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Spectrophotometric Determination of Iron(III) after Separation by Adsorption of Its 5-Chloro-7-iodo-8-quinolinol Complex on Microcrystalline Naphthalene

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A procedure is described for the spectrophotometric determination of iron(III) at ppm levels with 5-chloro-7-iodo-8-quinolinol. Iron(III) reacts with the reagent in an acidic solution to form a water-insoluble blue-black complex, which can be quantitatively adsorbed on the surface of freshly precipitated microcrystalline naphthalene at room temperature. The separated iron(III) complex is dissolved in *N,N*-dimethylformamide, together with the naphthalene, and the absorbance of the resulting solution is measured at 480 nm. Beer's law is obeyed over the range of 5—88 μg of iron in 10 ml of the solvent. The molar absorptivity of the complex was found to be 6.3×10^3 l mol^{-1} cm^{-1} at 480 nm. The effects of various factors, such as the pH, the amounts of the reagent and naphthalene, and diverse ions, were also examined. The proposed method was satisfactorily applied to the determination of iron in several selected samples, including standard reference materials, aluminum metal, and natural water.

5-Chloro-7-iodo-8-quinolinol, which is a derivative of 8-quinolinol, forms water-insoluble colored complexes with various metal ions, such as zinc, manganese, cobalt, nickel, cadmium, and iron(III). These complexes are easily extracted into chloroform or molten naphthalene under the optimum conditions. In this work, 5-chloro-7-iodo-8-quinolinol was chosen as a complexing reagent for the spectrophotometric determination of iron(III). This reagent reacts with iron (III) in the pH range of 1.8—4.5 to form a water-insoluble blue-black complex, which is quantitatively adsorbed on microcrystalline naphthalene at room temperature. The adsorbed naphthalene mixture is dissolved in *N,N*-dimethylformamide, and the absorbance of the solution is measured at 480 nm. The proposed method is characterized by the fact that the complex is easily adsorbed on micro crystalline naphthalene by vigorous shaking for a few seconds, even at room temperature, in contrast with the naphthalene-extraction method,[1–11)] in which heating above 81 °C is required. In this paper, we describe a simple and convenient spectrophotometric method for the determination of iron(III) in the N.B.S. reference materials (alloys) and environmental samples.

Experimental

Reagents. Standard iron(III) solution, 100 ppm. Prepared by dissolving 0.8635 g of ammonium iron(III) sulfate in 100 ml of 0.5 M(1 M=1 mol dm^{-3}) H_2SO_4 and by diluting to 500 ml with water.

5-Chloro-7-iodo-8-quinolinol solution, 0.2%. Prepared by dissolving 0.2 g of this reagent in 100 ml of ethanol.

Naphthalene solution, 20%. Prepared by dissolving 20 g of naphthalene in acetone and by then diluting to 100 ml.

Buffer solutions were prepared by mixing 1 M acetic acid and 1 M ammonium acetate solution at pH 3—6, and 1 M aqueous ammonia and 1 M ammonium acetate solution at pH 8—11.

Apparatus. The absorption measurements were made with a Hitachi Model 200-20 spectrophotometer with 10-mm glass cells.

All the pH measurements were done with a Toa-Dempa Model HM-6A pH meter, equipped with a combination glass and calomel electrode assembly.

Naphthalene was dried with a Tabai Model K-2 drier (Tabai Mfg. Co., Japan).

Procedure. Transfer a sample solution containing 5—88 μg of iron(III) to a tightly stoppered Erlenmeyer flask, and dilute with water to about 45 ml. Add 4.0 ml of a 0.2% 5-chloro-7-iodo-8-quinolinol solution and adjust the pH of the solution to 3.5 with 2.0 ml of an acetate buffer solution. Mix the solution well and let stand for 10 min at room temperature. Add 2.0 ml of 20% naphthalene in acetone to this sample solution as fast as possible, using a small nozzled pipet attached to a rubber bulb, and shake the mixture vigorously for 1 min. Collect the colored naphthalene mixture on a filter paper placed flat on a Teflon filter plate in a funnel or a sintered glass filter (No. 2) by filteration. Wash it with water and dry at 50—60 °C. Then dissolve the mixture in *N,N*-dimethylformamide and dilute to exactly 10 ml. Measure the absorbance of the solution in a 10-mm glass cell against the reagent blank.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of the reagent and the iron(III) complex in a naphthalene–*N,N*-dimethylformamide solution. The iron(III) complex has two absorption peak, at 480 and 620 nm. The reagent blank shows strong absorption below 375 nm.

Effect of pH. The effect of the pH on the absorbance of the complex was investigated. The pH measurements were made at room temperature after the adsorption of the complex on naphthalene. Figure 2 shows that the maximum absorbance is obtained between pH 1.8 and 4.5.

Effect of Reagent Concentration. Varying amounts of a 0.2% 5-chloro-7-iodo-8-quinolinol solution were added to a sample solution containing 50 μg of iron (III) and 2.0 ml of the buffer solution (pH 3.5). The results are shown in Fig. 3. The absorbance increased with an increase in the amount of this reagent up to 1.2 ml of the 0.2% solution. It was reasonably constant when 1.2—7.0 ml of this solution was used.

Effect of Buffer Solution and Digestion Time. The effect of the addition of buffer solution on the absorbance was also investigated. The absorbance was unaffected by the addition of up to 5 ml of the buffer solution. The effect of the digestion time on the absorbance was then investigated by digesting the iron(III) complex for 1—30 min. It was found that the absorbance was constant for this period of digestion.

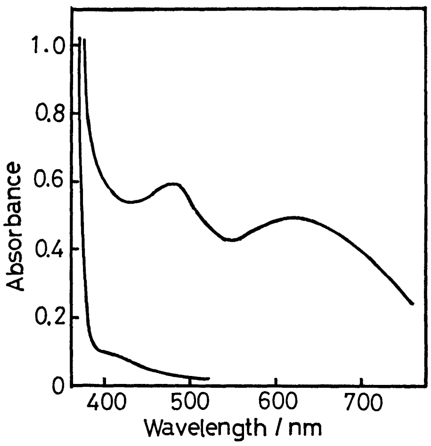

Fig. 1. Absorption spectra of reagent and iron(III)-complex in naphthalene–*N*,*N*-dimethylformamide solution.
Iron(III): 50 μg, 0.2% 5-chloro-7-iodo-8-quinolinol: 4.0 ml, pH: 3.5, 20% naphthalene–acetone: 2.0 ml, shaking time: 1 min, reference: water.

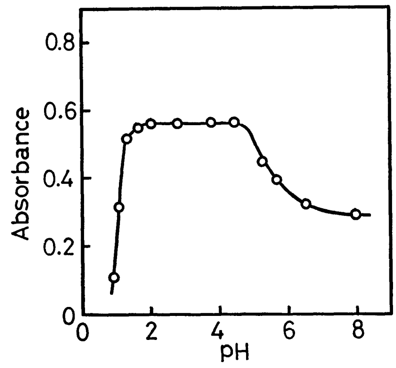

Fig. 2. Effect of pH.
Iron(III): 50 μg, 0.2% 5-chloro-7-iodo-8-quinolinol: 4.0 ml, wavelength: 480 nm, shaking time: 1 min, reference: reagent blank.

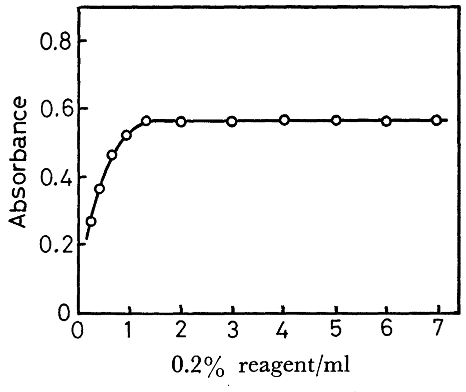

Fig. 3. Effect of reagent concentration.
Iron(III): 50 μg, wavelength: 480 nm, pH: 3.5, 20% naphthalene–acetone: 2.0 ml, standing time: 15 min, reference: reagent blank.

Effect of Naphthalene Concentration. 0.1—4.0 ml portions of 20% naphthalene in acetone were added to a sample solution containing the iron(III) complex. The results showed that the absorbance was independent of the amount of naphthalene.

Effect of Shaking and Standing Times. The effect of the shaking time on the absorbance of the complex was also examined. The rate of the adsorption of the complex on naphthalene was very fast, and no change in the degree of the adsorption was observed during the shaking period of 2—120 s. The adsorbed naphthalene mixture was dissolved in *N*,*N*-dimethylformamide. The color of the complex thus obtained is very stable, and the absorbance remained unchanged for a long time.

Calibration Curve. Based on the optimum conditions described above, a calibration curve for the iron(III) determination was prepared. A linear relationship was obtained between the concentration of iron(III) and the absorbance over the range of 5—88 μg of iron at 480 nm in 10 ml of *N*,*N*-dimethylformamide. The molar absorptivity was 6.3×10^3 l mol^{-1} cm^{-1} at 480 nm, the sensitivity being 0.009 μg/cm^2 for 0.001 absorbance. The relative standard deviation for ten replicate determinations was 0.72% for 50 μg of iron(III).

Choice of Solvent. Tests were made with various organic solvents to dissolve the adsorbed naphthalene mixture. This mixture is easily soluble in *N*,*N*-dimethylformamide, benzene, toluene, xylene, dioxane, chlorobenzene, chloroform, *o*-dichlorobenzene, acetonitrile, nitrobenzene, 1,2-dichloroethane, *etc.* at room temperature.

Effect of the Aqueous-phase Volume. Since the volume ratio of the organic to the aqueous phase is an important factor in the adsorption of the iron(III) complex on naphthalene, the effect of the volume of the aqueous phase on the absorbance was studied.

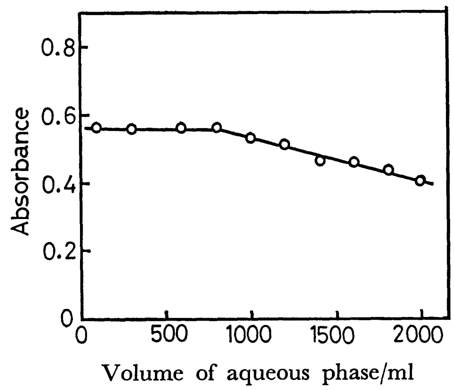

Fig. 4. Effect of volume of aqueous phase.
Iron(III): 50 μg, wavelength: 480 nm, pH: 3.5, 0.2% 5-chloro-7-iodo-8-quinolinol: 6.0 ml, 20% naphthalene–acetone: 4.0 ml, digestion time(30—35 °C): 20 min, reference: reagent blank.

TABLE 1. DETERMINATION OF IRON IN STANDARD REFERENCE MATERIALS(ALLOYS) AND ENVIRONMENTAL SAMPLES

Sample	Iron content (certified value) %	Number of determinations	Iron found: Present method (%)	Iron found: 1,10-phenanthroline method (%)
N.B.S. SRM-85b Al alloy	0.24	5	0.239±0.003	0.239±0.003
N.B.S. SRM-94c Zn alloy	0.018	5	0.017±0.001	0.017±0.001
N.B.S. SRM-158a Silicon-Bronze alloy	1.23	5	1.33 ±0.01	1.27 ±0.02
Metallic aluminum (powder)	—	5	0.135±0.001	0.139±0.002
Lake water (Kitagata, Fukui Pref.)	—	4	1.35 ±0.01 (ppm)	1.45 ±0.04 (ppm)

The results are shown in Fig. 4. Under the experimental conditions described, the absorbance remains almost constant up to about 800 ml of the aqueous phase. With further increases in the volume of the aqueous phase, however, the absorbance is gradually diminished.

Effect of Diverse Ions. The effect of diverse ions on the determination of 50 μg of iron(III) was studied. The following alkali metal salts and metal ions(present in the amounts given in parentheses) did not cause an error of more than ±5%: NaCl(8 g), Na_2SO_4 (8 g), NaI(8 g), NH_4Cl(8 g), KNO_3(7 g), sodium tartrate(5 g), sodium citrate(5 mg), sodium oxalate(3 mg), disodium EDTA(10 μg), Ca^{2+}(8 mg), Mg^{2+}(8 mg), Mn^{2+}(8 mg), Pb^{2+}(500 μg), Cr^{6+}(300 μg), Zn^{2+}(40 μg), Cd^{2+}(150 μg), Bi^{3+}(50 μg), Cu^{2+}(30 μg), Pd^{2+}(20 μg), Ni^{2+}(10 μg), Co^{2+}(5 μg). Most of the diverse metal ions gave a positive error, but the complexing reagents, such as sodium citrate, sodium oxalate, and disodium EDTA gave negative one.

Determination of Iron in Reference Materials and Environmental Samples. The proposed method was applied to the determination of iron in the reference materials, aluminum powder, and water samples. The results are in reasonably good agreement with those obtained by the standard spectrophotometric procedure employing 1,10-phenanthroline,[14] as is shown in Table 1. The analytical procedures were as follows: a 0.8279-g portion of standard aluminum alloy (N.B.S., SRM-85b) was gently dissolved in 40 ml of hydrochloric acid (1+1) and 2 ml of 30% hydrogen peroxide. The excess hydrogen peroxide was decomposed by gently heating the mixture on a boiling-water bath for a few minutes. After cooling, the volume of the sample was made up to 200 ml with water. A 5-ml aliquot was transferred to a 100-ml separatory funnel, and 50 ml of hydrochloric acid (1+3) was added. The iron(III) in this sample was extracted by vigorous shaking for 5 min with 20 ml of isobutyl methyl ketone (MIBK).[12] It was then back-extracted from the organic phase with 25 ml of water, and the proposed method was applied.

A 5.085-g portion of standard zinc alloy(N.B.S., SRM-94c) was dissolved in 60 ml of hydrochloric acid (1+1) and 1 ml of concentrated nitric acid. The excess of the acids was removed by evaporating the mixture on a boiling-water bath, and the volume of the sample made up to 200 ml with water. A suitable aliquot was transferred to a 100-ml separatory funnel, and 20 ml of hydrochloric acid (1+1) was added. The iron(III) in this sample was extracted by vigorous shaking for 3 min with 20 ml of an MIBK–isopentyl acetate(1+1) mixture.[13] The aqueous phase was drained off and discarded. The organic phase was washed first with 15 ml and then with 5 ml of hydrochloric acid(1+1). Then 20 ml of water was added to the organic phase, and the mixture was shaken for 3 min. After having been left standing for 5 min, the aqueous phase was drained off in a beaker. Again, 5 ml of water was added to the organic phase, followed by the same procedure. The combined aqueous solution was diluted to exactly 200 ml with water. To an aliquot of this sample solution, we then added 2.0 ml each of a 10% hydroxyammonium chloride solution and a 20% EDTA solution. The solution was then analyzed for iron by the proposed procedure and the 1,10-phenanthroline method.

A 108.6-mg portion of Silicon Bronze alloy(N.B.S., SRM-158a) was dissolved in 10 ml of hydrochloric acid(1+1), 1 ml of concentrated nitric acid, and 3 ml of concentrated sulfuric acid. The mixture was then gently heated on a boiling-water bath. The excess of the acids was evaporated, and then the volume of the sample was brought to 200 ml with water. This sample was used for the both methods.

Metallic aluminum powder was analyzed in the same way as in the case of the standard aluminum alloy.

Lake-water samples, adjusted to 0.1 M with hydrochloric acid immediately after collection, were filtered through a filter paper(No. 5C) to remove suspended particulates; the filtrates were analyzed for the total iron content using this method and the 1,10-phenanthroline method.[14]

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