October, 1984] © *1984 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 57, 2999—3000 (1984)* 2999

A Modification of the Method of Spectrophotometric Determination of Iron with Ethylenediamine-*N,N'*-bis(2-hydroxyphenylacetic acid)

Tetsuo Katsuyama* and Kyoko Watanabe

Depertment of Basic Technology, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992

(Received January 9, 1984)

Synopsis. Etylenediamine-*N,N'*-bis(2-hydroxyphenylacetic acid) (H_4eddha) reacts with iron to form a 1:1 complex having an absorption maximum at 480 nm. The method of the spectrophotometric determination of iron with eddha was modified by heating the colored solution in a boiling water bath for a few minutes. The molar absorption coefficient of the Fe^{III}-eddha complex formed was 4.72×10^3 l mol^{-1} cm^{-1} and the relative standard deviation for determination of 5.90×10^{-5} mol dm^{-3} (3.29 μg cm^{-3}) of iron was 0.21%. The effect of 45 diverse ions was examined; only a few metal ions interfered. Aluminium alloys were analyzed for iron by the present method.

Ethylenediamine-*N, N'*-bis(2-hydroxyphenylacetic acid) (H_4eddha) has been used for the spectrophotometric determination of iron.[1–4] This reagent reacts with either iron(III) or iron(II) in the molar ratio 1:1 to form a red iron (III) complex.[5] The stability constant of the Fe^{III}-eddha complex is particularly large among metal-eddha complexes,[6] and the iron(III) complex is so stable that the color development is maximal over a wide pH range and a large excess of the reagent is not necessary for the determination.

This reagent has desirable properties for the spectrophotometric determination of iron. However it is not widely used for this purpose in spite of it being available for analytical use at a reasonable cost. This can be attributed to the following facts. (1) The color reaction of eddha with iron is slow; (2) the effect of diverse ions has not previously been examined sufficiently.

Gordon V. Johnson *et al.* reported that when the resultant colored solution was allowed to stand 18 h before absorbance was measured, the adverse effect of foreign metals on the accuracy of the analysis could be minimized.[4] However, their method is not convenient for usual spectrophotometric analysis since the color-developing period is long. Recently we have found that when the resultant colored solution not showing maximum color intensity was heated in a boiling water bath for a few minutes, the maximum color development was obtained and the color, once developed, was stable. Further, when the heating treatment was used, the existence of moderately large amounts of diverse ions was permited and accurate results were obtained. The present method can be also applied to the determination of iron in aluminium alloys.

Experimental

Reagents. A 1×10^{-2} M (1 M=1 mol dm^{-3}) iron(III) solution was prepared by dissolving guranteed reagent grade iron(III) nitrate in 0.02 M nitric acid. The concentration of the iron(III) ion was determined titrimetrically with edta. This solution was diluted with 0.02 M nitric acid as required.

A 1×10^{-3} M eddha solution was prepared by dissolving the known amount of the reagent obtained from Dojindo Laboratories in dilute sodium hydroxide solution; the molar ratio of eddha to sodium hydroxide was one to two. The reagent solution is colorless. However it changes to light yellow on standing for about 15 d. Thus it is recommended that fresh reagent solution be prepared every two weeks.

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 less than about 8 μmol (450 μg) of iron was taken into a 50 cm^3 Erlenmeyer flask. Then, 12 cm^3 of 1×10^{-3} M eddha, 2 cm^3 of 1 M acetic acid, and 5 cm^3 of 1 M sodium acetate were added to the solution. After the Erlenmeyer flask was kept for three minutes in a boiling water bath, the solution was cooled with running water. The cooled solution was then transfered to a 50 cm^3 volumetric flask and diluted to the mark with water; final pH was 5.1. The absorbance of the solution was measured at 480 nm against water.

Results and Discussion

The solutions for absorbance measurements were prepared by the heating method unless otherwise stated.

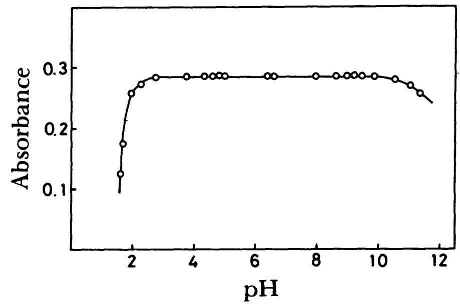

Fig. 1. Effect of pH on formation of the Fe^{III}-eddha complex.
Fe^{III}: 6.04×10^{-5} M (3.37 μg cm^{-3}), eddha: 2.40×10^{-4} M, wavelength: 480 nm, reference: water.

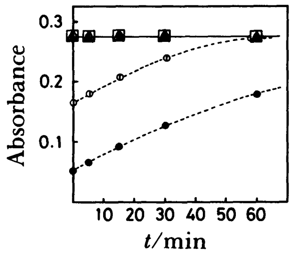

Fig. 2. The changes in absorbance of iron(III) eddha solution with time.
Fe^{III}: 5.83×10^{-5} M eddha: 2.40×10^{-4} M, Ni^{II}: 1.70×10^{-2} M pH: 5.0, room temperature (20 °C), wavelength: 480 nm, reference: water.
Heating time: ---●---, 0 min; ---◐---, 1 min; —▲—, 2 min; —○—, 3 min; —△—, 5 min; —□—, 8 min. The quantity of the solution heated was 25 cm^3.

Absorption Spectra and Effect of pH. The solution of Fe^{III}-eddha had an absorption maximum at 480 nm. The absorbance of the solution at 480 nm remained constant over a wide pH range 2.5—10.0 (Fig. 1).

Color Development. Without the heat treatment, the time to obtain the maximum color development was varied by changing the conditions.[7] However, when the solution not showing maximum color intensity was kept for a few minutes in a boiling water bath the color reaction was completed. Examples are shown in Fig. 2, in which it is seen that the maximum color development is obtained by the heat treatment of two minutes and above. As a rule, a heat treatment of three minutes was adequate for full color development if the quantity of the solution for the color reaction was less than 40 cm³. The color, once developed, was stable; the absorbance remained constant over a period of 5 h. The absorbance was independent of the temperature of measurement (10—35 °C).

Composition of the Complex and Effect of eddha Concentration. The composition of the complex was determined by a molar ratio study: The absorbance was plotted as ordinate against the $[\mathrm{eddha}]/[\mathrm{Fe^{III}}]$ ratio (iron concentration constant; ratio, 0.3—6.0). The absorbance increased linearly with the ratio but became constant above a ratio of unity. This suggests that iron(III) forms a 1:1 complex with eddha and a large excess of reagent is not needed for full color development.

Effects of 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 color intensity of the iron(III) complex was not affected by the addition of from 2 to 20 cm³ of the buffer solution (for 2.95 μmol of iron(III) in 50 cm³ solution). The color intensity of the iron(III) complex was also not affected by an ionic strength change of from 0.1 to 1.4 M.

Calibration Curve. The calibration curve under the conditions described in the standard procedure was linear in the concentration range 1×10^{-5}—1.6×10^{-4} M (0.6—9 μg cm⁻³) of iron(III). The molar absorption coefficient of the Fe^{III}-eddha complex was 4.72×10^{3} l mol^{-1} cm^{-1} (at 480 nm). These values are somewhat smaller than those reported in the literature,[1] in which it is stated that the linear concentration range and the molar absorption coefficient of the Fe^{III} -eddha complex are 0—2.5×10^{-4} M and about 5.6×10^{-3} l mol^{-1} cm^{-1} (at 470) respectively. The relative standard deviation of the absorbance was 0.21% for 5.90×10^{-5} M (3.29 μg cm^{-3}) of iron(III) (12 determinations). This value is smaller than that of the method of A. L. Underwood (0.5%).[1]

Effect of Diverse Ions. The effect of 45 diverse ions was examined by the standard procedure stated. The ion in question was introduced into the iron sample solution before addition of other reagents. The results are shown in Table 1.

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

Ions added	Tolerance amount added to 50 cm³
	μmol
K^+, Li^+, Na^+, NH_4^+, Rb^+, Tl^+, Ba^{2+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Mg^{2+}, Pb^{2+}, Sr^{2+}, Zn^{2+}, Ce^{3+}, La^{3+}	6000[b]
Al^{3+}	5400
Mn^{2+}	3000
Th^{4+}	1800
Ni^{2+}	1200
Hg^{2+}	900
Ag^+	450
UO_2^{2+}, Cu^{2+}	80
Co^{2+}, Cr^{3+}	3
Br^-, Cl^-, ClO_3^-, ClO_4^-, HCO_3^-, CH_3COO^- I^-, NO_3^-, $H_2PO_4^-$, SCN^-, SO_4^{2-}, thiourea	6000[b]
F^-	3000
tartrate	1500
citric acid, $P_2O_7^{4-}$	300
NO_2^-, oxalate	90
CN^-	60

a) Iron(III) taken in 50 cm³ was 2.95 μmol (165 μg). The tolerance limit was taken as the value in which an error is not more than 1%. Foreign ions were added as nitrates and sodium salts except following: K^+, KCl; NH_4^+, NH_4Cl; Hg^{2+}, $HgCl_2$; Al^{3+}, $K_2Al_2(SO_4)_4$; SCN^-, NH_4SCN; CN^-, KCN; tartrate, sodium potassium tartrate. b) Maximum tested.

A. L. Underwood tested several metal ions for interference in the measurement of 5.4 μmol (in 50 ml) of iron(III);[1] it was shown that the presence of the metal ions in the following amounts did not interfere with the determination of the iron(III). Ca^{2+}, 5000 μmol; Cu^{2+}, 32 μmol; Hg^{2+}, 100 μmol; Mg^{2+}, 8200 μmol; Mn^{2+}, 3600 μmol; Ni^{2+}, 34 μmol; Pb^{2+}, 97 μmol; UO_2^{2+}, 8 μmol; Zn^{2+}, 31 μmol; Al^{3+}, 7400 μmol; Th^{4+}, 9 μmol in 50 ml. Comparing Table 1 with the results tested by A. L. Underwood, it seems that in many cases the interferences in the present method are smaller than those in A. L. Underwood's results. Thus, it may be said that the tolerance limit of diverse ions increases by use of heat treatment.

Determination of Iron in an Aluminium Alloy. Aluminium alloys furnished by the National Bureau of Standards were analyzed for iron. The sample solution was prepared by dissolving the aluminium alloy (NBS 85: 1.2 g, NBS 87a: 0.5 g) in perchloric acid using the method describcd previously.[8] The results of the three repeated determinations of iron (starting from the weighing of the alloy) were as follows. NBS 85 (certified, 0.24%): 0.24, 0.23, and 0.24%. NBS 87a (certified, 0.61%): 0.61, 0.61, and 0.61%. Satisfactory results were obtained.

References

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

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

3) R. Kono and T. Maikawa, *Kei Kinzoku*, **51**, 35 (1962).

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

5) Fe^{II}-eddha complex formed is oxidixed instantly to Fe^{III}-eddha complex even without addition of any oxidizing agent.

6) $\log K_{\mathrm{Fe^{III}\text{-}eddha}}=33.9$,[a] $\log K_{\mathrm{Mg^{II}\text{-}eddha}}=8.0$,[b] $\log K_{\mathrm{Ca^{II}\text{-}eddha}}=7.2$,[b] $\log K_{\mathrm{Ni^{II}\text{-}eddha}}=19.7$,[b] $\log K_{\mathrm{Cu^{II}\text{-}eddha}}=23.9$,[b] $\log K_{\mathrm{Zn^{II}\text{-}eddha}}=16.8$,[b] $\log K_{\mathrm{Cd^{II}\text{-}eddha}}=13.1$[b]: a) G. Anderegg and F. L'Eplattenier, *Helv. Chim. Acta*, **47**, 1067 (1964); b) A. E. Frost, H. H. Freedman, S. J. Westerback, and A. E. Martell, *J. Am. Chem. Soc.*, **80**, 530 (1958).

7) When a buffer was added to an iron solution before the reagent was added, or the pH was raised to about 5 in the absence of reagent, and/or an excess of foreign species was present, long color-developing periods were necessary in order to attain maximal color intensity.

8) T. Katsuyama and T. Kumai, *Bull. Chem. Soc. Jpn.*, **54**, 1544 (1981).