Spectrophotometric Determination of Trace Iron after Collection and Elution as Its 8-Hydroxyquinoline-5-sulfonate Chelate on Protonated Chitin

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A collection and elution method for anionic metal chelate on protonated chitin has been applied to the spectrophotometric determination of iron. Iron is collected as its anionic 8-hydroxyquinoline-5-sulfonate (8-HQ-5-S) chelate on a column of chitin in weak acidic medium. The iron(III)-8-HQ-5-S chelate collected on the chitin is effectively eluted with a small volume of 0.1 mol dm^{-3} ammonia buffer solution (pH 9), and the absorbance of the eluent is measured at 571 nm. Beer's law is obeyed over the concentration range of 0.5 to 5 μg of iron in 1 cm^3 of the eluent. Some metal ions and common inorganic anions do not interfere in concentration range of 100 to 1000 times that of iron, but the tolerance limit for Co, Ni and Cu is low due to the competitive reaction with 8-HQ-5-S. The present method can be applied to the determination of iron in tap and spring water samples.

Keywords Preconcentration, spectrophotometric determination, iron, iron(III)-8-hydroxyquinoline-5-sulfonate chelate, protonated chitin

Attention has been paid to the preconcentration of some inorganic ions as their appropriate species on a natural polymer chitin. The spectrophotometric methods for some metal ions have been developed after the collection and elution of their colored metal complexes on a chitin in the presence of suitable counter ions.[1-4] In those process their colored metal complexes were rapidly collected on chitin and readily eluted with a small volume of the suitable eluents.

The acetylamino groups of chitin are protonated in an acidic medium, acting as an anion exchanger. This property of chitin was applied to the determination of some metal ions with atomic absorption spectrometry after preconcentration as their maleonitriledithiolate[5] and 1-nitroso-2-naphthol-3,6-disulfonate[6,7] anionic chelates, and to the spectrophotometric determination of phosphate after collection and elution as its phosphomolybdenum blue anion.[8] The functionalyzed chitin containing dithiocarbamate group has been also synthesized and used for preconcentration of some metal ions.[9]

In this paper, we report on the spectrophotometric determination of iron following the preconcentration procedures as follows: first the collection as its anionic 8-hydroxyquinoline-5-sulfonate chelate, which has the specific absorption spectrum at longer wavelength, on protonated chitin, and second the elution with a small volume of ammonia buffer solution (Fig. 1). The proposed method was applied to the determination of iron in water samples.

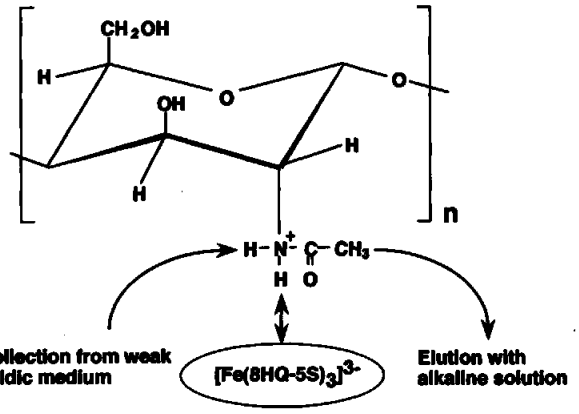

Fig. 1 Collection and elution scheme on protonated chitin.

Experimental

Reagents and apparatus

A commercially available chitin powder (Funakoshi Co., Ltd.) was washed successively with a 1 mol dm^{-3} hydrochloric acid solution, distilled water and acetone; it was then kept at 40° C for 24 h in a vacuum dry oven.

A standard iron(III) solution (1 mg cm^{-3}) was prepared by dissolving 0.7234 g of iron(III) nitrate enneahydrate, 99.9% (Wako Pure Chemicals) in 0.1 mol dm^{-3} nitric acid and diluting to volume in a 100 cm^3 volumetric flask, and standardized by titration with EDTA. This was further diluted as required. A 8-hydroxyquinoline-5-sulfonic acid (8-HQ-5S) solution (1×10^{-2} mol dm^{-3}) was prepared by dissolving 0.4504 g of 8-hydroxyquinoline-5-sulfonic acid (Wako Pure Chemicals) in 0.01 mol dm^{-3} sodium hydroxide and *diluting* to volume in a 200 cm^3 volumetric flask. Other chemicals used were of analytical grade.

All absorbance measurements were made with a Hitachi U-2000 spectrophotometer. A Hitachi–Horiba Model F-7_{AD} pH meter was used for all pH measurements.

Standard procedure

To a solution containing up to 5 μg of iron(III), add 1 cm^3 of 1×10^{-2} mol dm^{-3} 8-HQ-5-S solution and 1 cm^3 of 0.1 mol dm^{-3} acetate buffer solution (pH 4.5); the solution is then diluted with water in a 100 cm^3 volumetric flask. Then pass the solution through a chitin column (polyethylene column, 6 mm i.d.×60 mm long, 50 mg of chitin) fitted with a porous polyethylene disk with a 20-μm pore size at a flow-rate of 10 cm^3 min^{-1}. Elute the iron(III)-8-HQ-5S chelate from chitin with 1 cm^3 of 0.1 mol dm^{-3} ammonia buffer solution (pH 9.0), and measure the absorbance of the eluent at 571 nm.

Results and Discussion

Overall capacity

The overall capacity for 8-HQ-5S and its iron(III) chelate on protonated chitin at pH 4.5 (0.01 mol dm^{-3} acetate buffer solution) was examined by batch equilibration of 50 mg of chitin with 100 cm^3 of each solution containing 5×10^{-5} mol dm^{-3} of 8-HQ-5S and its iron(III) chelate, respectively. The equilibration could be achieved by agitating for over 60 min. After filtration, the amounts collected on chitin for 8-HQ-5S and the iron(III) chelate were decided by comparing the concentration of the solutions before and after equilibration spectrophotometrically. Their overall calculated capacities were 6.07 for 8-HQ-5S and 57.31 μmol g^{-1} for the iron(III) chelate, respectively. It is known that a larger charged ion is adsorbed on an ion-exchanger more than a smaller one, especially in the low concentration range of ion. The negative charge of the species increases from the charge of 8-HQ-5S to that of the iron chelate by the chelation. It is likely that the difference of the amount adsorbed on the protonated chitin between 8-HQ-5S and the iron chelate may be caused by mentioned above. A systematic study using various types of anionic species is required to clarify the adsorption mechanism on protonated chitin in detail.

Absorption spectra

The absorption spectra of iron(III)-8-HQ-5S chelate and the reagent blank in the eluent are shown in Fig. 2. The iron chelate has absorption maximum at 571 nm, where the absorption of reagent blank is negligible. All absorption measurements were, therefore, carried out at 571 nm in this study.

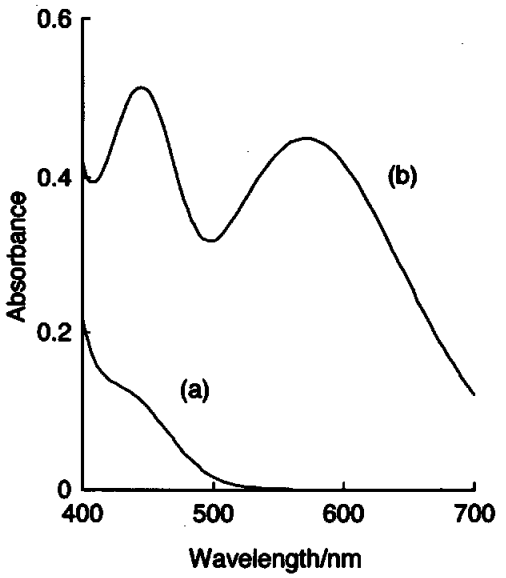

Fig. 2 Absorption spectra of reagent blank and iron(III)-8-hydroxyquinoline-5-sulfonate chelate in eluent. Conditions as standard procedure for 5 μg of iron(III): (a) reagent blank (reference: water); (b) the iron(III) chelate against reagent blank.

Effect of pH on complex formation and collection

The effect of pH on the formation of the iron chelate was examined with a sample containing 1×10^{-4} mol dm^{-3} of iron(III) and 1×10^{-3} mol dm^{-3} of 8-HQ-5S in aqueous solution. The absorbance was found to remain constant over the pH range 4.0 to 9.5.

Figure 3 shows the effect of pH on the collection of the iron chelate on chitin. The iron chelate was quantitatively collected from aqueous solution over a pH range of 4 to 6. It is likely that the collection percentage for iron on chitin decreases due to the insufficient complex formation with 8-HQ-5S below pH 4 and due to the decrease in the amount of the effective protonated chitin above pH 6. This behavior was similar to those of metal-1-nitroso-2-naphthol-3,6-disulfonates.[6,7] In this study, the optimum pH of the solution on the collection was adjusted to be 4.5 by adding 0.1 mol dm^{-3} acetate buffer solution.

Effect of reagent concentration

The effect of the reagent concentration on the collection was also examined. The quantitative collection was obtained in the concentration over a 10-fold molar excess of 8-HQ-5S to iron(III), when the sample solution contained 5 μg of iron(III). The reagent concentration was chosen as described in the standard procedure.

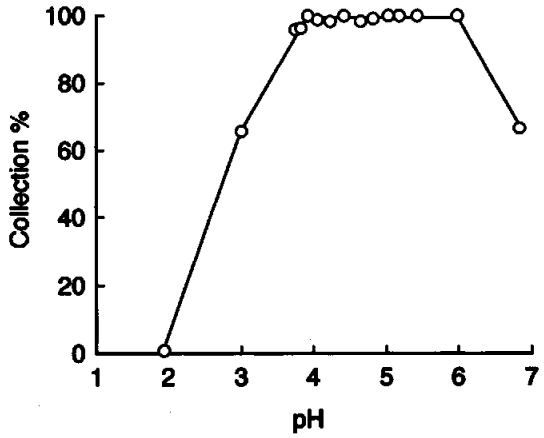

Fig. 3 Effect of pH on collection of iron(III)-8-hydroxyquinoline-5-sulfonate chelate. Conditions as standard procedure except pH of the sample solution.

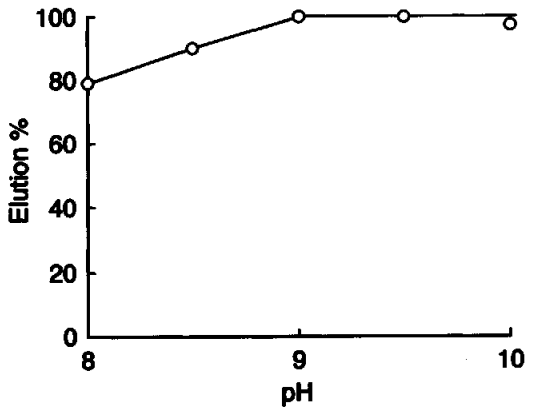

Fig. 4 Effect of pH of eluent on elution of iron(III)-8-hydroxyquinoline-5-sulfonate chelate from chitin. Eluent: 1 cm^3 of 0.1 mol dm^{-3} ammonia buffer solution. Conditions as standard procedure except pH of eluent.

Eluent

The elution of the iron(III) chelate collected on a column of chitin was examined by using 0.1 mol dm^{-3} ammonia buffer solution over a pH range of 8 to 10 (Fig. 4). The elution of the iron(III) chelate was not quantitative with the ammonia buffer solution of pH 8 and 8.5 due to insufficient neutralization of the protonated chitin, while the iron(III) chelate was quantitatively eluted with the ammonia buffer solution of pH $\geqq$ 9. In this study, 0.1 mol dm^{-3} ammonia buffer solution of pH 9.0 was used as the eluent.

Calibration curve, precision and other factors

The calibration curve obtained by the standard procedure was linear over the concentration range of 0.5 to 5 μg of iron in 1 cm^3 of the eluent. The apparent molar absorptivity was 5000 dm^3 mol^{-1} cm^{-1} at 571 nm.

Table 1 Effect of diverse ions

Ion	Added as	Ion/Fe ratio	Recovery, %
Al^{3+}	$Al(NO_3)_2 \cdot 9H_2O$	100	98.5
Cd^{2+}	$Cd(NO_3)_2$	100	100.4
SO_4^{2-}	Na_2SO_4	100	98.9
CrO_4^{2-}	K_2CrO_4	100	99.6
MoO_4^{2-}	Na_2MoO_4	100	100.4
WO_4^{2-}	Na_2WO_4	100	101.2
VO_3^-	NH_4VO_3	100	98.4
Co^{2+}	$Co(CH_3COO)_2$	10	99.6
Ni^{2+}	$Ni(CH_3COO)_2$	10	98.8
Cu^{2+}	$Cu(NO_3)_2$	10	101.9

Fe taken, 2.5 μg.

The relative standard deviation was 1.85% for 2.5 μg of iron (5 measurements).

The effect of flow rate on the collection and elution was examined. The flow rate of sample solution on the collection was varied from 5 to 15 cm^3 min^{-1}. The column was aspirated. The iron chelate was quantitatively collected even when the flow rate was 15 cm^3 min^{-1}. The iron chelate collected on the chitin was readily eluted with 1 cm^3 of the eluent within 1 min.

Collection from 100 cm^3 solution containing 5 μg of iron on a column with various amounts of chitin over the range of 12.5 to 62.5 mg was examined. The iron chelate was quantitatively collected on a column containing down to 25 mg.

Recoveries of 5 μg of iron from various volumes over the range of 100 to 500 cm^3 of sample solution were examined. The iron chelate was quantitatively collected in this range; up to 500-fold concentration could be easily achieved.

Five successive collection and elution cycles with 5 μg of iron on the same chitin gave almost identical results.

Effect of diverse ions

Table 1 shows the effect of diverse ions on the determination of iron. The tolerance limit was taken as being the amount causing an error ±3% in the absorbance of the eluent for iron alone. For the determination of 2.5 μg of iron, Al^{3+}, Cd^{2+}, SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-} and VO_3^- in concentration up to 100-times that of iron were tolerable, but Co^{2+}, Ni^{2+} and Cu^{2+} were tolerated only in concentration up to 10-times that of iron, and gave negative error at more than the concentration range due to the competitive reaction with 8-HQ-5S. It is likely that an increase in the reagent concentration improves the tolerance limits for metal ions. Ca^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, F^-, Cl^-, NO_3^-, ClO_4^-, CO_3^{2-}, PO_4^{3-} and NH_4^+ did not interfere in concentrations up to 1000-times that of iron.

Application

Our method was applied to the determination of iron in tap and spring water samples around Kitami city. Five replicate portions of sample, after pretreatment with

concentrated nitric acid, were analyzed by the standard procedure individually and gave an average value of 8.8 ppb with a relative standard deviation (RSD) of 3.2% for tap water, and a value of 20.4 ppb with an RSD of 3.2% for spring water. The same sample was also analyzed by the spectrophotometric method with 4-(2-pyridylazo)-resorcinol[10] after pretreatment with concentrated nitric acid and 10-fold preconcentration with evaporation. It gave a value of 8.1 ppb with a RSD of 2.5% for tap water, and a value of 18.1 ppb with an RSD of 0.8% for spring water. The results obtained by both methods show reasonable agreement.

In conclusion, the collection of iron-8HQ-5S chelate on chitin is affected by the pH of the solution. The elution of the iron chelate from chitin is easily achieved with aqueous alkaline solution. These facts suggest that most of the anionic iron chelate is collected by the electrostatic interaction between the anionic species and the surface of the protonated chitin. The presented method has the advantages of simplicity, rapidity and a high concentration factor. The proposed method may be applicable to the preconcentration of various colored anionic species used for spectrophotometry.

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