Digital Derivative Spectrophotometric Determination of Micro Amounts of Iron with 1,10-Phenanthroline

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Digital first-order derivative spectrophotometry was applied to the determination of iron with 1,10-phenanthroline. Under the recommended conditions, a linear relationship was confirmed between the first-derivative value and the iron concentration. The present method gives accurate results for iron, ranging from 1.6×10^{-7} to 8×10^{-5} mol dm^{-3} (8.9 μg dm^{-3}—4.5 mg dm^{-3}). The relative standard deviations for the determination of 4.8×10^{-5}, 4.8×10^{-6}, and 4.8×10^{-7} mol dm^{-3} of iron(III) were 0.37, 0.38, and 0.93%, respectively. The effects of 63 diverse ions were examined. The present method was applied to the determination of iron in practical samples, *i.e.*, river water, waste water and sea water.

There are many reagents used in the spectrophotometric determination of iron.[1—4] Among these, 1,10-phenanthroline (phen) is the most widely used. A standard procedure is usually established and the effects of diverse ions are carefully examined.[5—7] The above-mentioned reagent is not highly sensitive.

Derivative spectrophotometry, which uses a derivative spectrum, is effective for increasing sensitivity.[8—13] In the work reported in this paper derivative spectrophotometry was introduced to make the determination more sensitive.

The methods for obtaining a derivative spectrum are divided into two groups, *i.e.*, optical and electrical. The optical group includes the dual-wavelength and wavelengh-modulation methods. The electrical group includes a shift-memory method, an analogue-differentiation method, and a digital-differentiation method.[14] These methods have their individual advantages and disadvantages. In analytical applications, the digital-differentiation method (using a computer) is of interest for several reasons. (1) Absorption-spectrum data are at first stored in the main memory of the computer. Thus, it is easy to calculate a derivative spectrum from the stored data. The S/N ratio of the derivative spectrum can be much improved by the use of smoothing treatments. (2) An exact derivative spectrum is derived (a distorted spectrum is obtained in the case of analogue method). (3) A calibration curve (derivative value *vs.* concentration) is linear and passes through the origin even if the wavelength interval for the differentiation becomes large. (4) After a measurement of the absorption spectrum, the final results of the analysis may be obtained automatically, since all calculations are performed by the computer. Thus, in this study the digital-differentiation method was adopted.

The present method can be applied to iron existing at one-hundredth of the concentration which can be determined by ordinary spectrophotometry with phen.

Experimental

Reagents. A 1×10^{-2} M (1 M=1 mol dm^{-3}) iron(III) solution was prepared by dissolving guaranteed reagent-grade iron(III) nitrate in dilute nitric acid. The solution was standardized by edta titration using Variamine Blue B as an indicator. This solution was diluted with 0.02 M nitric acid, as required.

A 2×10^{-3} M phen solution was prepared by dissolving a weighed amount of the reagent in 0.01-M nitric acid.

The other reagents used were of a guaranteed reagent grade.

Apparatus. The absorption spectra and their derivative spectra were measured with a Hitachi 228 double-beam spectrophotometer system. This system is composed of a photometer part and a personal computer equipped with a CRT (display part) and a mini-floppy disk. With this system, the derivative spectrum is obtained as follows. The absorption spectrum measured with the photometer part (spectrum data are stored in the computer memory) is differentiated on the personal computer from one to four times (corresponding to first to fourth derivative spectrum, respectively). The derivative-spectrum data are also stored in computer memory. Then, the derivative spectrum is displayed on a CRT and on the chart of the printer of the photometer part.

In the present system, the output signals from the photometer are fed to the personal computer through an 8-bit AD converter. After the absorption-spectrum data are stored in the main memory of the computer, a most appropriate derivative spectrum can be easily calculated from the data; *e.g.*, when the ordinate of the spectrum are not suitable, the calculation is done again while changing the scale of the ordinate. The length of the time at which the derivative spectrum is calculated and shown on the CRT and the peak-to-trough value of the spectrum is recorded on the printer, was 45 s. in the present conditions (485—600 nm). Thus, the present method can be used over a wide iron-concentration range (without altering the concentration) since the scale of the ordinate of the derivative spectrum can be easily changed.

The flow chart of the present computer program is shown in Fig. 1.

Standard Procedure. A sample solution containing from 8 nmol to 4 μmol of iron is placed in a 50-cm^3 volumetric flask. Then, 5 cm^3 of 0.5 M hydroxylamine hydrochloride, 8 cm^3 of 2×10^{-3} M phen, 5 cm^3 of 0.2 M acetic acid, and 5 cm^3 of 0.2 M sodium acetate are successively added to the flask. Next, water is added up to the mark of the flask; the final pH is 4.4. The flask is kept for about thirty minutes in a water bath held (thermostatically) at 25 °C. The absorption spectrum of the solution is measured in a 10-mm cell against a reagent blank as the reference. Then, the first-order derivative spectrum is calculated at around 540 nm using wavelength intervals ($\Delta\lambda$) of 10 nm. The vertical distance from the base line to a trough of the spectrum, which is written on a chart, is then determined.

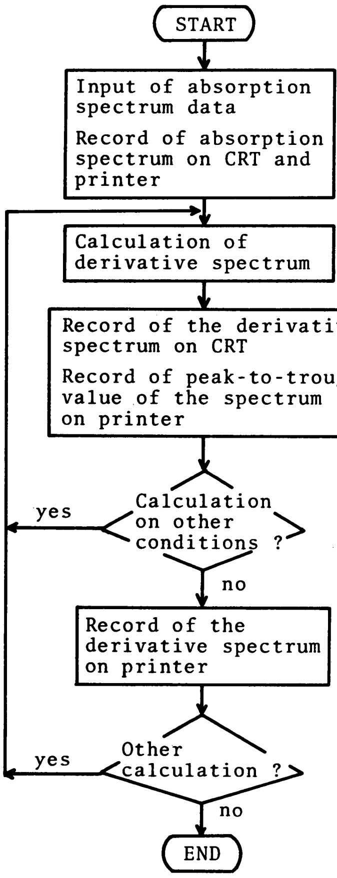

Fig. 1. Flow chart of the computer program for the derivative spectrum.

Results and Discussion

Derivative Spectrum. After the absorption spectrum of the Fe^{II}-phen complex solution was measured, the derivative spectra (first, second, third, and fourth order) were calculated from the measured absorption spectrum by use of the personal computer. Figure 2 shows a measured absorption spectrum and its first- and second-order derivative spectra (third- and fourth-order spectra are omitted). The value of the vertical distance between a peak and a trough of the derivative spectrum was greatest for a first-order derivative spectrum.

The value of the vertical distance from the base line to a trough (or a peak) of the derivative spectrum depended upon the value of $\Delta\lambda$, which can be selected between 1 to 10 nm in this program; the greater the value of $\Delta\lambda$, the longer the vertical distance (Fig. 3). Thus, in order to make the determination more sensitive, first-order derivative spectrophotometry was adopted and the value of $\Delta\lambda$ was set to 10 nm.

Reaction Time. In the color reaction, if the iron content is low, the time for a maximum color development may be long. In order to ascertain this point, the reaction time for the solution prepared by the above stated procedure was measured. When the

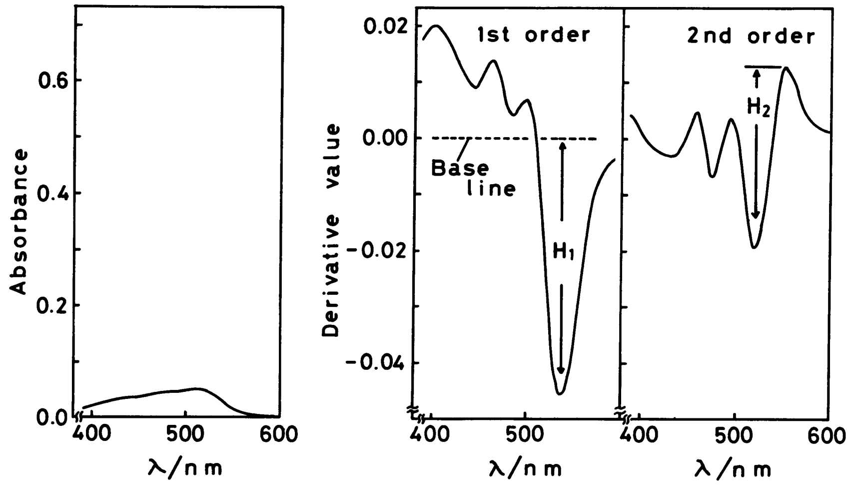

Fig. 2. Absorption spectrum and derivative spectra of Fe^{II}-phen complex solution.
Fe: 4.3×10^{-6} M, phen: 3.2×10^{-4} M, pH: 4.4, $\Delta\lambda$: 10 nm.
H_1 denotes the vertical distance from the base line to a trough of the first-order derivative spectrum and H_2 is the vertical distance between a peak and a trough of the second-order derivative spectrum.

iron content was 2 μmol, 0.2 μmol, and 0.02 μmol per 50 cm^3, the vertical distance from the base line to a trough of the first-order derivative spectrum did not vary for more than about twenty minutes at 25 °C, in respective cases. Thus, in this study, the standing time of the colored solution was set at thirty minutes for a temperature of 25 °C.

Calibration Curves. The first-order derivative spectrum of the Fe^{II}-phen complex solution at around 540 nm was recorded on a chart of the printer of the photometer by the stated standard procedure. The vertical distance from the base-line to a trough (*i.e.*, derivative value) was measured. The first-order derivative value *vs.* the iron concentration gave a straight line passing through the origin as shown in Fig. 4, where the recorder sensitivity was set so that the values of the derivatives, 1.0 in A, 0.1 in B, and 0.01 in C, gave a signal of 15 cm on the chart (full scale: 15 cm). The relative standard deviations of the first-order derivative values were 0.37, 0.38, and 0.93% for 4.8×10^{-5}, 4.8×10^{-6}, and 4.8×10^{-7} M of iron(III), respectively (11 measurements).

Effect of Diverse Ions. The effects of the 63 diverse ions were examined. The experiments were run as follows: a sample solution containing 0.202 or 0.0204 μmol of iron(III) was placed in a 50-cm^3 volumetric flask and then the ion in question was added to the flask; next, the stated standard procedure was applied.

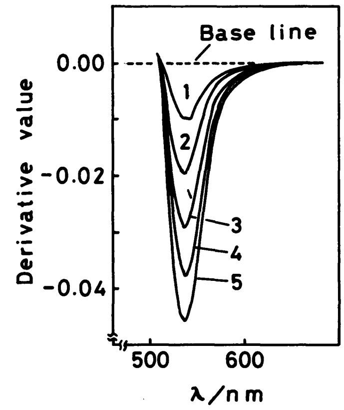

Fig. 3. Effect of Δλ on the first-order derivative spectrum of Fe^{II}-phen complex solution.
Fe: 4.3×10^{-6} M, phen: 3.2×10^{-3} M, pH: 4.4.
1: Δλ=2, 2: Δλ=4, 3: Δλ=6, 4: Δλ=8, 5: Δλ=10.

In this study it was decided that the diverse ion concentrations for 500 times the concentration of iron should be sufficient to test for interference; *i.e.*, when this amount did not interfere, a furfher test was not undertaken. Diverse ions were added in the form of nitrate and sodium salt except for the following: K^+, Na^+, NH_4^+, Hg^{2+}, Sn^{2+}, As^{3+}, Sb^{3+}, Ce^{4+}, Sn^{4+}, Zr^{4+}, CN^-, IO_3^-, SCN^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, $Mo_7O_{24}^{6-}$, and tartrate, which were added as KCl, NaCl, NH_4Cl, $HgCl_2$, $SnCl_2$, As_2O_3, $SbCl_3$, $CeSO_4$, $SnCl_4$, $ZrO(NO_3)_2$, KCN, KIO_3, NH_4SCN, K_2CrO_4, $K_2Cr_2O_7$, $(NH_4)_6Mo_7O_{24}$, and potassium sodium tartrate, respectively.

The results are summarized in Tables 1 and 2, from which it can be seen that in the determination of 4.04×10^{-6} M iron (Table 1) silver, mercury, molybdenum, and tungsten interfere with the determination when present at a concentration of 5 times that of iron, and that in the case of 4.08×10^{-7} M iron (Table 2), only mercury(II) ion interferes when present at a concentration of 5 times that of iron.

Determination of Iron in Practical Samples. *Iron Ion in River Water*: The water sample was collected at the Matsukawa river in Aioicho, Yonezawa, Yamagata (at August, 1983). It was instantly drawn through a membranefilter (pore size 0.45 μm), then, the determination of the iron ion of the filtrate was carried out using the stated standard procedure. The results are shown in Table 3.

Iron in Waste Water: Waste water included the following: (No. 1) water exhausted from the Faculty of Engineering, Yamagata University, and (No. 2) that from T electric company in Yonezawa, Yamagata. To these samples, concentrated hydrochloric acid was added (to become 0.1 M) to keep the iron ions from being adsorbed by the vessel.

Pretreatment of the waste water was done as follows. 100 cm^3 of the sample and 5 cm^3 of concen-

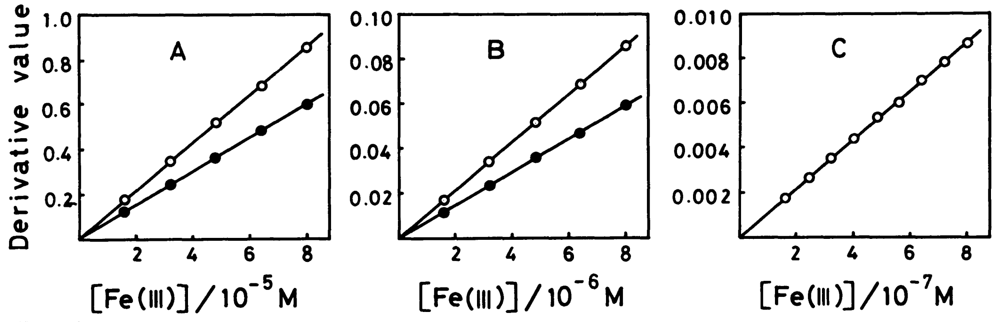

Fig. 4. Relationship between derivative value and iron(III) concentration.
phen: 3.2×10^{-4} M, pH: 4.4, reference: reagent blank, Δλ: 10 nm.
—○—: the results of first-order derivative spectrophotometry (base line-to-trough values are plotted).
—●—: the results of second-order derivative spectrophotometry (peak-to-trough values are plotted).[16]

TABLE 1. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 4.04×10^{-6} M IRON[a] AT pH 4.4±0.1

Ion	Tolerable amount[b] added to 50 cm^3 μmol
K^+, Li^+, Na^+, NH_4^+, Rb^+, Tl^+, Ba^{2+}, Be^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Sr^{2+}, Al^{3+}, As^{3+} c), Ce^{3+}, La^{3+}, Ce^{4+} d), Zr^{4+} e)	100
Th^{4+}	40
UO_2^{2+}, Zn^{2+}	20
Cd^{2+}, Cr^{3+}, Sb^{3+} f)	10
Co^{2+}, Cu^{2+}, Ni^{2+}, Sn^{2+}, Sn^{4+}	4
Bi^{3+}	1
Ag^+	0.4
Hg_2^{2+}	0.2
Hg^{2+}	0.1
Br^-, CH_3COO^-, Cl^-, ClO_3^-, ClO_4^-, F^-, HSO_3^-, I^-, NO_2^-, NO_3^-, SCN^-, HPO_4^{2-}, SiO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, citric acid, tartrate, salicylate	100
IO_3^-, $HAsO_4^{2-}$	40
CN^-, CO_3^{2-}, $B_4O_7^{2-}$, oxalic acid	20
CrO_4^{2-}, $Cr_2O_7^{2-}$, $P_2O_7^{4-}$	4
$Mo_7O_{24}^{6-}$, WO_4^{2-}	0.4

a) Iron taken in 50 cm^3 was 0.202 μmol. b) Tolerable amount was taken as that which caused an error of not more than 2%. c) pH: 4.0. d) pH: 3.8. e) pH: 4.2. f) pH: 2.8.

TABLE 2. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF 4.08×10^{-7} M IRON[a] AT pH 4.4±0.1

Ion	Tolerable amount[b] added to 50 cm^3 μmol
K^+, Li^+, Na^+, NH_4^+, Rb^+, Tl^+, Ba^{2+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Sr^{2+}, Zn^{2+}, Al^{3+}, As^{3+}, Ce^{3+}, La^{3+}, Ce^{4+}, Th^{4+}, Zr^{4+}	10
Sn^{4+}, UO_2^{2+}	4
Cu^{2+}, Ni^{2+}, Sn^{2+}, Cr^{3+}, Sb^{3+} c)	2
Co^{2+}	1
Ag^+, Bi^{3+}	0.4
Hg_2^{2+}	0.1
Hg^{2+}	0.04
Br^-, CH_3COO^-, Cl^-, ClO_3^-, ClO_4^-, CN^-, F^-, HSO_3^-, I^-, IO_3^-, NO_2^-, NO_3^-, SCN^-, CO_3^{2-}, $HAsO_4^{2-}$, HPO_4^{2-}, SiO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, citric acid, oxalic acid, tartrate, salicylate	10
$B_4O_7^{2-}$, $P_2O_7^{4-}$	4
CrO_4^{2-}	1
$Cr_2O_7^{2-}$, $Mo_7O_{24}^{6-}$	0.4
WO_4^{2-}	0.2

a) Iron(III) taken in 50 cm^3 was 0.0204 μmol. b) Tolerable amount was taken as that which caused an error of not more than 4%. c) pH: 4.2.

TABLE 3. DETERMINATION OF IRON ION IN RIVER WATER

Sample taken in 50 cm^3 cm^3	(A) Iron added to 50 cm^3 nmol	(B) Iron found in 50 cm^3 nmol	(B)—(A)	Iron concentration in sample mol dm^{-3}
20.00	0	17.9	17.9	9.0×10^{-7} (50 ppb)
20.00	0	17.7	17.7	8.9×10^{-7} (50 ppb)
20.00	0	17.9	17.9	9.0×10^{-7} (50 ppb)
20.00	0	17.7	17.7	8.9×10^{-7} (50 ppb)
20.00	17.2	34.9	17.7	8.9×10^{-7} (50 ppb)
20.00	17.2	34.9	17.7	8.9×10^{-7} (50 ppb)

trated nitric acid was added to a 250-cm^3 porcelain dish. The solution was concentrated to about 10 cm^3 on a boiling-water bath. Then, 5 cm^3 of concentrated nitric acid and 10 cm^3 of concentrated perchloric acid were added. The solution was then heated on a hot plate until white fumes of pherchloric acid were produced. After this, the solution was cooled to room temperature, was transfered to a 100-cm^3 volumetric flask and water was added up to the mark of the flask.

The determination of the iron was performed by the standard procedure, using 5 cm^3 of the prepared solution. In the determination, however, 4 cm^3 of 2-M sodium acetate was added in order to adjust the pH to 4.4. The analyses were run three times, starting from the pretreatment of the waste water. The results are shown in Table 4.

Iron in Sea Water: Sea water was collected at Ishinomaki bay. The collection was done at a place 200-m from the beach in Nobiru, Naruse, Miyagi. The sea water was placed in a polyethylene vessel and concentrated hydrochloric acid was added (to become 0.03 M).

4 cm^3 of concentrated hydrochloric acid was added to 500 cm^3 of the sea water. Then, the sea water was concentrated to about 80 cm^3 on a boiling-water bath (using porcelain dish). Infrared heating was used simultaneously. After cooling, the solution was transfered to a 100-cm^3 volumetric flask and then water was added up to the mark of the flask. The determination of iron was carried out by the standard procedure, using 20 cm^3 of the prepared solution. In the determination, 11 cm^3 of 2-M sodium acetate was added as a buffering agent. The results are shown in Table 5.

The waste water and the sea water were also ana-

TABLE 4. DETERMINATION OF IRON IN WASTE WATER

Sample number	Sample taken in 50 cm^3	Iron found in 50 cm^3	Iron concentration in waste water	Iron concentration by atomic absorption method
	cm^3	nmol	mol dm^{-3}	mol dm^{-3}
	5.00	46.6	9.3×10^{-6} (0.52 ppm)	
No. 1	5.00	45.7	9.1×10^{-6} (0.51 ppm)	9.1×10^{-6} (0.51 ppm)
	5.00	47.5	9.5×10^{-6} (0.53 ppm)	
	5.00	18.8	3.8×10^{-6} (0.21 ppm)	
No. 2	5.00	16.1	3.2×10^{-6} (0.18 ppm)	3.6×10^{-6} (0.20 ppm)
	5.00	19.7	3.9×10^{-6} (0.22 ppm)	

TABLE 5. DETERMINATION OF IRON IN SEA WATER

Sample taken in 50 cm^3	Iron found in 50 cm^3	Iron concentration in sample	Iron concentration in sea water	
			mol dm^{-3}	
cm^3	nmol	mol dm^{-3}	Present method	Atomic absorption method
20.00	193	9.7×10^{-6} (0.54 ppm)	1.9×10^{-6} (0.11 ppm)	
20.00	193	9.7×10^{-6} (0·54 ppm)	1.9×10^{-6} (0.11 ppm)	1.8×10^{-6} (0.10 ppm)
20.00	183	9.2×10^{-6} (0.51 ppm)	1.8×10^{-6} (0.10 ppm)	

lyzed for iron by atomic-absorption spectrometry (Tables 4 and 5).[15] The results agreed with those in the present method.

Characteristics of the Present Method. The base line of the absorption spectrum sometimes moved from the zero line. However, the shift of the base line of the first-order derivative spectrum from the zero line was not seen; thus, the calibration curves passed through the origin even in the case of a low iron-ion concentration as shown in Fig. 4.

In ordinary spectrophotometry, a variation of the zero point influences the results. In the present method, the results were not influenced by the deviation of the base line of the absorption spectrum. This is considered to be attributed to the fact that a determination by the derivative method does not depend directly on the absorbance (of the absorption spectrum) but mainly on the shape of the spectrum. Consequently, a derivative value may be magnified without error.

The iron ion of $1.6—8\times10^{-7}$ M (0.009—0.045 mg dm^{-3}) could be determined by the present method; this concentration level is one-hundredth of the concentration $1.6—8\times10^{-5}$ M (0.9—4.5 mg dm^{-3}) which is presented to the ordinary spectrophotometry with phen. The procedures of the present method are not complicated; thus the ppb level of an iron ion (10—50 μg dm^{-3}) can be easily determined by the present method. The concentration of iron ions in ordinary spectrophotometry when using a highly sensitive reagent, *e.g.*, 4,7-diphenyl-1,10-phenanthroline (ε of iron(II) complex: 22400 l mol^{-1} cm^{-1} at 533), 2,4,6-tris(2-pyridyl)-*s*-triazine (ε of iron(II) complex: 22600 l mol^{-1} cm^{-1} at 593) is more than about 0.1 mg dm^{-3};[4] thus, the present method can be said to be very sensitive.

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15) A Hitachi model 180-80 polarized Zeeman atomic absorption spectrophotometer was used.
16) Peak-to-trough values of the second-order derivative spectrum *vs.* the iron concentration also gave a straight line passing through the origin.