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Fractional Spectrophotometric Determination of Ethylenediaminetetraacetate and nitrilotriacetate as Their Iron(III) Complexes by Use of H- and Na-form Ion Exchange Resin Columns

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The fractional determination of ethylenediaminetetraacetate(EDTA) and nitrilotriacetate(NTA) was carried out by use of hydrogen- and sodium-form ion exchange resin columns. After the conversion of free and complexed EDTA and NTA to the corresponding iron(III) complexes, two aliquots of the sample solution were separately passed through the columns. The iron(III)–EDTA complex was stable in both columns but iron(III)–NTA complex was completely decomposed in the hydrogen-form resin column, therefore, both of iron(III)–EDTA and –NTA were found in the effluent of sodium form resin column but only iron(III)–EDTA was found in the effluent of hydrogen-form resin column. The complexes in the respective effluents were determined spectrophotometrically at 255 nm. The recovery tests of EDTA and NTA from the synthetic sample solutions containing various metal ions were examined and the results observed were satisfactory.

The determination of chelating agents has recently been required for the estimation of the complexing capacity and for the speciation of trace metals in water. The general method was based on the conversion of chelating agents to the corresponding copper(II) complexes with the addition of excess copper(II) ion. After the removal of excess copper(II) by means of the chelating resin column,[1] or as copper(II) oxide,[3,4] the resulting copper(II) complexes were determined by atomic absorption spectrometry[1–3] or spectrophotometry.[4] A CuO-loaded ion exchange resin column was used to determine EDTA as the copper(II) complex.[5] Chelating agents were also determined as iron(III) complexes.[6,7] The fractional determinations of chelating agents were carried out with various methods, *i.e.*, gas chromatography as methyl esters,[8] liquid chromatography as copper(II) complexes,[9] and polarography as cadmium(II) complexes.[10]

In the present paper a simple spectrophotometric method of fractional determination of EDTA and NTA is described.

Experimental

Reagents. All chemicals used were of analytical reagent grade. The stock solutions of EDTA and NTA were prepared from the Dotite reagents (Dojindo Lab.). A 10^{-2} M (1 M=1 mol dm^{-3}) EDTA solution was made by dissolving dried disodium dihydrate salt (80 °C, 2 h) in deionized water. A 10^{-2} M NTA solution was prepared by dissolving dried acid (110 °C, 2 h) in a sodium hydroxide solution, the pH of final solution being around 8. Ammonium iron(III) sulfate dodecahydrate was dissolved into acidified water (pH 1) to give a 2×10^{-2} M solution. Other metal ion solutions were made from the nitrate or chloride salts.

Ion Exchange Resin. Dowex 50W-X8 (100—200 mesh) was used in H- and Na-forms, respectively. Hydrogen-form resin was packed in a column (23 cm long, 1 cm i.d.) to make a 2-cm resin bed, and it was washed with 0.025 M sulfuric acid. Sodium-form resin was packed in another column of the same size to give a 1-cm resin height, and the column was washed with a buffer solution (pH 3.1) composed of 0.05 M formic acid and 0.01 M sodium formate.

Apparatus. A Shimadzu spectrophotometer, UV-240, was used with 1-cm quartz cells.

General Procedure. The sample solution containing EDTA and NTA was divided in two equal aliquots and placed in 50-ml volumetric flasks.

A) Procedure by the H-form Resin Column. To one of the sample aliquot were added 2.5 ml of 0.5 M sulfuric acid and 0.5 ml of 0.02 M iron(III) solution. The mixture was filled up to the mark with deionized water, the pH of final solution being 1.4. The solution was then passed through the hydrogen-form resin column at a flow rate of 2—3 ml min^{-1}. The first 10-ml portion of effluent was discarded and the next 5-ml portion was collected. The absorbance of iron(III)–EDTA complex in the effluent was measured at 255 nm against deionized water. The blank value was also determined without addition of chelating agents.

B) Procedure by the Na-form Resin Column. To another aliquot of sample solution were added 2.5 ml of 0.5 M sulfuric acid, 0.5 ml of 0.02 M iron(III) solution, and finally 3 ml of 1 M sodium formate solution. The mixture was filled up to the mark, the pH of final solution being 3.1. This solution was passed through the sodium-form resin column and the effluent was collected as described in the above procedure. The absorbance corresponding to the sum of EDTA and NTA was also determined at 255 nm.

Results and Discussion

Absorption Spectrum. Absorption spectra of iron(III)–EDTA and –NTA complexes were shown in Figs. 1 and 2. The iron(III)–NTA complex in the formate buffer solution differed from that in dilute sulfuric acid, the adduct formation of the complex with formate being suggested. The absorbance due to the excess iron(III) was successfully removed by use of the cation exchange resin column. While the photosensitivity of iron(III)–EDTA complex is known,[11,12] the complex was found to be stable at least for 3 h, when the solution was protected from the direct sunlight.

Stability of Iron(III)–NTA Complex in H- and Na-form Resin Columns. The iron(III)–NTA complex was completely dissociated during the passage of the 2-cm column packed with hydrogen-form resin, being not found in the effluent (Fig. 3). By use of a 1-cm column, however, a part of iron(III)–NTA was eluted from the column indicating that the degree of decomposition depends on the column length. On the other hand, iron(III)–NTA complex in the formate buffer solution passed safely through the sodium-form resin column.

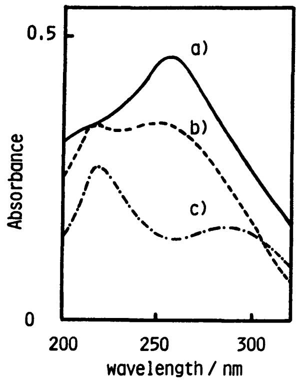

Fig. 1. Absorption spectra of iron(III) complexes in formate buffer solution (0.05 M HCOOH—0.01 M HCOONa, pH 3.1). a) 50.0 μM iron(III)-EDTA, b) 50.0 μM iron(III)-NTA, c) 50.0 μM iron(III), reference: reagent blank.

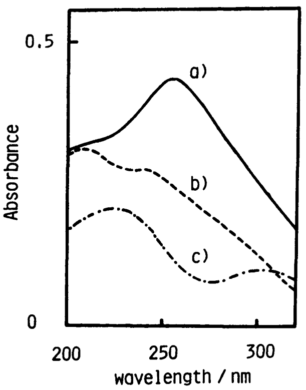

Fig. 2. Absorption spectra of iron(III) complexes in 0.025 M sulfuric acid solution (pH 1.4). The symbols have the same meanings as in Fig. 1.

The absorbance of iron(III)-NTA complex in the effluent increased with increasing pH, probably due to the adduct formation of the complex with formate.

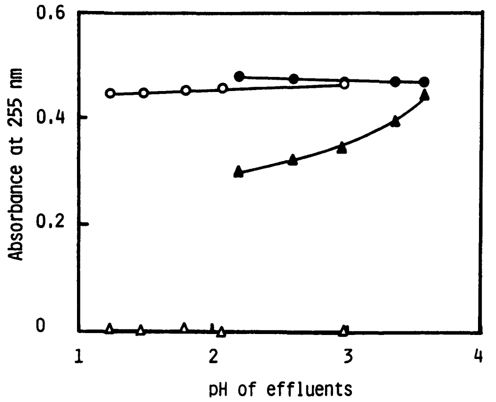

Fig. 3. Effects of pH on the stability of iron(III) complexes after passing the H- and Na-form resin columns. Iron(III)-EDTA: 51.3 μM, (○) H-form, (●) Na-form. Iron(III)-NTA: 51.0 μM, (△) H-form, (▲) Na-form.

Stability of Iron(III)-EDTA Complex in H- and Na-form Resin Column. Iron(III)-EDTA complex was stable in both columns (Fig. 3).

Calibration Curves. The calibration curves of EDTA and NTA were linear over the concentration range 20—100 μM; the regression equations were shown by

$$A_{\mathrm{H}}^{\mathrm{EDTA}} = 8762[\mathrm{EDTA}] - 0.003, \qquad (1)$$

$$A_{\mathrm{Na}}^{\mathrm{EDTA}} = 9185[\mathrm{EDTA}] - 0.001, \qquad (2)$$

$$A_{\mathrm{Na}}^{\mathrm{NTA}} = 6664[\mathrm{NTA}] - 0.002, \qquad (3)$$

where A denotes the absorbance and the suffixes H and Na indicate the signal obtained with the hydrogen- or sodium-form resin column. The relative standard deviations for 5.13×10^{-5} M EDTA were 0.3% (n=5) in the procedure A and 0.2% in the procedure B, respectively, and the value for 5.10×10^{-5} M NTA was 0.6% in the procedure B.

TABLE 1. RECOVERY OF EDTA AND NTA AS THEIR IRON(III) COMPLEXES

Metal(II) added in 0.1 mM	EDTA				NTA	
	Procedure A		Procedure B		Procedure B	
	Absorbance at 255 nm	Recovery %	Absorbance at 255 nm	Recovery %	Absorbance at 255 nm	Recovery %
None	0.458		0.471		0.344	
Mg	0.462	101	0.460	98	0.345	100
Mg[a]	0.457	100	0.471	100	0.335	97
Ca	0.459	100	0.460	98	0.346	101
Ca[a]	0.459	100	0.469	100	0.337	98
Co	0.453	99	0.474	101	0.345	100
Cd	0.450	98	0.472	100	0.347	101
Zn	0.459	100	0.460	98	0.341	99
Pb	0.460	100	0.457	97	0.340	99
Ni	0.160	35	0.230	49	0.343	100
Ni[b]	0.452	99	0.465	99	—	—
Cu	0.340	74	0.472	100	0.343	100
Cu[b]	0.453	99	—	—	—	—
Mixture[b,c]	0.455	99	0.471	100	0.344	100

a) [M]=1 mM. b) Heated for 10 min at pH 1.4. c) Mg, Ca, Co, Cd, Zn, Pb, Ni, and Cu each in 0.1 mM. [Fe(III)]=0.2 mM, [EDTA]=51.3 μM, [NTA]=51.0 μM.

TABLE 2. FRACTIONAL DETERMINATION OF EDTA AND NTA IN SYNTHETIC MIXTURES

Sample	Procedure A Absorbance	Procedure B Absorbance	EDTA			NTA		
			Taken/μM	Found/μM	Error/%	Taken/μM	Found/μM	Error/%
1	0.178	0.735	20.5	20.6	+0.5	81.6	82.3	+0.9
2	0.356	0.789	41.0	40.9	−0.2	61.2	62.4	+2.0
3[a)]	0.441	0.800	51.3	50.7	−1.2	51.0	50.7	−0.6
4	0.540	0.841	61.5	62.0	+0.8	40.8	41.3	+1.2
5	0.718	0.891	82.0	82.5	+0.6	20.4	20.8	+2.0

a) Mg(II), Ca(II), Co (II), Cd(II), Zn(II), Pb(II), Ni(II), and Cu(II), each in 0.1 mM, were added.

TABLE 3. RECOVERY OF EDTA FROM TOYOHIRA RIVER WATER

Sample	Volume/ml	Procedure A		Procedure B	
		Found[a)]/μM	Recovery/%	Found[a)]/μM	Recovery/%
A (upstream)	5	51.2	100	51.5	100
	25	50.4	98	51.5	100
B (midstream)	5	50.9	99	51.9	101
	25	51.0	99	50.7	99
C (downstream)	5	50.6	99	52.6	103
	25	51.2	100	51.3	100

EDTA taken: 51.3 μM. a) Mean of three determinations.

Effect of Diverse Ions. By the addition of excess iron(III), both the free and complexed NTA's were quantitatively converted to the iron(III)–NTA complex at room temperature. In the case of EDTA, however, the conversion of copper(II) and nickel(II) complexes to the iron(III) complex was first achieved by heating the acidified reaction mixture (pH 1.4) for 10 min on a water bath (Table 1).

Fractional Determination of EDTA and NTA. The determination was carried out as follows. The concentration of EDTA in the sample solution was determined by the procedure A; namely, from Eq. 1, one has

$$[\mathrm{EDTA}] = 1.141(A_{\mathrm{H}}^{\mathrm{EDTA}}+0.003)\times10^{-4}\ \mathrm{M}. \quad (4)$$

On the other hand, the absorbance corresponding to the sum of EDTA and NTA was determined by the procedure B; namely,

$$A_{\mathrm{Na}} = A_{\mathrm{Na}}^{\mathrm{EDTA}} + A_{\mathrm{Na}}^{\mathrm{NTA}}. \quad (5)$$

By introducing Eqs. 2, 3, and 4 into Eq. 5, the following relationship was obtained.

$$[\mathrm{NTA}] = [1.501(A_{\mathrm{Na}}+0.003)-1.573(A_{\mathrm{H}}^{\mathrm{EDTA}}+0.003)] \times10^{-4}\ \mathrm{M} \quad (6)$$

The results show the good accuracy, as shown in Table 2.

Recovery of EDTA from River Water Samples. The water samples were filtered through membrane filters (0.45 μm) and the various amounts of EDTA were added. After the addition of excess iron(III), the samples were heated for 10 min on a water bath and subjected to the determination according to the procedures A and B and Eqs. 1 and 2, NTA being assumed to be absent in the original sample solutions. The complete recovery of EDTA was observed in the both procedures (Table 3), which indicated that no appreciable amount of EDTA and NTA was contained in the original sample waters.

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