Ultraviolet Spectrophotometric Determination of Iron

By Masayoshi ISHIBASHI, Tsunenobu SHIGEMATSU, Yuroku YAMAMOTO,
Masayuki TABUSHI and Toyokichi KITAGAWA

(Received July 18, 1955)

In the previous publications,[1,2] an ultraviolet spectrophotometric determination of iron was reported. The method was based on measuring optical densities of the absorption peak at 300 mμ, which may be due to the formation of ferric sulfate complex, and it was necessary to conduct measurement under the constant concentration of sulfuric acid, because the optical densities were affected by the concentration of sulfuric acid.

E. Rabinowitch and W. H. Stockmayer[3] have studied the absorption curves for the ferric perchlorate solutions in the presence of different amounts of OH^-, Cl^- and Br^-, and could separate the absorption curve of free (hydrated) Fe^{3+} ions from that of $Fe(OH)^{++}$ ions. It was observed by A. R. Olson and T. R. Simonson[4] and confirmed by T. H. Siddall and W. C. Vosburgh[5] that an isosbestic point exists for dilute iron (III) perchlorate solutions at about 273 mμ. Recently R. M. Milburn and W. C. Vosburgh[6] have measured optical densities in this region for 10^{-4}, 10^{-3} and 10^{-2}M iron (III) solutions. For each concentration the acidity was varied while the ionic strength was held at constant and it was observed that the isosbestic point at 273 mμ was apparent for the 10^{-4}M solutions, but not for the 10^{-2}M solutions. They took this as confirmatory evidence for the presence of polynuclear species in the 10^{-2}M solutions.

We have studied the absorption curves for the ferric perchlorate solutions (10 p. p. m.) at various acidities and confirmed that two isosbestic points exist at 271 mμ and 223 mμ, and then established a method for spectrophotometric determination of iron in which the absorbancies at this isobestic point have been measured. The proposed method is very convenient and useful, since no reagents are needed except the dilute perchloric acid to dissolve the sample, and almost no attention needs to be given to test the acidity and temperature in the solutions. Applying the proposed method, the purity of iron alloy has been determined by means of differential absorptiometry.

Apparatus

Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, with 1cm. silica transmission cells.

A Beckman glass electrode pH meter, Model H-2, was used for all pH measurements.

Materials

The stock solutions of iron (III) were prepared as follows.

Ferric perchlorate was formed by dissolving proper amounts of electrolytic iron in perchloric acid (about 4 N), oxidizing by hydrogen peroxide (30%) and evaporating the solution until the crystals appear. After perchloric acid was added to dissolve the deposit, the solution was evaporated again. The procedure was repeated until the solution gave negative test for chloride and iron (II) ions. The violet crystals separated on cooling were filtered with a sintered glass filter and recrystallized twice from distilled water. A stock solution of iron was prepared by dissolving the crystal of ferric perchlorate in water to the concentration of 100 p. p. m. All of the solutions for absorbance measurements were prepared by diluting the required quantity of the stock solution.

---

1) R. Bastian, R. Weberling and F. Palilla, *Anal. Chem.*, **25**, 284 (1953).

2) M. Ishibashi, T. Shigematsu, Y. Yamamoto, M. Tabushi and T. Kitagawa, *J. Chem. Soc. Jap.* (*Pure Chem. Sec.*) **76**, 758 (1955).

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

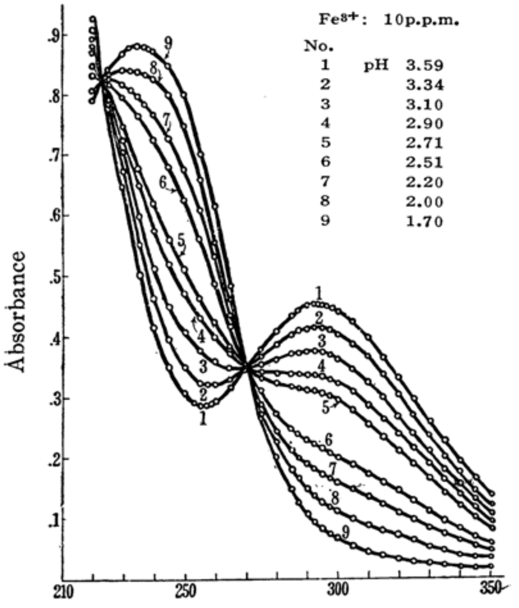
4) A.R. Olson and T. Simonson, *J. Chem. Phys.* **17**, 1322 (1949).

5) T.H. Siddall and W.C. Vosburgh, *J. Am. Chem. Soc.* **73**, 4270 (1951).

6) R.M. Milburn and W.C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955).

Experimental

The Isosbestic Point.—Fig. 1 shows the absorption curves of the solutions for iron (III) of 10 p. p. m. at various acidities.



Wave length mμ

Fig. 1. Absorption curves of ferric perchlorate in aquaous solution at various acidity

Since the acidity could be adjusted by adding a few drops of perchloric acid to a larger volume of the solution, the constancy was held for both the concentration and the ionic strength in each solution. It is found that, with increasing acidity in the solution, the absorption in the region 230 mμ increased, while that of 300 mμ decreased, and there existed two isosbestic points at 223 mμ and 271 mμ.

Further measurements were conducted for the iron solutions (10 p. p. m.) varying concentration of perchloric acid from 1N to 9.5N, and it was found that the band at 238 mμ (curve 9 in Fig. 1) did not suffer any change either in the absorbance or in the position of the peak. As other workers reported, the absorption band with peak at 238 mμ can be considered as belonging exclusively to Fe$^{3+}_{aq}$ ions, and the peak at 295 mμ must be due to Fe(OH)$^{++}$. It will be very useful to utilize this isosbestic point at 271 mμ for the determination of iron (III), since the absorbance is not affected by acidity in solutions. Although the other isosbestic point at 223 mμ is not affected by the acidity either too, it is not adequate for the iron determination, since the interferences of diverse ions and perchloric acid are great in the region of such shorter wave lengths.

Since the isosbestic position might shift by the great variation in the concentration of iron, investigation was made concerning the effects of the content of iron (III) to absorption curve in this region. Differential absorptiometry was applied and the solutions containing 10∼50 p. p. m. of iron were used as references.

As shown in Table I, it is found that a variation in iron content from 10 to 40 p. p. m. gave no change in the position of the isosbestic point at 271 mμ, but in the concentrations higher than 50 p. p. m., the isosbestic point was observed to have a tendency shifting to the shorter wave length.

Temperature.—The effects of the temperature for absorbancies were investigated. The solutions

Table I

Effect of concentration of iron to isosbestic position

Concentration of ferric solution (p. p. m.)	pH	Reference	Width of slit (mm.)	Absorbancies at 267	268	269	270	271	272	273 mμ
10	2.81	water	0.3	—	0.296	.289	.283	.275	.269	.264
〃	2.61	〃	〃	—	.309	.296	.286	.275	.266	.256
〃	2.40	〃	〃	—	.319	.302	.289	.275	.265	.251
20	2.80	Fe (10 p. p. m.)	〃	—	.334	.311	.293	.274	.256	.239
〃	2.60	〃	〃	—	.361	.329	.303	.275	.253	.229
〃	2.41	〃	〃	—	.377	.341	.309	.276	.240	.220
30	2.80	Fe (20 p. p. m.)	0.4	—	.353	.325	.298	.275	.248	.226
〃	2.60	〃	〃	—	.384	.345	.308	.275	.239	.205
〃	2.40	〃	〃	—	.412	.365	.321	.276	.233	.193
40	2.82	Fe (30 p. p. m.)	0.6	0.385	.358	.328	.298	.272	.247	—
〃	2.62	〃	〃	.440	.398	.353	.310	.271	.229	—
〃	2.40	〃	〃	.496	.442	.381	.322	.271	.214	—
50	2.83	Fe (40 p. p. m.)	0.8	.410	.372	.333	.296	.265	.230	—
〃	2.54	〃	〃	.469	.413	.355	.296	.248	.196	—
〃	2.29	〃	〃	.523	.449	.370	.296	.231	.164	—
60	2.89	Fe (50 p. p. m.)	1.3	.385	.357	.328	.297	.270	.244	—
〃	2.61	〃	〃	.464	.412	.353	.296	.242	.192	—
〃	2.29	〃	〃	.550	.470	.385	.298	.220	.143	—

for measurements were of 10 p. p. m. concentration and pH value was 2.5. Tabe II shows that the absorbance at 271 mμ is constant at the temperatures in the range from 10° to 30°C. Furthermore it was observed that with rising temperature the absorbance in the region longer than 271 mμ increased, while that of shorter wave lengths decreases. This must be due to the expedited hydrolysis of iron at higher temperature.

TABLE II

EFFECTS OF TEMPERATURE

Ferric solution (p. p. m.)	Temp. C°	pH	Absorbance at 271 mμ
10	32	2.5	274
〃	28	〃	275
〃	22	〃	274_5
〃	17	〃	274_5
〃	15	〃	274_5
〃	10	〃	274_5

Acidity.—From the above experiments, it is shown that the control of acidity in the solutions is almost needless, except when the acidity is so low as to precipitate the hydroxide. It is observed that the absorbance at 270 mμ increases remarkably in the solutions with pH value over 3.5; this may be due to the formation of the colloidal ferric hydroxide. There is no lower limit for the allowable pH value in the solution, but it is desirable to adjust the acidity in the range of pH 2.5–3.5 for more accurate measurement.

Calibration Curve.—The preparation of the standard iron solution was as follows. A 1.002 g. of electrolytic iron (purity 99.8%) was dissolved in 4N perchloric acid. The same procedures of evaporations as the stock solution were conducted until chloride and iron (II) became absent. The resulting solution was diluted to 1 *l* in a volumetric flask with distilled water. First, for the ordinary absorptiometry, the calibration curve was made by measuring the absorbance of the ferric solution in such a concentration as 5, 10, 15 and 20 p. p. m. at 271 mμ, with pure water as reference. Results are shown in Fig. 2 and Beer's law is followed in the range of 0.2–20 p. p. m. of iron. But as the sensitivity in this methods is fairly low as compared with the other spectrophotometric methods for the determination of iron, it is more useful to use in the differential absorptiometry for the determination of higher contents of iron. For this purpose, the solution with 50 p. p. m. iron was used as reference, and the calibration curve was made in such concentrations as 55, 60, 65 and 70 p. p. m. at 270 mμ. Results are also shown in Fig. 2. and Beer's law is followed in the range from 50 to 70 p. p. m. As the reference, concentration higher than 50 p. p. m. of iron can not be used, because it reduces the sensitivity of the spectrophotometer.

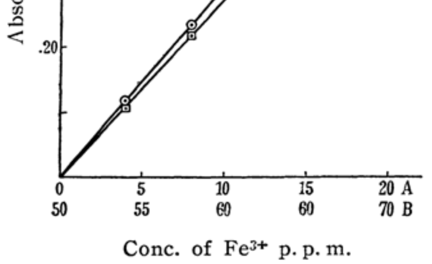


Fig. 2. Calibration curve for iron (III) in aquaous solution.

Effects of Diverse Ions.—A study was made on the effects of several cations and anions. The cations were present in solution as perchlorates and anions as sodium salts. Absorbance measurements were made for the solutions containing proper amounts of foreign salt with 10 p. p. m. of iron. The results are presented in Table III. It is found that the presence of such cations as Na^+, Ni^{++}, Co^{++}, Zn^{++}, Mn^{++} and Al^{3+} does not interfer at the concentration of 100 p. p. m. In the previous publication,[2] it was reported that the cupric and titanic sulfates in aqueous solution have intense absorption bands in far ultraviolet regions, and considerable absorptions were also obserbed at 270 mμ. in the perchloric acid. Thus the presence of cupric and titanic ions interferes the determination of iron (III); the limit concentration of them is about 10 p. p. m. The presence of anions such as Cl^-, NO_3^-, SO_4^{--} and PO_4^{---} interferes remarkably, but chloride and nitrate ions can be easily eliminated by evaporation.

TABLE III

ASBORBANCIES OF DIVERSE CATION WITH

10 p. p. m. Fe^{3+}

Ion	Concentration (p. p. m.)	Absorbance at 270 mμ
Fe^{+++}	10	0.275
Ni^{++}	+1000	0.276
Co^{++}	〃	0.280
Zn^{++}	〃	0.277
Mn^{++}	〃	0.275
Al^{++}	〃	0.277

Determination of Iron in Iron Base Alloy

In order to test the reliability of the proposed method, some iron base alloys were selected as samples. The determination of iron was done by means of differential absorptiometry.

Procedure.—A 200–150 mg. of sample (weighed correctly) was dissolved in 4N perchloric acid by warming on the 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 with distilled water. After being mixed thoroughly, an aliquot of 20 ml. was pipetted into a 100 ml. volumetric flask and then diluted to the volume with distilled water.

TABLE IV
ANALYSIS OF IRON SAMPLES

	Fe			
Sample	Present		Found	
	%	mg.	mg.	%
Haematite	61.32	4.911	4.922	61.46
(J. E. S. No. 23)			4.915	61.38
			4.915	61.38
			4.908	61.28
			av. 4.915	61.38
Iron	92.22	5.556	5.550	92.13
(J. E. S. No. 7)			5.559	92.28
			5.557	92.21
			5.550	92.13
			av. 5.554	92.20
Iron	92.46	5.548	5.557	92.62
(J. E. S. No. 12)			5.547	92.44
(low phosphor)			5.543	92.83
			5.547	92.44
			av. 5.548	92.46

The absorbance of the above solution was measured at 270 mμ, using an iron solution (50 p. p. m.) as the reference. The results are presented in Table IV, the errors in this method being 0.2–0.3%.

Summary

Absorption has been investigated for the solution of ferric perchlorate at various acidities in ultraviolet region and the existence confirmed of two isosbestic points at 223 mμ and 271 mμ. A method of spectrophotometric determination for iron has been proposed which involves the measurement of absorbance at the isosbestic point. Effects of temperature, acidity and diverse ions have been examined and the purity of iron base alloys has been determined by differential method.

The authors are grateful to Dr. R. Tsuchida for his sueful advice in the interpretation of the absorption spectra.

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto