Bull. Chem. Soc. Jpn., 54, 1544—1547 (1981)

Spectrophotometric Determination of Iron(III) with *N*,*N*′-Bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic Acid

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(Received September 26, 1980)

N,*N*′-Bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic acid (hbed) reacts with iron(III) to form a red complex having an absorption maximum at 485 nm. The iron(III) complex is so stable that the maximum absorbance of the solution is constant over the pH range from 2.5 to 13.2 and a large excess of reagent is not necessary. Beer's law is obeyed up to 1.6×10^{-4} mol dm^{-3} (9 μg cm^{-3}) of iron(III). The molar absorption coefficient is 3.95×10^3 l cm^{-1} mol^{-1}, and the relative standard deviation for determination of 3.5 μg cm^{-3} of iron was 0.29%. The molar ratio of iron(III) to hbed was found to be 1:1. The effect of 32 diverse ions was examined; only colored aqua metal ions interfere. The present method was applied to the determination of iron in aluminium alloys.

Spectrophotometric determination of iron(III) has been extensively studied by many authors.[1–9] In these studies, the method[6–8] using the reagent ethylenediamine-*N*,*N*′-di(2-hydroxyphenylacetic acid) (eddha) is peculiar: the reagent reacts with iron(III) to form a very stable complex (stability constant *ca.* 10^{34}); hence the color development is maximal over a wide pH range, and a large excess of the reagent is not necessary in the determination. These features are desirable in spectrophotometric determinations.

The reagent *N*,*N*′-bis(2-hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetic acid (hbed) gives a red color with iron(III) through the formation of a very stable complex whose stability constant is *ca.* 10^{40}. The constant is the highest of those of iron(III) complexes. Further, the constant is particularly large among metal–hbed complexes. So, in this study, hbed has been examined for the spectrophotometric determination of iron(III). The present method gives accurate results for iron(III) ranging from 1×10^{-5} to 16×10^{-5} M (1 M=1 mol dm^{-3}) (0.6—9 μg cm^{-3}), and has high selectivity.

Experimental

Reagents. *hbed Solution*: Material hbed·2HCl·2H$_2$O was prepared by the literature method.[10] Found: C, 48.75; H, 5.92; N, 5.65; Cl, 14.11%. Calcd for $C_{20}H_{24}N_2O_6\cdot2HCl\cdot2H_2O$: C, 48.30; H, 6.04; N, 5.64; Cl, 14.25%.

A 1×10^{-3} M hbed solution was prepared by dissolving a weighed amount of the prepared reagent in water.[11]

Iron(III) Solution: A 0.01 M iron(III) solution was prepared by dissolving guaranteed reagent grade iron(III) nitrate in 0.02 M nitric acid. The solution was standardized by edta titration using Variamine Blue B as indicator. This solution was diluted with 0.02 M nitric acid as required.

Iron(II) Solution: A 0.01 M iron(II) solution was prepared by dissolving GR grade iron(II) sulfate in 0.02 M nitric acid. The solution was standardized by the following procedure. Hydrogen peroxide was first added to the iron(II) solution. After the iron(II) was oxidized to iron(III), the excess hydrogen peroxide was expelled completely by warming the solution. Then the solution was titrated with edta, using Variamine Blue B as indicator.

Water: The ion-exchanged water was distilled with an allquartz distillation apparatus.

Apparatus. Absorbance and absorption spectra were measured with a Hitachi Perkin Elmer 139 spectrophotometer using 10 mm quartz cells. The pH values were measured with a Toa Electronics Model HM-15A digital pH-meter.

Standard Procedure. A sample solution containing up to 4 μmol (230 μg) of iron(III) is taken into a 50 cm^3 Erlenmeyer flask. Then 6 cm^3 of 1×10^{-3} M hbed, 1 cm^3 of 1 M acetic acid, and 2.5 cm^3 of 1 M sodium acetate are added. After being kept for about three minutes in a boiling water bath, the solution is cooled with running water. Next, the solution is transferred to a 25 cm^3 volumetric flask, and diluted to the mark with water (final pH: 5.1). The absorbance of the solution is measured at 485 nm against water.

Results and Discussion

Absorption Spectra. The red solution of Fe(III)–hbed complex had an absorption maximum at 485 nm. The reagent solution did not absorb light in the visible region.

Effect of pH. The pH of the Fe(III)–hbed complex solution was altered by the addition of nitric acid, acetic acid, acetic acid–sodium acetate, mannitol–boric acid–sodium borate, or sodium borate–sodium hydroxide buffer system. The absorbance of the solution at 485 nm remained constant over a wide pH range 2.5—13.2, as is shown in Fig. 1.

Stability of the Color. The color reaction of hbed with iron(III) seemed to take place rapidly, but the absorbance of the resultant colored solution increased very slowly. However, when the resultant solution was heated in a boiling water bath for about a few

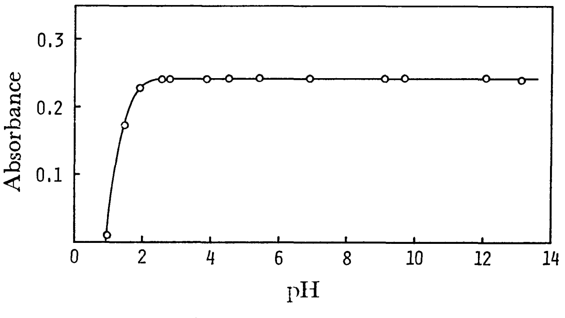

Fig. 1. Effect of pH on formation of Fe(III)–hbed complex.
Fe(III): 6.29×10^{-5} M (3.51 μg cm^{-3}), hbed: 1.03×10^{-4} M, wavelength 485 nm, reference: water, I= 0.1 M.

minutes, the maximum color development was obtained. The color, once developed, was very stable; the absorbance remained constant over a period of 72 h, and the absorbance was not affected by the measurement temperature (10—35 °C). Further, the reagent solution itself was stable; the concentration was unchanged for at least 40 d.

Effect of hbed Concentration. A constant absorbance was obtained over a [hbed]/[Fe(III)] ratio range 1.0—6.0. This fact shows that a large excess of reagent is not needed for full color development.

Effects of the Amount of Buffer Solution and Ionic Strength. A buffer solution was prepared by mixing 1 M acetic acid solution with 1 M sodium acetate solution in 1:2.5 ratio. The addition of from 1 to 10 cm^3 of the buffer solution (for 1.5 μmol of iron(III) in 25 cm^3 solution) had no effect on the color intensity of the iron(III) complex. The effect of ionic strength was also examined. The color intensity of the iron(III) complex did not change in ionic strengths from 0.1 to 0.4 M.

Calibration Curve. The calibration curve under the conditions described in the standard procedure was linear at least up to 1.6×10^{-4} M (9 μg cm^{-3}) of iron(III). The molar absorption coefficient of Fe(III)-hbed complex was 3.95×10^3 l mol^{-1} cm^{-1}, and the Sandell sensitivity for the absorbance of 0.001 was 1.41×10^{-2} μg cm^{-2}. The relative standard deviation of the absorbance was 0.29% for 6.3×10^{-5} M (3.5 μg cm^{-3}) of iron(III) (12 determinations).

Effect of Diverse Ions. The effect of diverse ions was investigated, as is shown in Table 1. It was seen that a large excess of colored metal ions interfered to some extent, and other metal ions did not interfere even if they were present at a concentration of 2000 times that of iron(III). The interferences from the metal ions such as chromium(III), cobalt(II), nickel(II), and uranyl(II) are considered to be attributed to the absorption of light by the colored aqua metal ions, since positive error occurs.

Composition of the Complex. The results obtained by the molar ratio study are shown in Fig. 2. It is seen that iron(III) forms a 1:1 complex with hbed. The same results were also obtained by the continuous variation method.

Determination of Iron(II). It seemed that hbed reacted with iron(II) and the Fe(II)-hbed complex formed was oxidized instantly to the red complex Fe(III)-hbed. Thus, the determination of iron(II) was run by use of the present method. The results of the three repeated determinations for 1.54 μmol/25 cm^3 of iron(II) were 1.53, 1.54, and 1.53 μmol/25 cm^3; iron(II) could be determined without addition of any oxidizing agent. Consequently, the total iron content, iron(II) and iron(III), is determined by the present method.

Determination of Iron in an Aluminium Alloy. Aluminium alloys were furnished by the National Bureau of Standards. 85b wrought: Fe, 0.24; Cu, 3.99; Si, 0.18; Mn, 0.61; Ni, 0.084; Cr, 0.21; Ti, 0.022; Pb, 0.021; Mg, 1.49; Zn, 0.03%. 87a Al-Si: Fe, 0.61; Cu, 0.30; Si, 6.24; Mn, 0.26; Ni, 0.57; Cr, 0.11; Ti, 0.18; Pb, 0.10; Mg, 0.37; Zn, 0.16%.

TABLE 1. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF IRON(III)

Ion	Added as	Amount added to 25 cm^3 μmol	Iron(III) found in 25 cm^3 μmol
K^+	KCl	3000	1.51
Li^+	$LiNO_3$	3000	1.51
Na^+	$NaNO_3$	3000	1.51
NH_4^+	NH_4Cl	3000	1.51
Rb^+	$RbNO_3$	3000	1.52
Tl^+	$TlNO_3$	3000	1.51
Ba^{2+}	$Ba(NO_3)_2$	3000	1.51
Be^{2+}	$Be(NO_3)_2 \cdot 3H_2O$	3000	1.53
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	3000	1.52
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	3000	1.51
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	20	1.54
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	750	1.43[20]
		300	1.51
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	3000	1.51
Mn^{2+}	$Mn(NO_3)_2 \cdot nH_2O$	3000	1.55
		750	1.53
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	750	1.53
Pb^{2+}	$Pb(NO_3)_2$	3000	1.52
Sr^{2+}	$Sr(NO_3)_2$	3000	1.50
UO_2^{2+}	$UO_2(NO_3)_2 \cdot 6H_2$	30	1.55
		15	1.52
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	3000	1.52
Al^{3+}	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	3000[a]	1.50
Ce^{3+}	$Ce(NO_3)_3 \cdot 6H_2O$	3000	1.52
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	20	1.58
		5	1.53
La^{3+}	$La(NO_3)_3 \cdot 6H_2O$	3000	1.51
Cl^-	NaCl	3000	1.51
ClO_4^-	$NaClO_4$	3000	1.52
F^-	NaF	3000	1.52
NO_2^-	$NaNO_2$	3000	1.52
NO_3^-	$NaNO_3$	3000	1.51
SCN^-	NH_4SCN	3000	1.52
SO_4^{2-}	$Na_2SO_4 \cdot 10H_2O$	3000	1.51
Citrate	$C_6H_8O_7 \cdot H_2O$	1300	1.50
Phosphate	$NaH_2PO_4 \cdot 2H_2O$	3000	1.52

Iron(III) taken: 1.52 μmol(84.9 μg) in 25 cm^3 solution.
a) The pH was adjusted to 3.2.

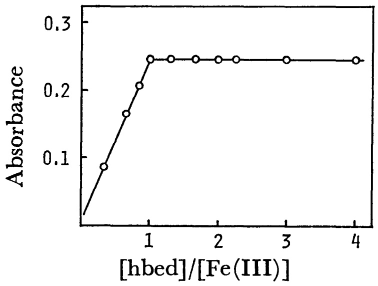

Fig. 2. Molar ratio plot at 485 nm.
Fe(III): 6.29×10^{-5} M, reference: water, pH=5.5, I=0.1 M.

A weighed amount of the alloy (85b wrought: 0.5 g, 87a Al-Si: 1.2 g) was taken in a 50 cm^3 Erlenmeyer flask, and concentrated hydrochloric acid

TABLE 2. ANALYTICAL RESULTS OF IRON IN ALUMINUM ALLOYS

Sample	Certified (%)	Found (%)
NBS 85, Wrought	0.24	0.23 0.24 0.24
NBS 87a, Al-Si	0.61	0.61 0.61 0.61

was added drop by drop. After the dissolving was complete, a small amount of concentrated nitric acid was added and the solution was boiled gently for several minutes. Next, the solution was transferred to a 100 cm^3 volumetric flask and diluted to the mark with water. Then, 3 cm^3 of the solution prepared was used for determination of iron. In the determination, the pH was adjusted to 3.2. The analyses were run three times, starting from the weighing of the sample. As shown in Table 2, satisfactory results were obtained.

Conditional Stability Constants. The stability constants for the hbed complexes of iron(III), copper(II), nickel(II), manganese(II), cadmium(II), lead(II), magnesium(II), calcium(II), cobalt(II), and zinc(II) are known.[10] Thus, the conditional stability constants[12] ($K_{\mathrm{M'L'(ML)'}}$) for the hbed complexes were calculated from Eq. 1[13] with the aid of an electronic computer (OKITAC 50).

$$K_{\mathrm{M'L'(ML)'}} = \frac{[(\mathrm{ML})']}{[\mathrm{M'}][\mathrm{L'}]} = \frac{\alpha_{\mathrm{ML(H)}}}{\alpha_{\mathrm{M(OH)}}\alpha_{\mathrm{L(H)}}}K_{\mathrm{ML}}, \qquad (1)$$

where

$$\alpha_{\mathrm{M(OH)}} = 1 + \sum_{m=1}^{m} \beta_{\mathrm{M(OH)}_m}[\mathrm{OH}^-]^m,$$

$$\alpha_{\mathrm{L(H)}} = 1 + \sum_{n=1}^{n} \beta_{\mathrm{H}_n\mathrm{L}}[\mathrm{H}^+]^n,$$

$$\alpha_{\mathrm{ML(H)}} = 1 + \sum_{i=1}^{i} \beta_{\mathrm{MH}_i\mathrm{L}}[\mathrm{H}^+]^i.$$

Here, K_{ML} refers to the stability constant of the complex ML, $\beta_{\mathrm{M(OH)}_m}$ and $\beta_{\mathrm{H}_n\mathrm{L}}$ are the over-all stability constant of the metal complex with hydroxide ion and the over-all protonation constant of the ligand, respectively, and $\beta_{\mathrm{MH}_i\mathrm{L}}$ is the over-all protolytic stability constant of the acid complex $\mathrm{MH}_i\mathrm{L}$ $\left(\prod_{i=1}^{i}\frac{[\mathrm{MH}_i\mathrm{L}]}{[\mathrm{MH}_{i-1}\mathrm{L}][\mathrm{H}^+]}\right)$. The formation of an acid complex with known constant was taken into consideration. In Fig. 3, the conditional constants calculated at various pH values are plotted. Figure 3 shows that the value of the conditional constant of Fe(III)–hbed complex is considerably higher than those of the hbed complexes of other metals.

Conditional stability constants of metal–eddha complexes were also calculated from the stability constants[14,15] of the related complexes, and compared with those of the metal–hbed complexes. The conditional constant of Fe(III)–hbed complex is higher than that of Fe(III)–eddha complex, as shown in Fig. 3. For other metals, however, the consitional constant of the hbed complex is similar in magnitude to that of eddha complex. Consequently, it may be seen that reagent hbed is superior to reagent eddha in the determination of iron(III).

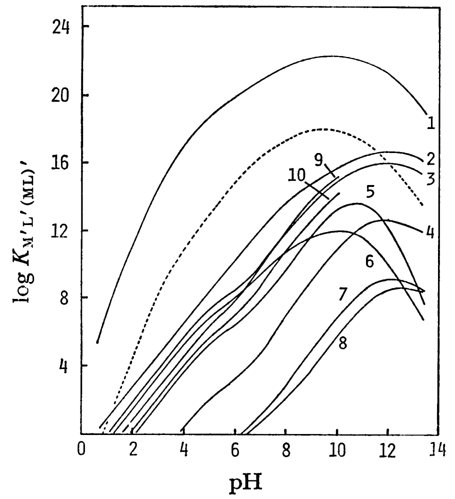

Fig. 3. Conditional stability constants, $K_{\mathrm{M'L'(ML)'}}$, of various metal-hbed complexes as functions of pH. Metal: 1, Fe(III); 2, Cu(II); 3, Ni(II); 4, Mn(II); 5, Cd(II); 6, Pb(II); 7, Mg(II); 8, Ca(II); 9, Co(II); 10, Zn(II). The dotted line shows the conditional stability constant of Fe(III)–eddha complex.

Characteristics of the Present Method. The present method has high selectively without masking agents (Table 1). This is attributable to the following reasons: (1) the stability constant of Fe(III)–hbed complex is particularly large among those of metal–hbed complexes; (2) the absorption spectrum of Fe(III)–hbed complex in the visible region differs from those of other metal–hbed complexes, whose spectra are similar in shape and magnitude to those of aqua metal ions. The precision is relatively high (relative standard deviation: 0.29%); this seems to be attributable to the high stability of the developed color. On the other hand, the sensitivity is small. In selectivity the present reagent hbed is superior to other reagents, *e.g.*, eddha,[6] 5-sulfosalicylic acid,[16] tiron,[17] edta,[18] and salicylic acid,[19] whose sensitivities are also small.

References

1) "Zikken Kagaku Koza," 3rd ed, ed by the Chemical Society of Japan, Maruzen, Tokyo (1966), Vol. 15, Part II, p. 268.

2) "Shin Zikken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1976), Vol. 9, Part I, p. 331.

3) "Bunseki Kagaku Binran," 2nd ed, ed by the Japan Society for Analytical Chemistry, Maruzen, Tokyo (1971), p. 102.

4) "Muki Oyo Hishoku Bunseki," Kyoritsu Shuppan, Tokyo (1974), Vol. 2, p. 323.

5) T. Takeuchi and Y. Shijo, *Bunseki Kagaku*, **14**, 930 (1965).

6) A. L. Underwood, *Anal. Chem.*, **30**, 44 (1958).

7) A. L. Underwood, *Anal. Chim. Acta*, **20**, 228 (1959).

8) G. V. Johnson and R. A. Young, *Anal. Chem.*, **40**, 354 (1968).

9) J. Ueda, *Bull. Chem. Soc. Jpn.*, **51**, 773 (1978).

10) F. L'Eplattenier, I. Murase, and A. E. Martell, *J. Am. Chem. Soc.*, **89**, 837 (1967).

11) The material prepared is slightly soluble in water. A 2×10^{-3} M solution may be prepared at room temperature. The velocity of dissolution is very slow. However, the velocity is accelerated by the addition of sodium hydroxide.

12) A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers Inc., New York (1963), p. 35.

13) The formation of a basic complex was not taken into consideration since the formation constants of basic hbed complexes are not known.

14) A. E. Frost, H. H. Freedman, S. J. Westerback, and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 530 (1958).

15) G. Anderegg and F. L'Eplattenier, *Helv. Chim. Acta*, **47**, 1067 (1964).

16) M. Kennard and C. R. Johnson, *Proc. Trans. Texas Acad. Sci.*, **27**, 45 (1944).

17) J. H. Yoe, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1964).

18) H. J. Cluley and E. J. Newman, *Analyst*, **88**, 3 (1963).

19) R. O. Scott, *Analyst*, **66**, 142 (1941).

20) The negative error can be attributed to the formation of a Cu(II)–hbed complex (with dissociation of Fe(III)–hbed complex) since the stability constant of the Cu(II)–hbed complex is high.