution.

Rabinowitch and Stockmeyer(3) have analyzed the absorption spectra for the ferric perchlorate solution in the presence of various amounts of OH^-, Cl^- and Br^-, and Mc. Connell and Davidson(6) have investigated the nature of the absorption spectra due to the equilibrium between ferric and ferrous ion, but they almost never refered to the absorption in the ultraviolet region. Recently, Gamlen and Jordan(4) have investigated the nature of the iron chloro-complex in the concentrated hydrochloric acid solution by ultraviolet spectrophotometry, and concluded that the highest chloro-complex formed have the formula $FeCl_4^-$.

DeSesa and Rogers(5) reported a method of spectrophotometric determination of iron based upon measurement at 342.5 mμ in 6 M hydrochloric acid solution. A recent A. S. T. M. publication(7) recommends the use of constant boiling hydrochloric acid as reagent and measurment at 370 mμ for the determination of traces of iron in copper and copper alloys.

The present paper reports an investigation of the absorption of iron(III) in a hydrochloric acid solution, and also of a differential method of spectrophotometric determination for iron using this acid as reagent. Applying this method, the purity of iron alloys has been determined by means of differential spectrophotometry.

Apparatus and Materials.—Spectrophotometric measurements were made with a Beckman Quartz spectrophotometer Model DU with 1 cm. silica cells.

The stock solution of ferric perchlorate was prepared to the concentration of 100 p.p.m. as previously described(2). The hydrochloric acid was purified by distillation untill it gave negative test for iron. The reagent grade perchloric acid which contains no chloride and iron ions was used.

Experimental

Absorption Spectra.—The absorption spectra of ferric perchlorate in 6 M-perchloric and 6 M-hydrochloric acid solutions are shown in Fig. 1.

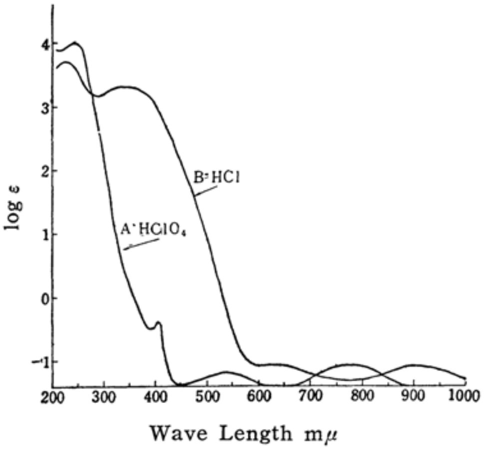

Fig. 1. Absorption Spectra of Iron(III) in 6 M Perchloric Acid and 6 M Hydrochloric Acid.

Curve A has shown good agreement with that of Rabinowitch(3), and therefore this curve may be considered as belonging exclusively to ferric aquo

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1) M. Ishibashi, T. Shigematsu, Y. Yamamoto, T. Tabushi and T. Kitagawa *J. Chem. Soc. Japan* (*pure Chem. Sect.*) **76**, 758 (1955).

2) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, This Bulletin, **29**, 57 (1956).

3) E. Rabinowitch and W. H. Stockmeyer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

4) G. Gamlen and D. Jordan, *J. Chem. Soc.*, **1953**, 1435.

5) M. A. DeSesa and L. Logers, *Anal. Chim. Acta*, **6**, 534 (1952).

6) H. McConnel and N. Davidson, *J. Am. Chem. Soc.*, **72**, 5557 (1950).

7) A. S. T. M. Method for the chemical Analysis of Metals, American Society for Testing Materials. (1950).

ion. In the curve B, maxima shift to the longer region by the formation of ferric chloro-complex. As other workers have reported[3], the ordinate of curve B is the average of absorption coefficients, because the absorbing species are mixed.

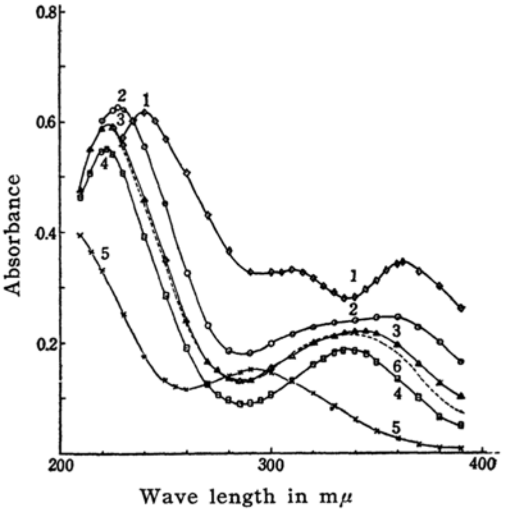


Fig. 2. Absorption Spectra of Iron(III) in the Hydrochloric Acid Solution

Fe^{3+} = ca. 4.5 p.p.m.	◈	1	9.6 N	HCl
Temp. 12°C	⊙	2	6.4 N	〃
Ref. coresponding acid	◬	3	4.8 N	〃
	⊡	4	2.4 N	〃
	×	5	—	(pH 3.4)
	……	6	48 *f*	NaCl (pH 2.58)

The effect of change in the concentration of hydrochloric acid was then studied. Fig. 2 shows the spectra of ferric perchlorate in solution of various concentrations of hydrochloric acid. The absorption maximum of ferric aquo ion at 238 mμ shifts to the region of 320–360 mμ by adding hydrochloric acid. The position of maximum in the region of 320–360 mμ shifts to longer, and the absorbance in these bands also rises, with increase in the concentration of this acid. Another band appears in the region of 220–230 mμ in the solution of hydrochloric acid, and considerable changes both in absorbance and in wave length of maxima are observed with the changes in acid concentration. Curves 5 and 6 indicate the spectra of ferric perchlorate solutions, but the former is that of extreme diluted perchloric acid solution (pH 3.4) and the latter is of the solution (pH 2.6) of 4.8 M sodium chloride. As previously reported[2], curve 5 belongs to the spectrum of the ferric hydroxo-ion $Fe(OH)^{2+}$, and thus it is considered that the hydroxo-complex has transferred to iron chloro-complex in such weak acidic medium under the considerable concentration of chloride. The similarity between curve 6 and 3 indicates that the effect of hydrogen ion concentration is little in such a concentration of chloride ion as 4.8 M.

As the formation of the ferric chloro-complexes may take place stepwise according to Bjerrum's theory of complex formation, it is necessary to investigate the effects of concentration of chloride ion under the constant acidity. Fig. 3 shows the absorption spectra in the following conditions. The concentration of iron(III) was kept constant and the constancy of the concentration of hydrogen ion could be approximately held by mixing the same molar concentration of hydrochloric and perchloric acid. The variations in the absorbance and location of the absorption bands are showed in detail as follows.

(1) 1.2 and 2.4 M H^+ (Fig. 3-1)

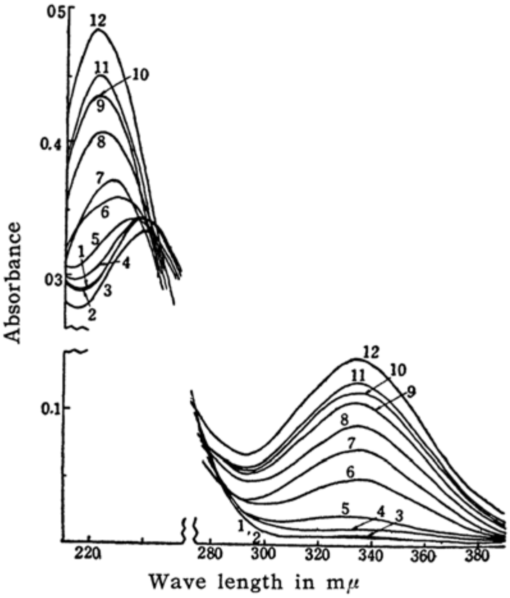


Fig. 3-1. Effect of Chloride Concn. (I) (Fe^{3+} = ca. 4.5 p.p.m, acidity = ca. 1.2 N)

	Vol. of Acid in 20 ml.		λmax.	
	HCl (ml.)	$HClO_4$ (ml.)		
1	0.05	18.95	239 mμ	—
2	0.1	18.90	238	—
3	0.3	18.70	238	—
4	0.5	18.50	237	—
5	1.0	18.00	236	—
6	3.0	16.00	227	334 mμ
7	5.0	14.00	225	334_5
8	7.0	12.00	223	334
9	10.0	9.00	222	333_5
10	13.0	6.00	222_5	333_5
11	15.0	4.00	222	334_5
12	19.0	—	222	334_5

In the region of a shorter wave length, the absorption shifts to shorter, while in the longer region the maximum is kept at constant. The absorbance increases continuously with rise of the concentration of chloride ion in both bands.

(2) 4.8 M H^+ (Fig. 3-2)

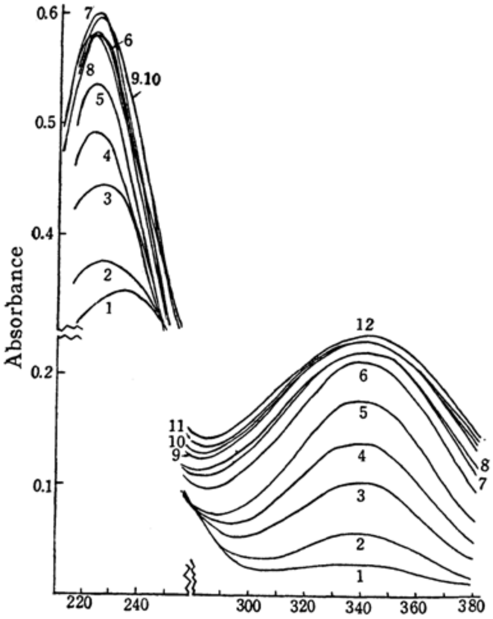


Fig. 3-2. Effected of Chloride Concentration(II) $[\mathrm{Fe}^{3+}=$ca. 4.5 p.p.m. acidity =ca. 4.8 N]

The numbers on the curves are the same as in Fig. 3-1.

	λmax.	
1	234 mμ	336 mμ
2	227	334
3	224	337
4	223	338
5	222	337
6	222	340
7	221	338
8	223	341
9	223	343
10	223	343
11	222	343
12	222	343

The maximum at shorter wave length becomes shorter, that of longer wave length becomes longer, and the absorbance increases continuously in both bands.

(3) 6.4 M H^+ (Fig. 3-3)

In shorter wave length, the position of maximum is kept at constant and the absorbance rises slightly with the increase of the concentration of chloride. In the region of longer wave length, the effect of change in the concentration of chloride ion is more complicated. The position of maximum changes continuously from 342 to 354 mμ until the concentration of chloride ion grows to 1.6 M, but when the concentration becomes greater than 1.5 M, another band appears at 310 mμ. The absorbance also increases continuously while only one band is present, but when the second band appears, the change in both bands becomes very slight.

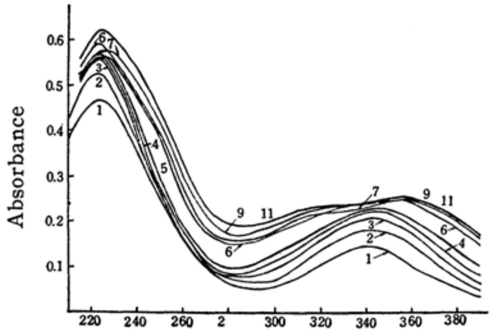
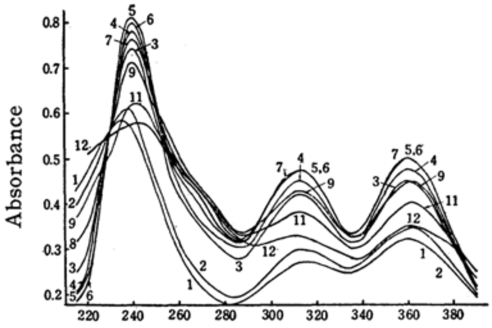


Fig. 3-3. Effect of Chloride Concn. (III) $[\mathrm{Fe}^{3+}=$ca. 4.5 p.p.m. acidity=ca. 1.4 N]

The numbers on the curves are the same as in Fig. 3-1.

	λmax.	
1	223 mμ	342 mμ
2	223	343
3	223	343
4	223	343
5	223	346
6	223	351
7	224	354
9	224	354.5
11	224	355

(4) 9.6 M H^+ (Fig. 3-4)



Wave length in mμ

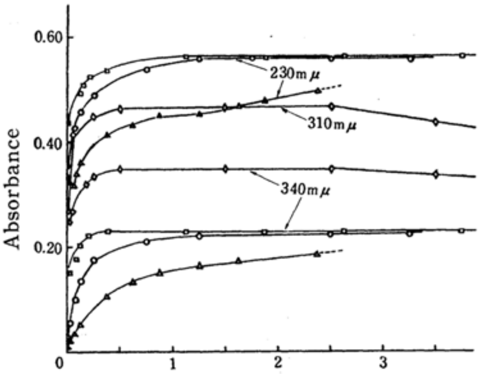
Fig. 3-4. Effect of chloride Concn. (IV) $[\mathrm{Fe}^{3+}=$ca. 4.5 p.p.m. acidity=ca. 9.6 N]

The numbers on the curves are the same as in Fig. 3-1

	λmax.		
1	236 mμ	315 mμ	360 mμ
2	237	313.5	360
3	240	312	360
4	240	312	360
5	240	312	360
6	240	312	359.5
7	240.5	312	260
9	241.5	312	361
11	242	312	361
12	242	310	363

In this case remarkable changes in location and absorbance of all bands occur.

The maximum in the region of shorter wave length shifts to longer. In the region of the longer wave length, two bands exist even at the small concentration of chloride ion, and the maxima of these bands shift from 315 to 310 mμ, from 360 to 363 mμ, respectively. With increase in the concentration of chloride ion, the absorbance in all bands rises at first, and then remains constant while the chloride concentration is in the range from 0.5 to 2.4 M (Curve 5, 6 and 7), and after that it begins to diminish gradually.



Chloride Concentration in Mol.

Fig. 4. Correlation of chloride concentration and Acidity.
Acidity: △ 2.4 N, ○ 4.8 N,
□ 6.4 N, ◇ 9.6 N

The complicated changes in absorption spectra are due to the stepwise formation of iron(III) chloro-complex as follows.

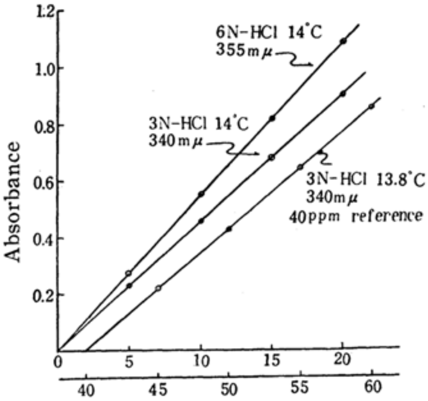
$$Fe^{3+} + Cl^- \rightleftarrows FeCl^{2+}$$
$$FeCl^{2+} + Cl^- \rightleftarrows FeCl_2^+$$
$$FeCl_2^+ + Cl^- \rightleftarrows FeCl_3$$
$$FeCl_3 + Cl^- \rightleftarrows FeCl_4^-$$

To survey the correlation of the effects of hydrogen and chloride ions, in Fig. 4 are shown the changes in absorbance at a given wave length plotted against the concentration of chloride ion at various constant acidities. From this figure, it is deduced that hydrogen ion expedites the formation of the chloro-complex when the chloride concentration is considerably low, but in the higher chloride solution, effects of acidity become small, except in the solution of 9.6 M. Since the curves in Fig. 3-4, are in accord with the spectrum of $FeCl_4^-$, calculated by Gamlen, it is found that the tetra chloro-complex is formed even at the small concentration of chloride ion when the acidity is considerably high, but it may not be formed even at higher chloride concentration if the acidity is low, as shown in Fig. 3-1, -2, and -3. The decrease in absorbance observed in Fig. 3-4, might be due to decrease of ferric ion, which may be caused by the reduction of ferric to ferrous ion in such a concentrated hydrochloric acid solution, but this assumption has not been confirmed experimentally.

Determination of Iron(III)

From the above preliminary survey it is necessary to conduct the measurement under the constant concentration of hydrochloric acid for the determination of iron (III).

Calibration curve.—The preparation of the standard iron solutions was as previously reported. A 1.002 g. of electrolytic iron (purity 99.8%) was dissolved in 4 M perchloric acid and evaporated until chloride and iron(II) became absent and then diluted to 1 l.



p.p.m. Fe

Fig. 5. Calibration Curves

First, for the ordinary absorptiometry, the calibration curve was made for the ferric solution in such concentration as 5, 10, 15 and 20 p.p.m. The concentration of the acid was held at constant in 3 M and 6 M, and the absorbance was measured at 340 and 355 mμ, respectively. In both cases Beer's law is followed in the range 0.2–20 p.p.m. of iron, as shown in Fig. 5. The sensitivity in this method is considerably low compared to the other methods; however, it is more useful by means of the differential absorptiometry. For this purpose, the solution with 40 p.p.m. of iron was used as reference, and the calibration curve was made in such concentration as 45, 50, 55 and 60 p.p.m. Results are also shown in Fig. 5 and Beer's law is followed up to 60 p.p.m. As the reference, concentration higher than 40 p.p.m. of iron is not favourable, because it reduces the sensitivity of the measurement.

Temperature.—The effects of the temperature on absorbance were investigated and the results are shown in Table I. It is seen that the effect of the temperature is almost negligible in the range 10–25°C.

TABLE I

EFFECT OF TEMPERATURE

Concn. of Iron(III): 10 p.p.m.

3 M-HCl		6 M-HCl	
Temp. °C	As. at 340 mμ	Temp. °C	As. at 355 mμ
9	0.440		
10	0.440	10	0.543
11	0.441	12	0.543
13	0.442	14	0.544
16	0.442	18	0.544
17	0.445	23	0.543
19	0.448	30	0.545
20	0.449		
24	0.451		
28	0.454		

TABLE II

EFFECT OF DIVERSE ION

Diverse Ion (p.p.m.)		Fe present (p.p.m.)	Fe found (p.p.m.)
Al^{3+}	200	10.0	9.9_5
Zn^{2+}	200	10.0	10.0_6
Mn^{2+}	200	10.0	10.0
Ni^{2+}	200	10.0	10.1
Co^{2+}	200	10.0	10.1
Ti^{4+}	200	10.0	10.1
Cu^{2+}	200	10.0	29.9
Cu^{2+}	10	10.0	11.1

concn. of HCl; 6 M, wave length: 355 mμ

Effect of diverse Ions.—Study was made on the effect of several cations. The cations were present in solution as perchlorate. Measurements were made for the solutions containing a proper amount of foreign salt with 10 p.p.m. of iron. The results are presented in Table 2. It is found that the presence of such cations as Na^+, K^+, NH_4^+, Co^{2+}, Zn^{2+}, Mn^{2+} and Al^{3+} do not interfere in the concentration of 200 p.p.m. As DeSesa has reported, the chloride of cations such as Cu^{2+}, Ti^{4+}, Bi^{3+} and V^{5+} in the solution of hydrochloric acid have intense absorption in the ultraviolet region, and thus their presence will interfere with the determination of iron. For Cu^{2+} and Ti^{4+}, it is found that the maximum allowable concentration was 2.0 p.p.m.

Determination of Iron in Iron-base alloy.—In order to test the reliablity of the proposed method, some iron-base alloys were shosen as samples, and the determination was done by means of differential absorptiometry.

Procedure:

A 200–150 mg of sample was dissolved in 4 M perchloric acid by warming on a sand bath. After cooling, several drops of H_2O_2 (30%) were added and then evaporated almost to dryness. The evaporation was repeated several times and the residue was dissolved in distilled water: then the solution was transferred to a 500 ml. volumetric flask and diluted to the volume. After being mixed thoroughly, an aliquot of 20 ml was pipetted into a 100 ml. volumetric flask and after 50 ml. of 6 M hydrochloric acid was added, diluted to the volume with water.

TABLE III

ANALYSIS OF IRON SAMPLES

Sample	Fe (%)		
	Present	Found	Error (%)
J. E. S. No. 12 (low phosphor iron)	92.46	92.91	$+0.4_9$
J. E. S. No. 21 (Haematite)	61.32	61.49	$+0.2_8$
J. E. S. No. 19 (Ferrovanadium)	57.44	71.12	+27.0
J. E. S. No. 13 (Ferromanganese)	15.78	15.71	-0.4_5

The absorbance of the above solution was measured at 340 mμ using an iron solution (40 p.p.m.) as the reference. Results are presented in Table 3, and the error is about 0.4%. In the case of ferrovanadium alloy, the reason for the high value must be the presence of vanadium (V).

Summary

The absorption spectra have been investigated for the solution of ferric perchlorate at various concentrations of hydrochloric acid. A method for spectrophotometric determination of iron has been studied using hydrochloric acid as reagent. Effects of temperature, acidity and diverse ions have been examined and the iron content of iron-base alloys has been determined by differential method.

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