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Chromatographic determination of commercial Fe(III) chelates of ethylenediaminetetraacetic acid, ethylenediaminedi(*o*-hydroxyphenylacetic) acid and ethylenediaminedi(*o*-hydroxy-*p*-methylphenylacetic) acid

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Abstract

The use of synthetic iron chelates is the most common and effective way to treat iron chlorosis in plants. Using an ion-pair HPLC method previously proposed by the authors, it was found that the older commercial products reached the percentage of Fe chelated indicated by the manufacturer, but in no case did the current products reach their nominal, or legal, composition. Moreover, the current products of Fe–ethylenediaminedi(*o*-hydroxyphenylacetic) acid (FeEDDHA) showed significant additional chromatographic peaks that, based on published synthesis pathways for these type of compounds, may correspond to *para–para* FeEDDHA or *ortho–para* FeEDDHA, sterically-hindered isomers of FeEDDHA which are of little or no value as an iron chelate for agricultural purposes. © 1997 Elsevier Science B.V.

Keywords: Fertilizers; Metal chelates; Iron; Ethylenediaminetetraacetic acid; Ethylenediaminedi(hydroxyphenylacetic) acids

1. Introduction

For many crops, iron chlorosis is a major obstacle to crop production in calcareous soils. Iron normally exists in nature in either ferrous or ferric form. The solubility of Fe^{3+} changes 1000-times with each pH unit change [1]. Among all methods used to correct iron chlorosis, synthetic iron chelates are currently, but for their cost, the first choice for remediation of iron deficiencies in plants [2]. Metal chelates are used for micronutrient fertilization in foliar, trunk and soil application and in hydroponic cultures. Iron is by far the most common element used in fertilizers in chelated form [3]. Nevertheless, sometimes the increased profit from using synthetic chelates is less than the cost of application [4]. It is therefore necessary to evaluate the effectiveness of the commercial products as well as to determine the most suitable chelate from a purely chemical standpoint.

The most common synthetic chelating agents used to hold Fe are the polyamine-carboxylic acids, which form ferric complexes of high stability [1,5–8]. In Europe, the 76/116/EC directive allows chelates of the elements Fe, Mn, Cu, Zn, and Co to be used as such or incorporated in mixed fertilizers. Six chelating agents, all polyamine-carboxylic acids, are permitted for this purpose: EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), HEDTA (hydroxy-2-ethylenediamine triacetic acid), EDDHA [ethylenediaminedi(*o*-hydroxyphenylacetic) acid, also known as EHPG: N,N′ - ethylene - bis - 2 - (*o* - hydroxyphenyl)glycine],

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EDDHMA [ethylenediaminedi(*o*-hydroxy-*p*-methylphenylacetic) acid] and EDDCHA [ethylenediaminedi(5-carboxy-2-hydroxyphenyl) acetic acid]. To comply with the EC directive, a commercial iron chelate fertilizer must furthermore contain a minimum of 5% water-soluble Fe (based on the dry mass of the dry substance), of which at least 80% must be chelated by the declared chelating agent, thereby corresponding to a minimum of 4% Fe chelated with the declared chelate. Moreover, the pH range in which the chelated fraction is guaranteed to be stable against Fe precipitation must be indicated on the manufacturer's label on the product. Pure, fully-ferrated chelates of the permitted types would contain either 15.2% Fe (EDTA, based on $NaFeC_{10}H_{12}O_8N_2$), 11.4% Fe (DTPA, based on $Na_2FeC_{14}H_{18}O_{10}N_3$), 15.9% Fe (HEDTA, based on $NaFeC_{10}H_{14}O_7N_2$), 12.9% Fe (EDDHA, based on $NaFeC_{18}H_{16}O_6N_2$), 12.1% Fe (EDDHMA, based on $NaFeC_{20}H_{20}O_6N_2$) and 10.7% Fe (EDDCHA, based on $NaFeC_{20}H_{16}O_{10}N_2$).

Chromatographic separations of Fe(III) chelates include paper chromatography [9], thin-layer chromatography [10], glass column chromatography [11,12] and high-performance liquid chromatography (HPLC) [13–19]. The first report of the separation of the two stereoisomers of the Fe(III)–EDDHA, as dark brown and violet spots, used paper chromatography [9]. While developing a HPLC technique for determining FeEDDHA in solutions containing dissolved soil organic matter, it was found that the two stereoisomers of FeEDDHA separated on a 30-mm anion-exchange column eluted with 5 m*M* H_2SO_4 + 0.01 m*M* $Fe_2(SO_4)_3$ [20]. Separation of the isomers by paper chromatography by the procedure of [9] and crystallization of Fe(*rac*-EDDHA) by the procedure of [21] permitted the identification by HPLC of the violet band found in paper chromatography as the meso complex and the red band as the racemic FeEDDHA complexes [20]. Given the great similarity in size and structure of the two isomers, differences in elution time by anion chromatography suggested that the racemic isomer may chelate Fe more strongly than the *meso* complex, thereby imparting a stronger anionic nature to the racemic complex. Later measurements of the stability constants for FeEDDHA isomers showed that the Fe–ligand stability constant was 2.26 log units greater for the racemic complex than the *meso* complex, indicating a 500-fold difference in iron chelating ability [12].

An isocratic HPLC ion-pair chromatographic method to identify and quantify iron chelates permitted for fertilizers has been reported [22]. Ferric chelates containing EDTA, DTPA, EDDHA, EDDHMA and also CDTA (*trans*-1,2-cyclohexanediaminetetraacetic acid), were well-separated by this method. For the Fe(III)–EDDHA, studies showed that Fe concentrations between 0.5 and 150 mg/l are within the linear range of the method, which permits the analysis of the concentrations found in commercial fertilizers. With this method, separation and identification of the ferric complexes were obtained with good resolution and selectivity, including the separation of the isomers of the complexes, in 15 min per analysis. The objective of this research was the application of the previously reported ion-pair HPLC method [22] to several samples of commercial Fe(III) chelates of EDTA, EDDHA and EDDHMA in order to evaluate the suitability of the technique for routine assay of commercial iron chelate materials.

2. Experimental

2.1. Reagents

Analytical-reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ and NaOH were obtained from Merck. Hydrochloric acid and acetonitrile, HPLC-grade, were obtained from Fisher Chemical. Tetrabutylammonium hydroxide (40% solution in water, 1.5 *M*) was obtained from Sigma. EDTA was obtained from Pfaltz and Bauer. H_4EDDHA was obtained from Sigma (98% pure, Lot No. 117F50221) and an older EDDHA standard (83% pure) was kindly provided by Dr. A. Wallace (labeled in this study as W1). Since the chelating agent EDDHMA could not be obtained in pure form commercially, several commercial products marketed in the Fe(III) form were chosen based on the quality of the chromatograms obtained [22] and on the previous results about the purity of various commercial iron chelates [23].

The commercial fertilizers tested are shown in Table 1, as well as some of the characteristics that

Table 1
Commercial name, manufacturer, nominal percentage of Fe chelated as the different Fe(III)–chelates (% Fe–Ch), range of pH at which the chelate is stable and lot No. used in this study

Product	Manufacturer	% Fe–Ch	pH interval	Lot No.
Fe(III)–EDDHA:				
Sequestrene 138 Fe G-100	Ciba-Geigy	6	6.5–11	718592
Crescal[1]	Scheering	6	4–12	018034
Ferrishell[1]	Shell	6	–	–
Fe(III)–EDDHMA:				
Bolikel	Argos	6	4–10	930222
Hampiron W.G.	Rhône-Poulenc	6.5	–	89101512
Fe(III)–EDTA:				
Fertrilon 13	Basf Española	13	–	496120690

[1] Products not currently commercially available.

the commercial label must contain in order to comply with the EC Directive. Four FeEDDHA test products (TP1, TP2, TP3 and TP4) were also analyzed; all of them were nominal 6% Fe as FeEDDHA, and for the TP4 product, samples of two different lots were available (TP41 and TP42). In addition, FeEDDHA products at least 25 years old, referred to here as W2 (nominal 6% Fe as Fe-EDDHA), W3 (experimental product, 7.2% Fe as Fe-EDDHA), W4 (garden product ''Kerx'', nominal 2% Fe as FeEDDHA) and W5 (6% Fe as FeEDDHA) were kindly provided by Dr. A. Wallace.

2.2. Preparation of the standards and samples

For preparing the standard solutions, ligands were dissolved in sufficient NaOH (normally 1:3 molar ratio). Then an amount of $Fe(NO_3)_3$ that was calculated to be 5% in excess of molar amount of ligand was added, the pH was adjusted to 7.0 with NaOH, and the solutions were left to stand overnight to allow excess Fe to precipitate as oxides. The final solutions, with a Fe concentration of 100 mg/l, were filtered with Whatman No. 2 filters and made to volume with water.

Solutions of the commercial products were prepared by dissolving the formulations in deionized water. The solutions were left to stand overnight, filtered with Whatman No. 2 filters and made up to volume. For both, standard and sample solutions, light exposure was avoided during their preparation process because of the potential photodecomposition of chelates [9].

2.3. Ion-pair chromatographic separation of chelates

Chelates were separated and quantified by the method of [22] using a Waters 600E Multisolvent Delivery System, a Waters 700 Satellite WISP autosampler and a Waters 486 tunable absorbance detector set to 280 nm. A LiChrospher RP-18, 150×4.6 mm I.D. and d_p=5 μm column, was used. The injection volume was of 20 μl and flow-rate 1.5 ml/min. The mobile phase contained 0.03 *M* tetrabutylammonium chloride and 30% acetonitrile at pH 6.0. The solution was filtered with 0.22 μm Millipore filters and sparged during the entire process with He. Data were processed using Baseline 810 software.

Solutions of the standards and samples containing 100 mg/l of Fe chelated by EDTA, EDDHA and EDDHMA as chelating agents, were passed through 0.22 μm Millipore filters prior to injection.

2.4. Characterization of impurities

Using a Waters Symmetry C_{18}, 150×3.9 mm column, and the eluent described in Section 2.2 above [22], impurities were separated by HPLC on a Waters 2690 Separation Module (Alliance) and absorption spectra (200–600 nm) recorded with a

Waters 996 photodiode array detector and Millennium 2010 chromatography data system.

3. Results and discussion

Even though the 76/116/EC directive allows the commercialization of products with 4% of the total Fe chelated, the most of the FeEDDHA and FeEDDHMA products found declared 6% or more of Fe chelated. For the FeEDTA products, it is possible to find formulations with 13% Fe chelated by this chelating agent.

3.1. Product purity

Commercial iron chelates of EDDHA (Fig. 1), EDDHMA (Fig. 2) and EDTA (Fig. 3) were injected and the percentage of iron chelated by both isomers was calculated by estimation of the peak areas in comparison with the standard solution (Table 2). Without exception, the more recent commercial FeEDDHA products tested presented chelated Fe levels significantly lower than those indicated by the manufacturer. The purest products were Crescal and Sequestrene 138, but in no case were chelated iron contents higher than 4%, in spite of the 6% indicated at the commercial label, and the 4% required by the 76/116/EC directive. By contrast, the nominal percentage of Fe as FeEDDHA was present in some of the older products tested (6% chelates W2 and W5 and 2% chelate W4).

The chromatograms obtained for the FeEDDHMA and FeEDTA commercial products are shown in Figs. 2 and 3. For the FeEDDHMA products, no quantitative data were obtained because the FeEDDHMA standard is not available on the market. Two peaks, as well as for the FeEDDHA chelates, were obtained in the HPLC separation, with only other small peaks present in the formulations tested, indicating high purity in the FeEDDHMA products. For the FeEDTA, only one commercial product was injected, no extraneous peaks were found, and the peak area obtained revealed the high purity of this product in comparison with the FeEDTA standard.

3.2. Product impurities

The difference in purity between the older and newer FeEDDHA products could be due to either the difference in synthesis techniques or degrees of product purification. The chromatograms obtained for some of the commercial products showed that two significant peaks (labeled as peaks III and IV in Fig. 4) with lower retention times were present in addition to the two peaks of the FeEDDHA isomers (labeled as peaks I and II in Fig. 4) and were absent in the standard FeEDDHA solution. When the HPLC detection was performed at 480 nm, the third peak was not particularly significant, but at 280 nm the peak size was approximately equal to that of the peaks of the racemic and meso isomers of the *ortho*-FeEDDHA. These third and fourth peaks were

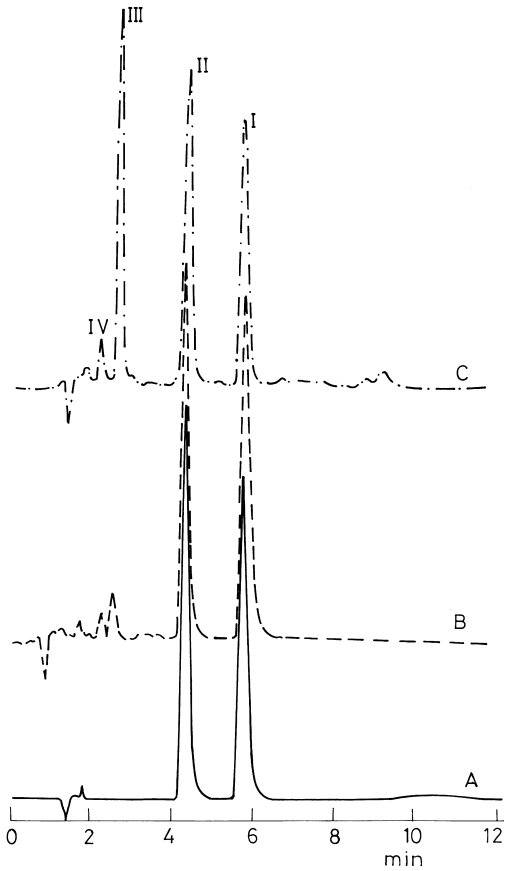

Fig. 1. Chromatograms obtained for (A) FeEDDHA standard, (B) Sequestrene 138 and (C) TP4,2. I: *meso* Fe–*ortho*-EDDHA; II: racemic Fe–*ortho*-EDDHA; III and IV: impurity peaks. Column, LiChrospher RP-18; eluent 0.03 *M* TBACl–30% acetonitrile (pH 6.0); flow-rate, 1.5 ml/min, injection volume, 20 μl; detection wavelength, 280 nm.

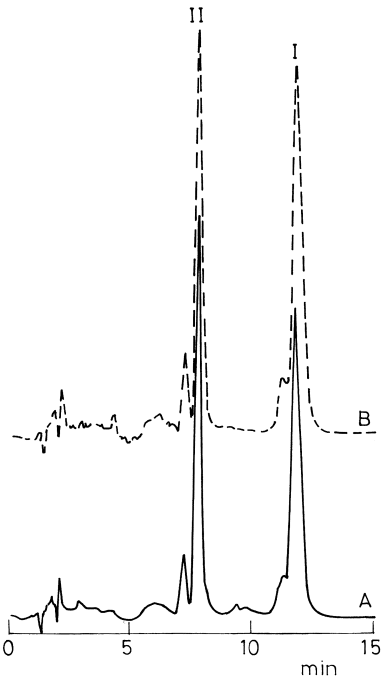

Fig. 2. Chromatograms for FeEDDHMA commercial products (A) Bolikel and (B) Hampirón. I: racemic Fe–*ortho*-EDDHMA; II: *meso* Fe–*ortho*-EDDHMA. Conditions as in Fig. 1.

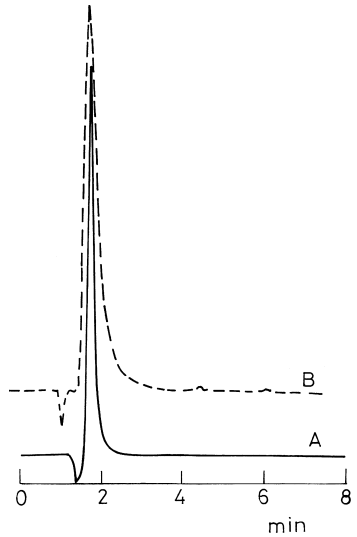

Fig. 3. Chromatograms for (A) FeEDTA standard and (B) commercial product Fertrilon. Conditions as in Fig. 1.

previously found together when analyzing two different commercial FeEDDHA fertilizers by HPLC [18] but no identification or explanation of them were given. Interestingly, the purest of the modern commercial products, Sequestrene 138 and Crescal, did not exhibit these peaks at all, indicating that the presence of the third and fourth peaks may be related to the overall purity of the FeEDDHA chelates.

The two *ortho*-FeEDDHA isomers (Fig. 4, I and II) have very similar absorbance spectra in the UV range, both exhibiting peaks at 206 and 280 nm, the first attributed to the benzene ring and the second due to the *ortho*-hydroxy substitution of the benzene ring [20,24]. Both isomers also show a broad band of absorption in the visible range typical of the Fe–phenol complexes, peaking at about 480 nm, with the slight difference in color between the two isomers due to a difference of about 10 nm in the placement of the peak [20]. By contrast, the third peak found in the chromatograms of the FeEDDHA commercial fertilizers does not have an important Fe–phenol interaction as evidenced by the insignificant absorption at 480 nm, although it is apparently phenolic in nature based on its absorption at 280 nm. The fourth peak has a spectrum similar to those of both *ortho* isomers (Fig. 4).

The third and fourth peaks may correspond to compounds formed as byproducts along the synthesis pathway of *o*-EDDHA. A number of synthesis paths have been reported for EDDHA, with the first among them a Strecker-type synthesis using ethylenediamine, HCN and 2-hydroxybenzaldehyde to force *ortho* configuration of EDDHA [25]. Another synthesis pathway starts with ethylenediamine, phenol and oxoacetic acid and is *ortho*-directing but may form significant amounts of *p*-EDDHA in the presence of water and certain organic solvents [26]. Yet another method employs an organic solvent to largely separate *ortho*-hydroxymandelic acid from a mixture of the *ortho* and *para* isomers, synthesized from oxoacetic acid and phenol, before oxidation to the keto acid and subsequent reductive amination with ethylenediamine [27]. Since two phenolic groups are present in EDDHA, *ortho–ortho* (known as *ortho*), *ortho–para* and *para–para* (known as *para*) positional isomers are possible. For the *ortho* (*ortho–ortho*) and *para* (*para–para*) configurations, three optical isomers are possible (*R*,*R*) and (*S*,*S*), which form the racemic-mixture [22], and the (*R*,*S*),

Table 2
Percentage of iron chelated by both isomers in respect to the percentage indicated by the manufacturer

	%Fe as racemic isomer	%Fe as *meso* isomer	%Fe total
FeEDDHA:			
Sequestrene 138 (6%)	1.64±0.02	1.75±0.01	3.39±0.03
Crescal (6%)	1.81±0.02	1.92±0.04	3.73±0.06
Ferrishell (6%)	0.50±0.00	0.48±0.01	0.98±0.01
TP1 (6%)	0.88±0.01	0.83±0.03	1.71±0.04
TP2 (6%)	0.16±0.01	0.10±0.01	0.26±0.02
TP3 (6%)	0.99±0.06	1.05±0.00	2.04±0.06
TP4 1 (6%)	1.38±0.07	1.31±0.01	2.69±0.08
TP4 2 (6%)	1.80±0.01	1.09±0.01	2.89±0.02
W1 (6%)	51.76±0.04[1]	47.07±0.12[1]	98.83±0.16[1]
W2 (6%)	3.24±0.07	2.63±0.01	5.87±0.08
W3 (7.2%)	0.13±0.00	0.09±0.01	0.22±0.01
W4 (2%)	0.91±0.06	0.87±0.01	1.78±0.07
W5 (6%)	3.27±0.02	3.04±0.06	6.31±0.08
FeEDTA:			
Fertrilon (13%)			12.23±0.02

Each value represents the %Fe–chelate (±S.D.) (n=3).
[1] Results expressed as percentage of chelating agent (instead of Fe) on dry matter basis.

which forms the meso isomer. Four optical isomers are possible for *ortho–para* EDDHA: (*R-ortho*, *R-para*) (Fig. 5), (*R-ortho*, *S-para*), (*S-ortho*, *R-para*) and (*S-ortho*, *S-para*). All four maintain a similar environment for the iron: five-fold coordination of the Fe(III) with the chelate through 2 amine, 2 carboxylate and one *ortho*-phenolate groups. Furthermore, two spatial arrangements for the *ortho*-phenolic half of *ortho–para*-EDDHA when binding Fe: one with the *ortho*-phenolic group in equatorial position and the other in an axial position, as shown in Fig. 5. The first seems to be of lesser importance according to previous discussions [22,28,29].

For a synthesis technique that generates, for example, an 80:20 split between *ortho*:*para* substitution and assuming that substitution on one side of the molecule is independent of the other side, then the expected distribution of synthesis products would be: 32% *o*-racemic, 32% *o*-meso, 16% *o–p*-racemic, 8% *R-o-S-p* and 8% *S-o-R-p* (32% total *ortho–para*), 2% *p*-racemic and 2% *p*-meso (4% total *para–para*).

The *para* positioning of the hydroxyl groups sterically hinders Fe–phenol binding within the chelate, leaving Fe(III) chelated only by the amine and carboxyl groups. Spectral considerations with respect to peak III (Fig. 4) reveals that although it is aromatic, it does not show any Fe–phenol interaction, as is therefore consistent with Fe–*para*-EDDHA (Fig. 5). For the fourth peak, an absorbance maximum at 448 nm reveals Fe–phenol binding, but its relative height is only half that of the *ortho* isomers (peaks I and II), consistent with an assignment of peak IV to the *ortho–para* isomer. If the four optical isomers of Fe–*o–p*-EDDHA present similar, and not particularly stable, Fe-chelating environments, then it would appear that they elute simultaneously using this chromatographic method, with a lower retention time than those of the isomers of the *ortho*-FeEDDHA.

Because of its low affinity for binding Fe under slightly alkaline conditions, Fe–*p*-EDDHA is of little or no value in commercial iron chelate intended for remedy of iron deficiencies in calcareous soils [26], and presumably the same is true of Fe–*o–p*-EDDHA. Further research, using synthesized Fe–*para–para*-EDDHA would be need to assure the proper assignment of the impurities.

4. Conclusions

The HPLC method previously described for separating and quantifying iron chelates appears applicable to the assay of commercial iron chelates

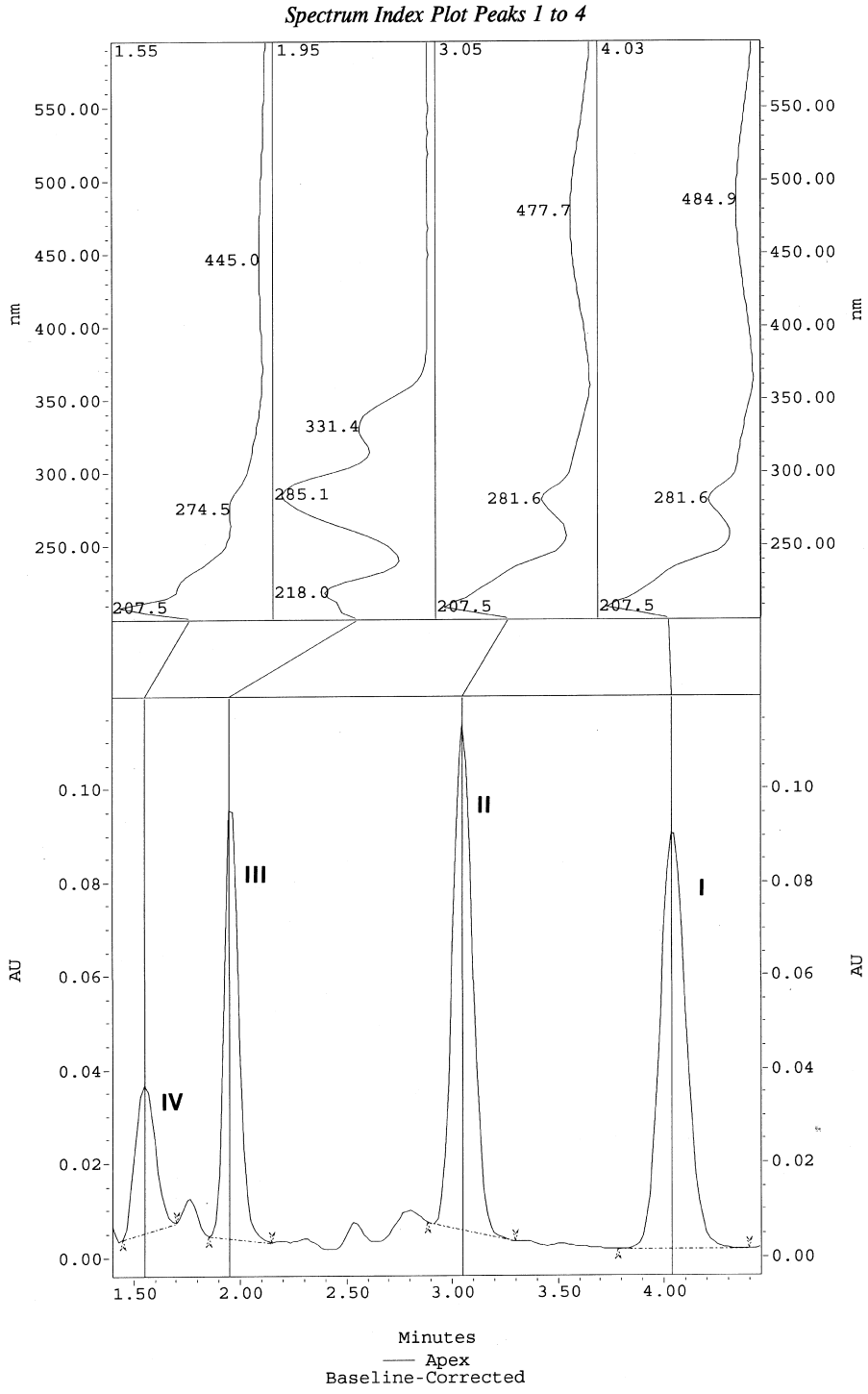

Fig. 4. Chromatogram and spectra of TP4,2 main peaks. I and II: *meso* and racemic Fe–*ortho*-EDDHA; III and IV main impurity peaks. Column, Symmetry C_{18}; eluent 0.03 *M* TBACl–30% acetonitrile (pH 6.0); flow-rate, 1.5 ml/min, injection volume, 20 μl; detection wavelength, 280 nm.

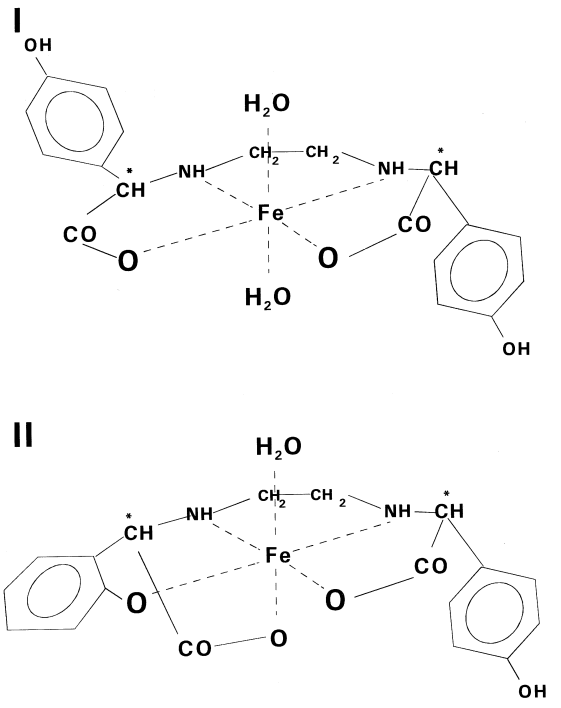

Fig. 5. Proposed structures for *R–R* isomers of I: Fe–*para*–*para*-EDDHA and II: Fe–*ortho*–*para*-EDDHA. H_2O molecules could be replaced by OH^- (depending on pH) or other anions.

marketed for the remedy of iron chlorosis in calcareous soils. A limited survey of commercial chelates indicates that current products tested do not meet the declared content of active ingredient. Several products do not meet the requirements of the 76/116/EC directive. Additional peaks were identified in a number of FeEDDHA products that are tentatively identified as Fe–*p*-EDDHA and Fe–*p*–*o*-EDDHA, synthesis byproducts that exhibit low stability of the Fe chelate and of little or no use as Fe fertilizers. Routine use of HPLC techniques such as those used in this study should permit both better control of product analysis during manufacture and better regulation of marketed product for protection of consumers.

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