Spectrophotometric Determination of Iron(II) with 2-Diethylamino-4-hydroxy-5-nitroso-6-aminopyrimidine¹

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2-Diethylamino-4-hydroxy-5-nitroso-6-aminopyrimidine (EHNA) is synthesized and used for the spectrophotometric determination of iron(II). EHNA reacts easily with iron(II), copper(II) or nickel(II) to form water-soluble complexes at pH 6.1. The iron(II)-EHNA complex, once formed, is stable even at pH 10.3, while the copper(II) and nickel(II) complexes are decomposed at this pH. The iron(II)-EHNA complex is extracted into an organic solvent such as isopentyl alcohol. The molar absorptivity of the iron(II) complex in an aqueous solution is $3.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 660 nm. The molar ratio of iron(II) to EHNA in the complex is 1:3, according to the continuous variation method. This method has been satisfactorily applied to the determination of iron in various samples, such as leaded brass, copper-nickel and magnesium-aluminum alloys.

Keywords Iron(II) determination, spectrophotometry, 2-diethylamino-4-hydroxy-5-nitroso-6-aminopyrimidine

Though various spectrophotometric methods for the determination of iron(II) have been reported²⁻⁸, many of the chromogenic reagents for iron(II) also react with copper(II) or nickel(II). Consequently, if these reagents are to be used for determining microgram amounts of iron(II) in materials containing relatively large amounts of copper or nickel, any iron present must be separated from the copper or nickel. We have already reported that 5-nitrosopyrimidine compounds are useful for the spectrophotometric determination of iron(II).⁹⁻¹¹ This paper describes a selective and improved spectrophotometric method for determining iron(II) with a new 2-diethylamino-4-hydroxy-5-nitroso-6-aminopyrimidine (EHNA) in an aqueous solution or after extraction into an organic solvent. The proposed method is more sensitive than the previously reported method¹¹, and has the advantages of simplicity, rapidity and stability of the color formed.

Experimental

Reagents

EHNA. The ligand (EHNA) was synthesized by condensation of equimolar quantities of ethyl cyanoacetate with 1,1-diethylguanidine sulfate (Tokyo Kasei Kogyo Co. Ltd.) in a methoxide media, as described elsewhere.⁹ The crude compound was recrystallized from ethanol-water (1:1) to give pink needles, m.p. 198°C.

Analytical results: found, C 45.34, H 6.15, N 32.88%; calculated for $\text{C}_8\text{H}_{13}\text{N}_5\text{O}_2$, C 45.49, H 6.16, N 33.17%.

A stock solution of $9.5 \times 10^{-3} \text{ M}$ EHNA in distilled water was stable for at least 1 month.

A standard iron(II) solution was prepared by dissolving 7.021 g of ammonium iron(II) sulfate hexahydrate in 10 ml of hydrochloric acid (1+1) and diluting to 1000 ml with distilled water.

Buffer solutions were prepared by mixing 1 M acetic acid with 1 M sodium acetate and 2 M ammonia with 2 M ammonium chloride.

Hydroxylammonium chloride solution was used as a 10% aqueous solution; impurity iron was removed by extraction.⁵

All of the reagents used were of analytical-reagent grade.

Apparatus

A Hitachi U-3200 spectrophotometer was used for absorbance measurements with matched 1.00-cm glass cells. A Hitachi-Horiba F-5 pH meter was used for pH adjustments. All measurements were made at 25°C.

Recommended procedure

Aqueous solution. A sample solution was placed into a 10-ml measuring flask; then, 1 ml of 1 M hydrochloric acid, 1 ml of 10% hydroxylammonium chloride and 2 ml of the (0.2 w/v%) EHNA solution, and 2 ml of a buffer solution (pH 10.3) were added successively. The mixture was diluted to the mark with ethanol. The absorbance was then measured in a glass cell of 1.00-cm path length at 660 nm against a reagent blank.

Extraction. A 5-ml aliquot of a sample solution was placed in a 30-ml separatory funnel; then, 1 ml of 1 M hydrochloric acid, 1 ml of 10% hydroxylammonium chloride and 3 ml of the (0.2 w/v%) EHNA solution, and 3 ml of a buffer solution (pH 10.3) were added

successively. The mixture was shaken with 8 ml of isopentyl alcohol for 30 s. (If a large amount of cobalt(II), copper(II) and nickel(II) coexisted, the organic phase was washed with 2 ml of a buffer solution (pH 10.3).) After the two phases were separated, the organic phase was transferred into a 10-ml measuring flask and diluted to the mark with ethanol. The absorbance was then measured in a glass cell with a 1.00-cm path length at 657 nm against a reagent blank.

Results and Discussion

Acid dissociation constant

The acid dissociation constant of EHNA was determined spectrophotometrically¹² in aqueous solution at $25 \pm 0.1^\circ\text{C}$. The ionic strength was adjusted to 0.1 with sodium perchlorate. The pK_a value was found to be 2.38.

Absorption spectra

The absorption spectra of the iron(II) complex were examined at pH 6.1 in an aqueous solution and after extraction into isopentyl alcohol. The absorption spectra of EHNA and its iron(II) complex are shown in Fig. 1. The maximum absorption of the complex

Fig. 1 Absorption spectra of EHNA and its iron(II) complex. EHNA: 1.90×10^{-3} M. In aqueous solution: Fe(II), 1.79×10^{-5} M; 1, reagent blank against water; 2, Fe(II)-EHNA complex against a reagent blank. In isopentyl alcohol: Fe(II), 1.07×10^{-5} M; 3, reagent blank against water; 4, Fe(II)-EHNA complex against a reagent blank.

Fig. 2 Effect of pH on the formation of the Fe(II)-EHNA complex. Fe(II), 1.79×10^{-5} M; EHNA, 1.90×10^{-3} M; ethanol, 10%; wavelength, 660 nm.

occurred at 660 nm in aqueous solution and at 657 nm in isopentyl alcohol. The absorption of the reagent, itself, at these wavelengths was very small.

Effect of pH

The effect of the pH on the formation of the iron(II)-EHNA complex was investigated. The absorbance of the complex was constant over the pH range from 5.5 to 6.8 when the EHNA concentration was 1.9×10^{-3} M, as shown in Fig. 2. The iron(II)-EHNA complex, once formed, is stable even at pH 10.3.

Stability of the complex

The time required for the maximum color development of the complex was found to be 10–20 s at room temperature. The absorbance was then stable for at least 20 h in aqueous solution and at least 30 h in isopentyl alcohol.

Shaking time

The minimum shaking time for the maximum extraction of the iron(II) complex with isopentyl alcohol was found to be 30 s at room temperature.

Choice of solvents

Various organic solvents such as chloroform, 1,2-dichloroethane, nitrobenzene, ethyl acetate, propyl acetate, isopentyl acetate, 2-propanol and isopentyl alcohol were tested as extractants for the iron(II) complex. Isopentyl alcohol was chosen as the best extractant because it exhibited the highest absorbance of the complex in the visible region in this solvent.

Composition of the iron(II) complex

The composition of the iron(II)-EHNA complex in aqueous solution and in isopentyl alcohol was determined by the continuous variation method. The obtained results showed that the molar ratio of iron(II) to the reagent in the complex was 1 : 3.

Calibration graph

A calibration graph for the determination of iron(II) was prepared according to a general procedure. A good linearity was obtained over the range 0–30 μg of iron(II) per 10 ml of aqueous solution and isopentyl alcohol. The Sandell sensitivity of the method in aqueous solution was $1.85 \text{ ng Fe cm}^{-2}$. When the determination of 5 μg of iron(II) was repeated 5 times by the standard procedure, the relative standard deviation was 0.32% in aqueous solution and 0.58% in isopentyl alcohol, respectively. Regarding sensitivity for iron(II), the present reagent, EHNA, is fairly or much superior to other colorimetric reagents such as 2,2'-bipyridyl², 1,10-phenanthroline³, 2,4,6-tripyridyl-1,3,5-triazine⁴, 4,7-diphenyl-1,10-phenanthroline⁵ and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine.⁶

Reactions of EHNA with metal ions

The reactions between EHNA and metal ions were

Table 1 Reactions of EHNA with metal ions

Ion	Wavelength/nm ($\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$)	
	pH 6.1 (acetate)	Final pH 10.3
K(I)	—	—
Na(I)	—	—
Li(I)	—	—
Ba(II)	—	—
Ca(II)	—	—
Cd(II)	—	—
Co(II)	385 ^a	385 ^a
Cu(II)	378 (1.5×10^4)	390 (5.7×10^2)
Fe(II)	370 (2.4×10^4), 660 (3.0×10^4)	377 (3.3×10^4), 660 (3.0×10^4)
Hg(II)	374 (3.2×10^2)	—
Mg(II)	—	—
Mn(II)	—	—
Ni(II)	371 (2.3×10^4)	390 (8.8×10^2)
Pb(II)	378 (2.0×10^2)	390 (5.6×10^2)
Pd(II)	364 (7.4×10^3)	379 (7.4×10^3)
Sn(II)	—	—
Sr(II)	—	—
Zn(II)	370 (3.3×10^2)	—
Al(III)	380 (3.4×10)	—
Bi(III)	385 (1.7×10^2)	400 (1.3×10^3)
Cr(III)	380 (2.3×10^2)	400 (2.0×10^2)
Fe(III)	377 (5.6×10^3)	404 (2.7×10^3)
Mo(VI)	—	—

a. Unstable absorbance.

—: no reaction.

 ϵ : molar absorptivity of complex ($1 \text{ mol}^{-1} \text{ cm}^{-1}$).EHNA: $1.90 \times 10^{-3} \text{ mol/l}$.

Reference: reagent blank.

examined and the results are summarized in Table 1. Among the 22 metal ions tested, only the iron(II)-EHNA complex was stable at pH 10.3; hence, the selectivity for the determination of iron(II) was improved at this pH. Under standard conditions the interference of various ions on the determination of $5 \mu\text{g}$ of iron(II) in isopentyl alcohol was studied. Many metal ions such as aluminum(III), cadmium(II), copper(II), lead(II), magnesium(II), nickel(II) and zinc(II) in 3 mg amounts and 0.5 mg of cobalt(II) did not interfere. Common anions such as acetate, chloride, nitrate and sulfate also did not interfere.

Influence of substituents on the pyrimidine ring

The effect of substituents on the pyrimidine ring on the molar absorptivity of the resulting iron(II) complexes is shown in Table 2.^{9,10} It was found that all of these derivatives reacted with iron(II) to form a water-soluble blue complex. The molar ratio of iron(II) to each reagent in these complexes in aqueous solution was 1:3, found by the continuous variation method. The molar absorptivity of the iron(II) complexes was the highest when the dimethylamino group and diethylamino group were used. This suggests that the charged quinone theory¹³ can be extended to these pyrimidine compounds, since chelates can take the charged quinone structure by the electron-donating dimethylamino group or the diethylamino group at the *para* position of the nitroso group.

Application to a magnesium-aluminum alloy

The proposed aqueous-solution method was applied to the determination of iron in two standard magnesium-

Table 2 Iron(II) complexes of 4-hydroxy-5-nitroso-6-aminopyrimidine derivatives

Compound	R ₁	R ₂	R ₃	pH ^b 6.1 (acetate)		pH ^c 10.3	
				$\lambda_{\text{max}}/\text{nm}$	$\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$
1 ^a		(C ₂ H ₅) ₂ N		660	3.0×10^4	660	3.0×10^4
2		(CH ₃) ₂ N		650	2.7×10^4	660	3.0×10^4
3		CH ₃ S		650	9.5×10^3	660	1.9×10^4
4		=S	CH ₃	650	5.5×10^3	670	1.7×10^4
5		=O	CH ₃	625	1.1×10^4	635	1.7×10^4
6		=O	C ₆ H ₅	630	1.1×10^4	645	1.7×10^4
7	CH ₃	=S	CH ₃	650	1.7×10^4	650	1.6×10^4
8		CH ₃		670	9.4×10^3	680	1.3×10^4
9		CH ₃ NH		650	6.2×10	660	5.0×10^3
10	CH ₃	=O	CH ₃	610	4.0×10^2	610	3.9×10^2

a. This work. b. Molar absorptivity measured at pH indicated. c. Molar absorptivity measured at final pH indicated.

 ϵ : molar absorptivity of complex ($1 \text{ mol}^{-1} \text{ cm}^{-1}$). Reagent concentration kept constant at $1.6 \times 10^{-3} \text{ M}$ throughout.

Reference: reagent blank.

Table 3 Determination of iron in magnesium-aluminum alloys

Sample	Composition, %	Sample taken (mg/100 ml)	Fe content, %	
			Certified	Found ^a
BCS 263/2 5% magnesium-aluminum alloy	Cu 0.019, Mg 4.67,	a) 23.7	0.26	0.26 ₂ ±0.002
	Si 0.14, Mn 0.36,	b) 29.0		0.26 ₄ ±0.003
	Zn 0.056, Ti 0.022,	c) 36.8		0.27 ₁ ±0.002
	Cr 0.074			
BCS 262/1 10% magnesium-aluminum alloy	Cu 0.039, Mg 10.75	a) 26.8	0.20	0.19 ₅ ±0.002
	Si 0.16, Mn 0.084	b) 28.6		0.20 ₃ ±0.003
	Ni 0.07, Zn 0.085,	c) 32.2		0.20 ₇ ±0.003
	Ti 0.005			

a. Av. of triplicate determinations by the non-extraction method.

Table 4 Determination of iron in leaded brass and copper-nickel alloy

Sample	Composition, %	Sample taken (mg/100 ml)	Fe content, %	
			Certified	Found ^a
BCS 385 Leaded brass	Cu 58.7, Sn 0.27,	a) 66.4	0.15	0.14 ₂ ±0.004
	Pb 2.24, Ni 0.13,	b) 71.6		0.15 ₃ ±0.005
	Zn 38.5	c) 76.1		0.14 ₈ ±0.005
BCS 180/2 Copper-nickel	Cu 68.12, Ni 30.35,	a) 17.4	0.68	0.70 ₁ ±0.004
	Mn 0.75, C 0.04,	b) 21.7		0.67 ₆ ±0.004
	S 0.006	c) 23.5		0.68 ₅ ±0.003

a. Av. of triplicate determinations by the extraction method.

aluminum alloy samples. The magnesium-aluminum alloy sample in a 100-ml beaker was treated with 10 ml of hydrochloric acid (1+1) plus 1 ml of concentrated nitric acid. The mixture was first heated on a hot-plate, then cooled to room temperature and transferred into a 100-ml calibrated flask. A suitable aliquot of this solution was used for the iron(II) determination. The analytical results shown in Table 3 are in reasonable agreement with the standard values.

Application to leaded brass and copper-nickel

The extraction method was applied to the determination of iron in leaded brass and copper-nickel. The samples were treated with 10 ml of nitric acid (1+1). The mixture was first heated on a hot-plate, then cooled to room temperature and transferred into a 100-ml calibrated flask. The analytical results are shown in Table 4. Iron in these sample solutions could be determined rapidly and simply.

In conclusion, EHNA is considered to be an excellent reagent for determining iron(II) because of its high selectivity and the stability of its iron(II) complex color as well as good reproducibility with a very low absorbance of the reagent blank. The molar absorptivity of the complex and the Sandell sensitivity are $3.0 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $1.85 \text{ ng Fe cm}^{-2}$, respectively. The molar ratio of metal to EHNA in the complex is 1:3 according to the continuous variation method. The proposed method can be satisfactorily applied to the determination of iron in leaded brass, copper-nickel and magnesium-aluminum alloys.

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