Ultraviolet Spectrophotometric Determination of Iron with Ethylenediaminetetraacetic Acid

By Yasumitsu UZUMASA, Masakichi NISHIMURA and Toshiko SEO

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When ethylenediaminetetraacetic acid, EDTA, is added to the solution containing a considerable amount of Fe^{3+} ion, a yellow color apparently akin to that produced by $Fe^{3+}-HCl$ complex develops. It was already pointed out by Schwarzenbach and Heller¹⁾ in 1951 that $Fe^{3+}-EDTA$ complex shows an absorption in the near ultraviolet region. The absorption at about 400 mμ was also reported by Jones and Long²⁾ who used in their observation a solution of considerably high concentration. In 1954, Goto and Kobayashi³⁾ illustrated an end absorption similar to that reported by Jones and Long while Nielsch and Böltz⁴⁾ described the fact that the solution of $Fe^{3+}-EDTA$ has an absorption maximum below 366 mμ which allows photometric estimation of the metal by EDTA. Uzumasa⁵⁾ and Nishimura⁶⁾ reported in their short communication that a dilute solution of $Fe^{3+}-EDTA$ compound has a characteristic absorption peak at 260 mμ which is available for ultraviolet spectrophotometric determination of iron. The conditions under which the analysis is carried out have been investigated since and the results will be reported here.

Experimental

An excess of disodium salt of EDTA was added to hydrochloric acid solutions containing various amounts of iron as Fe^{3+}. Each solution was diluted to a definite volume so that the resultant concentration should be 0.1 M with respect to hydrochloric acid and 0.001 M with respect to EDTA. The absorbance of the solutions was then measured with a Beckman DU spectrophotometer equipped with 1 cm. silica cells. Distilled water was referred to as blank throughout the present observation. In Fig. 1, curve I shows the absorption spectrum of EDTA under no iron; curves II, III and IV represent the absorption spectra of $Fe^{3+}-EDTA$ solutions which contain 5×10^{-5}, 1.5×10^{-4} and 2×10^{-4} mol. Fe^{3+}/l. respectively. The ferric ion when combined with EDTA shows, as already reported by the authors, a remarkable absorption at 260 mμ, whereas EDTA itself exhibits no absorption at this point.

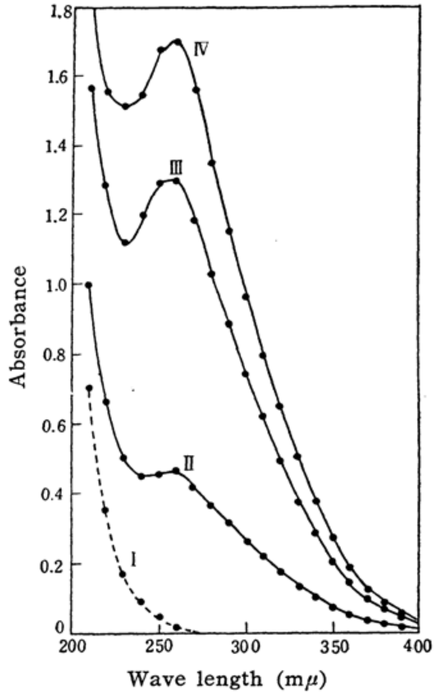

Fig. 1. Absorption of $Fe^{3+}-EDTA$ complex.
I: without iron
II: 5×10^{-5} M Fe^{3+}
III: 1.5×10^{-4} M Fe^{3+}
IV: 2×10^{-4} M Fe^{3+}

Fig. 2 indicates the calibration curve for iron at 260 mμ obtained by the present procedure. Conformity to Beer's law was found for concentrations up to 17 p.p.m. of iron. The sensitivity⁷⁾ of the method is 0.0065 γ Fe/cm², a little better than that of the thiocyanate method (0.008 γ/cm²; 480 mμ) and nearly comparable to that of the α, α′-bipyridyl method (0.007 γ/cm²; 522 mμ)⁷⁾.

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1) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

2) S. S. Jones and F. A. Long, *J. Phys. Chem.*, **56**, 25 (1952).

3) H. Goto and J. Kobayashi, *J. Chem. Soc. Japan*, **75**, 964 (1954).

4) W. Nielsch and G. Böltz, *Mikrochim. Acta*, **1954**, 481.

5) Y. Uzumasa, *Japan Analyst*, **3**, 255 (1954).

6) Y. Uzumasa and M. Nishimura, This Bulletin, **28**, 88 (1955).

7) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed. Interscience Publishers, Inc., New York, N. Y. (1950). p. 364.

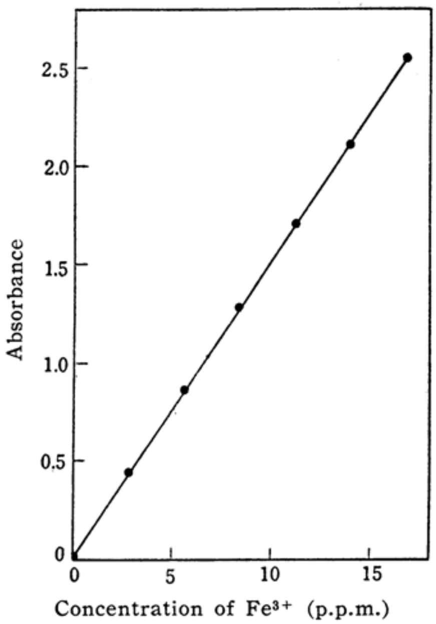

Fig. 2. Calibration curve for iron at 260 mμ.

Jones and Long[2] described in their discussion on the mechanism of the reaction that a part of Fe^{3+}—EDTA complex in the solution is converted into Fe^{2+}—EDTA complex by light, the latter returning to the former in the dark. It was also established by the present authors that the absorbance of the Fe^{3+}—EDTA solution decreases when irradiated by light while it recovers when placed in the dark (Fig. 3). The complex is stable in the dark, its absorbance remaining unchanged when even it is left for 13 hours.

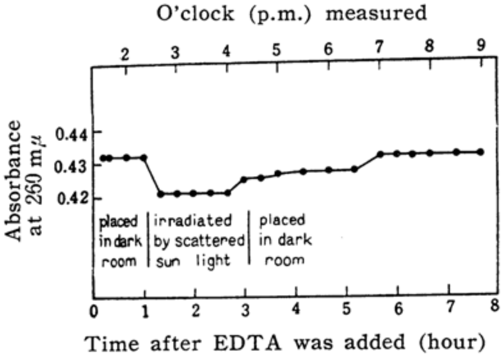

Fig. 3. Effect of light on Fe^{3+}—EDTA complex.

According to Schwarzenbach and Heller[1], the ratio Fe : EDTA in the complex is 1 : 1, which was ascertained by Jones and Long[2] after Job's continuous variation method. In the present study, a series of solutions was prepared by mixing 0.0002 M ferric iron solution and the EDTA solution of the same concentration in different ratios so that the acidity of the resultant liquid should be maintained to be constant, i. e., 0.1 M with respect to hydrochloric acid. Using these solutions, the absorbance at 260 mμ was observed, the result being in good accord with that of Jones and Long. Theoretically 1 mole EDTA is thus considered to react with 1 mole Fe^{3+} (Fig. 4). In the practical determination of iron, however, as shown in Fig. 5, EDTA might as well be used in excess, at least one and one half times as much as iron.

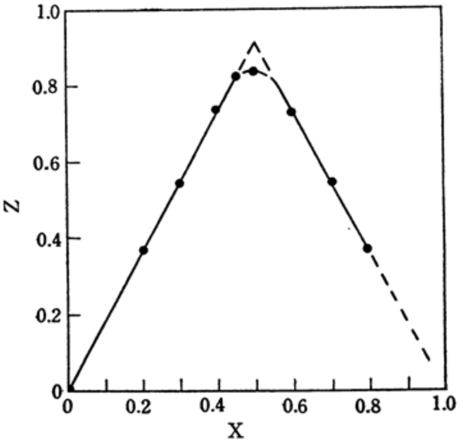

Fig. 4. Continuous variation study of the system Fe^{3+} and EDTA.
X = mol. ratio of (EDTA)/(Fe^{3+} + EDTA)
$Z=\varepsilon_2/(\varepsilon_2-\varepsilon_1)\{(As)_{obs.}-\varepsilon_1 M(1-X)\}$
Where ε_1 and ε_2 are molar extinction coeff. for Fe^{3+}—HCl and Fe^{3+}—EDTA solutions, respectively. $(As)_{obs.}$ is the absorbance observed at 260 mμ.

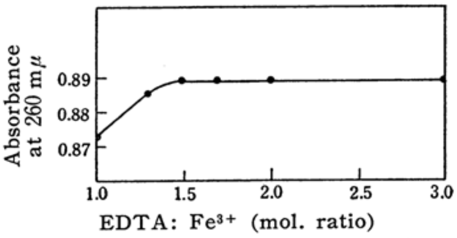

Fig. 5. Values of maximum absorbance of 1×10^{-4}M Fe^{3+} solutions at varying concentrations of EDTA.

Influence of pH.—Nielsch and Böltz[4] found the extinction of Fe^{3+}—EDTA complex depends upon the pH. This was further verified in the present investigation. By varying the amount of hydrochloric acid or sodium hydroxide to be added, a series of solutions, each of which was 5×10^{-5} M with respect to Fe^{3+} and 1×10^{-3} M with respect to EDTA, only differing in pH values, was obtained. Their absorbance was then examined at 260 mμ. As shown in Fig. 6, Fe^{3+}-EDTA complex seems to be stable on the acid side, although its absorbance decreases rapidly below pH 0.5. In the solution containing as much as 1 M hydrochloric acid, it develops an absorption similar to that which contains no EDTA: in other words, it corresponds to the absorption of Fe^{3+}–HCl. The absorbance is also reduced on the alkaline side.

In place of hydrochloric acid, sulfuric, perchloric or acetic acid may be used since these acids have, like hydrochloric acid, no characteristic absorption at 260 mμ. In case of nitric acid, even though it has an absorption peak at 300 mμ, its absorption is minimum at 260 mμ so that the absorbance of Fe^{3+}–EDTA in presence of nitric acid at 260 mμ remains unchanged provided that the concentration of the acid is kept lower than 0.01 M (Fig. 7).

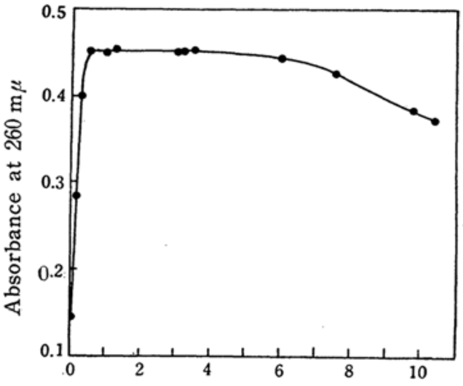

Fig. 6. Absorbance maxima for Fe^{3+}–EDTA complex. Its change with pH.

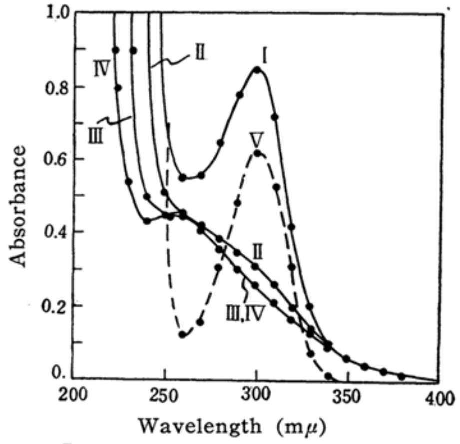

Fig. 7. Absorption of Fe^{3+}–EDTA complex (5×10^{-5} M) at varying concentrations of HNO_3.

I: in 0.1 M HNO_3
II: in 0.01 M HNO_3
III: in 0.001 M HNO_3
IV: in 0.0001 M HNO_3
V: 0.1 M HNO_3 itself

Influence of coexisting ions.—In their study of photometric determination of iron with EDTA, Nielsch and Böltz⁴⁾ confirmed that weaker complex formers such as tartaric acid do not interfere. No observations were carried out by them on the effects of metallic ions. In order to examine the influence of the coexisting foreign substances, the absorbance measurements were carried out by the authors using the solutions with or without foreign ions. Each solution was prepared so that it was 0.1 M with respect to sulfuric or hydrochloric acid and 0.0005 M with respect to EDTA, the amount of Fe^{3+} being always kept to be 2.45 p.p.m. After each solution to which the EDTA reagent had been added was placed in the dark for 30 min., the absorbance was measured. Other conditions were kept as constant as possible throughout the measurement. The results are summarized in Table I.

Among the cations examined, alkalies and alkaline earths do not interfere. Cu^{2+}, Hg^{2+} and Ti^{4+} interfere seriously when combined with EDTA. As indicated in Fig. 8 and 9, these cations unite like Fe^{3+} with EDTA in the 0.1 M sulfuric acid solutions forming

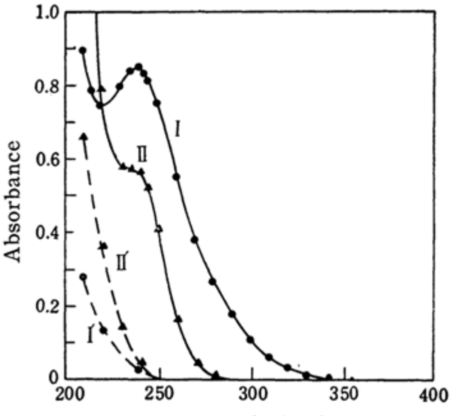

Fig. 8. Absorptions of Cu^{2+}— and Hg^{2+}—complexs in 0.1 M H_2SO_4.

I: 0.0002 M Cu^{2+} soln. with EDTA
I′: 0.0002 M Cu^{2+} soln. without EDTA
II: 0.0002 M Hg^{2+} soln. with EDTA
II′: 0.0002 M Hg^{2+} soln. without EDTA

Table I

Influence of foreign substances on the absorbance of Fe^{3+}—EDTA complex

(2.45 p.p.m. Fe^{3+} in 0.1 M H_2SO_4 solution)

Substance added	Ion	Concentration (p.p.m.)	Absorbance at 260 mμ
None	—	0.0	0.432
NaCl	Cl^-	4,000	0.427
		10,000	0.432
NaF	F^-	20	0.431
		60	0.432
$NaNO_3$	NO_3^-	248	0.436
		620	0.442
K_2SO_4	SO_4^{2-}	1,200	0.432
		2,500	0.428
		3,700	0.432
H_3BO_3		570	0.432
		1,140	0.432
NaH_2PO_4		125	0.434
		250	0.444
$Na_2C_2O_4$		150	0.468
		300	0.495
Na-citrate		100	0.444
		200	0.435
Na-tartrate		130	0.432
		260	0.432
Li_2CO_3+HCl	Li^+	8.0	0.432
		16.0	0.432
NaCl	Na^+	2,600	0.427
		6,500	0.432
K_2SO_4	K^+	1,000	0.432
		2,000	0.428
		3,000	0.432
$MgSO_4$	Mg^{2+}	960	0.437
		4,800	0.430
$CaCO_3+HCl$	Ca^{2+}	128	0.437
		240	0.445
$MnSO_4$	Mn^{2+}	30	0.432
		70	0.434
$CuSO_4$	Cu^{2+}	0.19	0.438
		0.32	0.444
		2.0	0.613
$ZnSO_4$	Zn^{2+}	200	0.432
		400	0.437
$CdSO_4$	Cd^{2+}	1,140	0.432
$HgCl_2$	Hg^{2+}	10.3	0.456
		51.4	0.495
$SnCl_2$	Sn^{2+}	700	0.437
$CoCl_2$	Co^{2+}	6	0.433
		20	0.434
$NiSO_4$	Ni^{2+}	7	0.435
		20	0.436
		60	0.438
$Cr_2(SO_4)_3$	Cr^{3+}	10	0.433
		18	0.446
$Al_2(SO_4)_3$	Al^{3+}	100	0.427
		200	0.432
		350	0.438
$Ti(SO_4)_2$	Ti^{4+}	0.7	0.438
		20	1.004
$Ge(SO_4)_2$	Ge^{4+}	100	0.433

(2.45 p.p.m. Fe^{3+} in 0.1 M HCl solution)

Substance added	Ion	Concentration (p.p.m.)	Absorbance at 260 mμ
None	—	0.0	0.420
$BaCl_2$	Ba^{2+}	40	0.420
		70	0.422
$SrCO_3+HCl$	Sr^{2+}	400	0.436

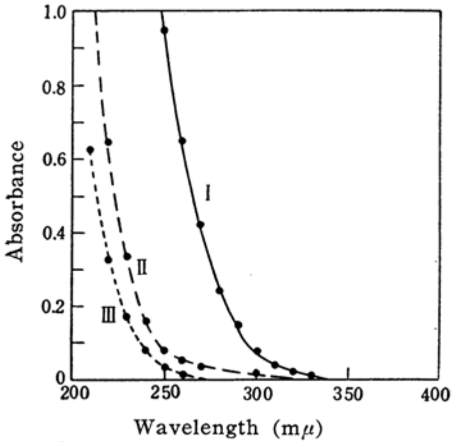

Fig. 9. Absorption of Ti^{4+}— complex in 0.1 M H_2SO_4.

I: 4×10^{-4} M Ti^{4+} soln. with EDTA
II: 4×10^{-4} M Ti^{4+} soln. without EDTA
III: EDTA only, 0.1 M H_2SO_4

complexes which exhibit remarkable absorption in the ultraviolet region. As expected from the curves in Fig. 1, 8 and 9, the effect of Cu^{2+}, Hg^{2+} or Ti^{4+} may be reduced to a certain extent if the measurement of Fe^{3+} is carried out in the range longer than 260 mμ.

Fe^{2+} can be determined by the present method if the ion is previously oxidized to Fe^{3+} by adding a dilute potassium permanganate solution in acid medium until the solution develops pink color. In this case, the absorbance changes for some time after EDTA is added. It is therefore desirable that the measurement is carried out 90 min. after the addition of the reagent.

Nitrate interferes when it exists at a certain concentration. As described above, this is certainly due to the absorption of the nitrate ion itself.

Summary

A dilute solution of Fe^{3+}—EDTA complex has a characteristic absorption peak at 260 mμ which is available for ultraviolet spectrophotometric determination of iron. An excess of disodium salt of EDTA was added to 0.1 M hydrochloric acid solution containing various amounts of iron as Fe^{3+} and the absorbance was measured with a Beckman DU spectrophotometer. A calibration curve for iron at 260 mμ was obtained and conformity to Beer's law was found for concentrations up to 17 p.p.m. of iron. The sensitivity of the method is 0.0065 γ/cm^2.

The absorbance of Fe^{3+}—EDTA solution decreases when irradiated by light, while it recovers when placed in the dark.

Fe^{3+}—EDTA complex is stable in acidic medium, although its absorbance decreases rapidly below pH 0.5. The absorbance is also reduced on the alkaline side.

Hydrochloric, sulfuric, perchloric or acetic acid can be used in the determination. Nitric acid is used only when the concentration is kept in a certain limited value, this acid having the absorption maximum at 300 mμ and the minimum at 260 mμ.

Influence of the coexisting substances on the absorption measurement of Fe^{3+}—EDTA complex was examined. Among the cations examined, alkalies and alkaline earths do not interfere. Cu^{2+}, Hg^{2+} and Ti^{4+} interfere seriously when combined with EDTA, because their EDTA complexes show remarkable absorption in the ultraviolet region, which may suggest a new ultraviolet spectrophotometric determination of the metals.

After the work reported herein had been completed, the authors were informed of the work of Hill-Cottingham[8], who reports a somewhat similar study on iron complexes of EDTA and other chelating agents.

Department of Chemistry
Faculty of Science
Hokkaido University, Sapporo

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[8] D. G. Hill-Cottingham, *Analyst*, **80**, 906 (1955).