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Photometric Determination of a Trace Amount of Nitrite by Its Kinetic Effect†

Satori Utsumi, Tadao Okutani, Akio Sakuragawa,* and Akira Kenmotsu**

College of Science and Technology, Nihon University, 1-8, Kanda-Surugadai, Chiyoda-ku, Tokyo 101

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A new photometric method has been developed for determining nitrite ions. This method is based on the kinetic effect of nitrite ions on the color-fading of the iron(III) thiocyanate complex in dilute nitric acid solution in the presence of iodide ions. The reaction is initiated by adding an ammonium iron(III) sulfate solution to the sample solution containing a mixture of potassium thiocyanate and potassium iodide at 25 °C. A concentration of nitrite ions, ranging from 0.0005 to 10 ppm can be determined by measuring the absorbance at 460 nm at a given time after the initiation using four appropriate calibration curves. Silver, mercury(II), iron(II), sulfide, sulfite, thiosulfate, chromate and cyanide ions in the concentration range from 0.1 to 1 ppm level interfered with the determination.

It has been established that the orange color of iron(III) thiocyanate, which was formed by the reaction with potassium thiocyanate and an excess of iron(III) salt in dilute nitric acid solution, faded more rapidly in the presence of iodide than in its absence.[1] The catalytic action of iodide ions on this reaction has been studied colorimetrically, and a new micro-determination method for iodide ions established.[1,2] It was also found that the catalytic reaction was characterized by an induction period, the length of which depended on the nitrite ion concentration.[2,3] This kinetic effect has been utilized to determine the amounts of iodide ions in the presence of nitrite ions.[4] Iodides in silicate rocks,[5] and iodide and iodate ions in sea water[6] have also been determined.

Successive investigations on the behavior of nitrite ions have shown that the kinetic effect can be applied to the determination of nitrite ions. This paper proposes a new method for the determination of nitrite ions on the basis of the kinetic effect mentioned above.

The proposed method gives accurate results for nitrite ions ranging from 0.0005 to 10 ppm. The determination can be made by measuring the absorbance at a given time after the addition of an ammonium iron(III) sulfate solution using calibration curves obtained under identical conditions.

Experimental

Apparatus. A Hirama IIC type photometric colorimeter with a 460 nm filter and 10 mm glass cells was used to measure the absorbance. The reaction was performed at 25.00±0.05 °C using a water bath with a Komatsu-Yamato Coolnicks circulator Model CTE/CTR-120 unit.

Reagents. All of the chemicals used were of guaranteed reagent grade. The ion-exchanged water was distilled in a borosilicate still prior to use.

Standard Nitrite Solution: Sodium nitrite (1.4997 g) was dissolved in distilled water, diluted to exactly 1 litre (1000 ppm NO_2^-), and stored in a brown glass bottle. The working solution was diluted as required.

Potassium Thiocyanate Solution(0.01 M): A potassium thiocyanate solution(0.1 M), standardized by Volhard's method, was diluted to 0.01 M and stored in a brown glass bottle.

Potassium Iodide Solution (2×10^{-3} M): A potassium iodide solution (0.1 M), standardized by Volhard's method, was diluted to 2×10^{-3} M and stored in a brown glass bottle.

Potassium Thiocyanate–Potassium Iodide Mixed Reagent Solution (Mixed Reagent Solution): The mixed reagent solution was prepared by mixing potassium thiocyanate solution (0.01 M) with an equal volume of potassium iodide solution (2×10^{-3} M) just before the experiment was started.

Ammonium Iron(III) Sulfate–Nitric Acid Solution (Iron(III) Reagent Solution): The iron(III) reagent solution was prepared by dissolving ammonium iron(III) sulfate (6.0 g) in nitric acid (7.0 M), and then diluting to 100 ml with 7.0 M nitric acid. After urea (10 mg) was added to the solution, it was heated in boiling water with a reflux condenser for 10 min and then cooled rapidly in water. This reagent solution was stored in a brown glass bottle at room temperature, and could be used for approximately 30 days.

Procedure and Calibration Curves. The sample solution (10 ml) was placed in a 20 ml glass tube fitted with a stopper. The mixed reagent solution (1 ml) was then added and the glass tube placed in a water bath at 25.00±0.05 °C for 10

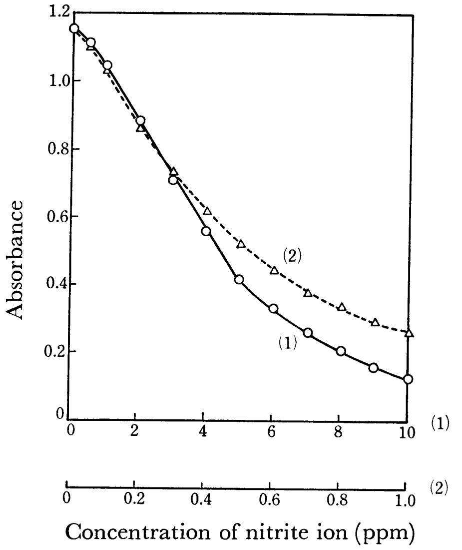

Fig. 1. Calibration curves 1.
(reaction temperature: 25 °C)
(1) Reaction time: 7 min, (2) reaction time: 13 min.

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** Present address: Nippon Electronics Engineering College, 5-23-22, Nishi-Kamata, Ohta-ku, Tokyo 144.

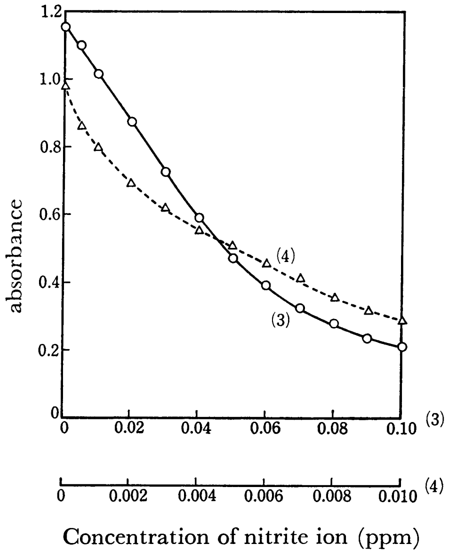

Fig. 2. Calibration curves 2.
(reaction temperature: 25 °C)
(3) Reaction time: 19 min, (4) reaction time: 24 min.

min. The reaction was initiated by adding the iron(III) reagent solution (2 ml, at the same temperature), mixing thoroughly and then replacing the glass tube in the water bath. The absorbance was measured at 460 nm using water as a reference at a given time after the addition of the iron(III) reagent solution. It is recommended that the solution in the glass tube is removed from the water bath and poured into the cell 20 s before measurement of the absorbance. By employing 7, 13, 19, or 24 min of reaction time, nitrite ions in the concentration range of 0.5—10, 0.05—1, 0.005—0.1, or 0.0005—0.01 ppm, respectively, could be determined. The calibration curves shown in Figs. 1 and 2 were obtained by the procedure described above.

Results and Discussion

The Reaction Rate Curves. The kinetic reactions were examined for each solution (10.0 ml) containing 10, 1, 0.1, or 0.01 ppm nitrite ions, and for distilled water. The curves shown in Fig. 3 were obtained by measuring the absorbances of these solutions at various reaction times. In the absence of nitrite ions (curve 5 in Fig. 3), the color-fading of the iron(III) thiocyanate complex began approximately 20 min after the initiation and after 32 min, the solution became almost colorless. In the presence of nitrite ions, the color-fading was accelerated with an increase in the concentration of nitrite ions. These results indicate that the length of the induction period is greatly affected by the concentration of nitrite ions, and that nitrite ions ranging in concentration from 0.0005 to 10 ppm can be determined by measuring the absorbances at different reaction times.

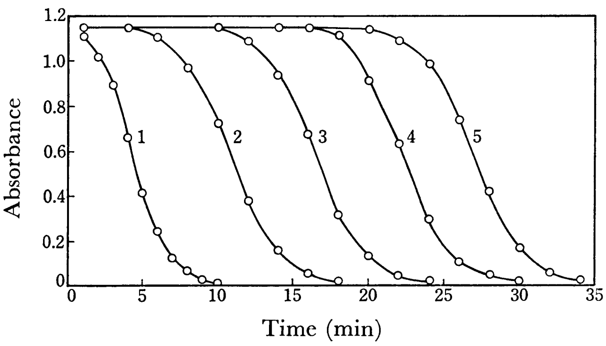

Fig. 3. The changes in absorbances of iron(III) thiocyanate solution with time in the presence of various concentrations of nitrite ions.
(reaction temperature: 25 °C)
1: 10 ppm, 2: 1 ppm, 3: 0.1 ppm, 4: 0.01 ppm, 5: distilled water.

The Effect of Iodide Ion Concentration in the Mixed Reagent Solution. The concentration of potassium thiocyanate in the mixed reagent solution was chosen as 5×10^{-3} M, which was the same value as in a previous paper.[4] Three concentrations of iodide ion (5×10^{-4}, 1×10^{-3}, and 2×10^{-3} M) were adopted to examine the effect of the iodide ion concentration in the mixed reagent solution on the color-fading. It was found that, as the concentration of iodide ion increased, the start of the color-fading was delayed, but once initiated the speed of the color-fading increased. For example, in the reagent blank, the color-fading of the iron(III) thiocyanate complex began approximately 19 min after the initiation at a concentration of 5×10^{-4} M of iodide ions, whereas it began approximately 24 min after the initiation at 2×10^{-3} M of iodide ions. In the present work, the concentration of iodide ions was adjusted to 1×10^{-3} M to make four calibration curves effective for the concentration range from 0.0005 to 10 ppm of nitrite ions. Consequently, the mixed reagent solution used was of 5×10^{-3} M potassium thiocyanate and 1×10^{-3} M potassium iodide.

The Effect of the Concentration of Nitric Acid in Iron(III) Reagent Solution. This effect was studied using the three reagent solutions in which ammonium iron(III) sulfate was dissolved in 6.00, 7.00, or 8.00 M nitric acid, the experimental results of which are shown in Fig. 4. With regard to the sensitivity and the length of time required to determine the amounts of nitrite ions, the iron(III) reagent solution prepared from 7.00 M of nitric acid was selected. Figure 4 illustrates the effect of nitric acid on the color-fading which is remarkable. Therefore, it is necessary to accurately adjust the concentration of nitric acid.

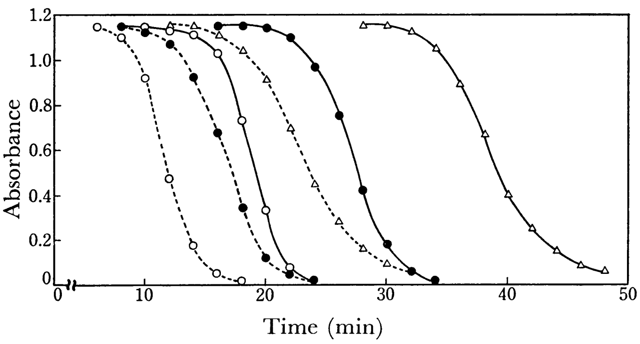

Fig. 4. Effect of concentration of nitric acid in the iron(III) reagent solution.
(reaction temperature: 25 °C)
——: Blank, ------: 0.1 ppm NO_2^-.
Nitric acid: △: 6.00 M, ●: 7.00 M, ○: 8.00 M.

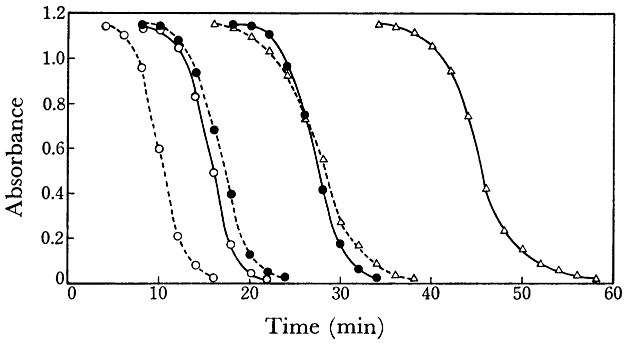

Fig. 5. Effect of the temperature.
——: Blank, ------: 0.1 ppm NO_2^-.
Reaction temperature: △: 20 °C, ●: 25 °C, ○: 30 °C.

TABLE 1. EFFECT OF UREA ON ABSORBANCE OF SOLUTION

Amount of urea[a] (mg/100 ml)	Absorbance 24 min	Absorbance 28 min
0[b]	0.652	0.161
2	0.865	0.260
5	0.921	0.327
10	0.987	0.426
20	1.009	0.445

a) Urea mg/100 ml iron(III) reagent solution, heated for 10 min in boiling water. b) Untreated.

TABLE 2. EFFECT OF THE HEATING PERIOD ON ABSORBANCE

Time (min)	Absorbance 24 min	Absorbance 28 min
—[a]	0.886	0.280
5	0.967	0.390
10	0.987	0.426
20	0.833	0.227

10 mg urea/100 ml iron(III) reagent solution.
a) Untreated.

TABLE 3. THE TREATMENT WITH UREA ON THE VARIOUS GRADES OF NITRIC ACID

Grade of nitric acid	Absorbance 24 min Untreated	Absorbance 24 min Urea treated	Absorbance 28 min Untreated	Absorbance 28 min Urea treated
SSG[a]	0.648	0.987	0.162	0.426
JIS-GR[b]	0.580	0.983	0.110	0.423
JIS-EP[c] 1	0.550	0.975	0.105	0.420
JIS-EP 2	0.535	0.979	0.100	0.415

10 mg urea/100 ml iron(III) reagent solution, heated for 10 min in boiling water.
a) Super Special Grade. b) Guaranteed Reagent of Japanese Industrial Standards. c) Extra Pure Japanese Industrial Standards.

The Effect of Temperature. Measurements were made at temperatures 20, 25, and 30 °C to study the effect of temperature. The induction period of the color-fading decreased with an increase in temperature. For example, in the reagent blank, the color-fading of the iron(III) thiocyanate complex began approximately 20 min after the initiation at 25 °C, and 36 min after the initiation at 20 °C (Fig. 5). A temperature of 25.00±0.05 °C was used throughout this work.

The Removal of Nitrite Ions in Nitric Acid. Commercially available nitric acid usually contains trace amounts of nitrite ions as impurity. If such nitric acid is used as a reagent, nitrite ion concentration of less than 0.01 ppm in the sample will prove impossible to determine. Thus, several attempts were made to remove the trace amounts of nitrite ions in the iron(III) reagent solution. It was found that the nitrite ion was readily decomposed

TABLE 4. EFFECT OF VARIOUS IONS ON THE DETERMINATION OF NITRITE

Ion	Added as	Concn (ppm)	Absorbance (19 min) Blank	Absorbance (19 min) 0.05 ppm NO_2^-
None			1.155	0.475
Cl^-	NaCl	1000	1.119	0.372
		500	1.149	0.470
Br^-	KBr	1000	1.143	0.393
		500	1.149	0.480
F^-	NaF	100	1.119	0.456
		10	1.143	0.472
NO_3^-	KNO_3	1000	1.108	0.403
		500	1.149	0.472
SO_4^{2-}	K_2SO_4	1000	1.137	0.527
		500	1.149	0.472
ClO_4^-	$KClO_4$	1000	1.149	0.472
$H_2PO_4^-$	$NaH_2PO_4 \cdot 2H_2O$	500	1.108	0.461
		200	1.149	0.472
CO_3^{2-}	Na_2CO_3	500	1.137	0.502
		250	1.155	0.475
S^{2-}	$Na_2S \cdot 9H_2O$	0.1	1.137	0.620
		0.01	1.143	0.484
SO_3^{2-}	Na_2SO_3	1	1.155	0.551
		0.1	1.149	0.482
CN^-	KCN	1	1.155	0.602
		0.1	1.149	0.480
CrO_4^{2-}	K_2CrO_4	1	1.114	0.416
		0.1	1.143	0.469
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	0.1	1.155	0.509
		0.05	1.155	0.479
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	100	1.149	0.467
Mg^{2+}	$MgSO_4 \cdot 7H_2O$	100	1.149	0.479
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	100	1.149	0.479
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	100	1.155	0.472
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	100	1.155	0.472
Pb^{2+}	$Pb(NO_3)_2$	100	1.149	0.474
Cd^{2+}	$CdSO_4$	100	1.149	0.471
Mn^{2+}	$MnSO_4$	100	1.155	0.474
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	100	1.155	0.476
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	100	1.149	0.478
Ag^+	$AgNO_3$	1	1.149	0.526
		0.1	1.149	0.478
Hg^{2+}	$HgSO_4$	1	1.119	0.513
		0.1	1.137	0.482
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	10	1.149	1.032
		1	1.143	0.480

by the addition of urea. Therefore urea was added to the iron(III) reagent solution, and the solution heated in boiling water under different conditions. As Table 1 illustrates, the absorbance of the reagent blank increases with an increase in the amount of urea. As shown in Table 2, maximum absorbance was obtained after a heating period of 10 min. Heating of the solution over 10 min, causes the complete decomposition of urea, which is succeeded by the decomposition of nitric acid to produce the nitrite ion. By using 10 mg of urea and a heating period of 10 min, nitrite ions can be almost completely decomposed (Table 3). Less than 0.1 ppm of the nitrite ion in the iron(III) reagent solution can also be removed by treating the solution in the same way. The iron(III) reagent solution thus treated could be used for at least 30 days.

The Effect of Various Ions. To establish the effect of various ions on the proposed method, experiments were conducted, both in the presence of nitrite ion (0.05 ppm) and its absence. The experimental results are given in Table 4.

Metal ions, such as silver, mercury(II), and iron(II) interfered with the determination of nitrite ion. Oxidizing or reducing anions, such as sulfide, sulfite, thiosulfate, chromate, and cyanide at 0.1 to 1 ppm level also interfered.

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