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Identification of Fe-polycarboxylic complexes by electrospray ionization mass spectrometry and reduction of interferences by ion chromatography/inductively coupled plasma mass spectrometry with an octopole reaction system

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Stable complexes are required during the ion chromatographic (IC) separation of Fe-polycarboxylic acid complexes. Electrospray ionization mass spectrometry (ESI-MS) was used to identify 1:1 stoichiometric complexes of Fe[HEDTA], Fe[EDTA]$^{1-}$ and Fe[DTPA]$^{2-}$, and the spectra showed that these Fe complexes were stable in solution. Furthermore, inductively coupled plasma mass spectrometry (ICP-MS) using an octopole reaction system (ORS) reduced polyatomic ion $^{40}Ar^{16}O^{+}$ interference in the detection of ^{56}Fe via the addition of either H_2 or He to the ORS, with He at a flow rate 3.5 mL min^{-1} being the optimum collision gas. Finally, IC/ICP-MS was used for the separation and detection of Fe complexes with an eluent containing 30 mM $(NH_4)_2HPO_4$ at pH 8.0, but only Fe[HEDTA], Fe[EDTA]$^{1-}$ and Fe[DTPA]$^{2-}$ were observed within 10 min with reasonable resolution. Detection limits in the range of 10–13 μg L^{-1} were achieved using He as the collision gas. The proposed method was used for the determination of Fe species in soil solutions. Copyright © 2010 John Wiley & Sons, Ltd.

In the last decade, chelate-induced phytoremediation for the cleanup of soils contaminated with heavy metals has received great attention.[1,2] Phytoextraction is based on the application of mobilizing or chelating agents, such as ethylenediaminetetraacetic acid (EDTA), applied to soils in an attempt to increase plant metal uptake and shoot accumulation, in particular where metals are not readily bioavailable.[1,2] For efficient metal uptake, the chelating agent must present a strong affinity for the target metal and be readily translocated as a metal-chelate complex from roots to harvestable parts of the plant. One study has shown enhanced uptake of Fe, Mn and Cu by *Zea mays* after 6 weeks growth when the soil was dosed with EDTA or DTPA prior to planting in a heavy-metal-contaminated soil from an abandoned gold mine.[3] However, the successful use of plants to extract metals from contaminated soils requires a better understanding of the mechanisms of metal uptake, translocation and accumulation within the plant. Usually, the total metal content can be determined by atomic absorption spectrometry (AAS) and the concentration of metal complexes calculated by running, for example, the GEOCHEM-PC model.[4] However, these simple speciation programs are often insufficient to obtain a complete understanding of the distribution of metal species in a complex chemical equilibrium. Therefore, the direct chemical speciation of Fe complexes in environmental samples is still necessary and remains an analytical chemistry challenge due to the complex matrix and the low concentrations of analytes in environmental samples. However, 'hyphenated' techniques, such as liquid chromatography/mass spectrometry (LC/MS) and liquid chromatography with inductively coupled plasma mass spectrometry (LC/ICP-MS), can be used to determine speciation at trace levels in biological samples.[5]

Ion chromatography (IC) with electrospray ionization (ESI) tandem mass spectrometry (MS/MS) was used to identify and quantify metal-EDTA complexes in soil solution and plant xylem exudates with detection limits ranging from 0.1 to 1 μM.[6] Liquid chromatography (LC)/ESI-MS was also used to determine EDTA in industrial effluents by forming the Fe(III)-EDTA complex,[7] as well as to determine EDTA and DTPA in influents and effluents of waste water treatment plants.[8] More recently, zwitterionic hydrophilic interaction liquid chromatography (ZIC-HILIC) coupled to ESI-MS has been developed to identify different phytosiderophores (PS) and their metal complexes in plants.[9] An LC/ESI-MS method was developed for the simultaneous determination of seven major Fe(III)-chelates used as fertilizers.[10] These methods are useful for the identification of metal complexes since ESI-MS provides molecular information. However, the detection limits obtained from these methods are poor. This lack of sensitivity can be addressed by using LC/ICP-MS due to its ultra-sensitive

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elemental detector; for example, trace metal complexes in water were determined using IC coupled with ICP-MS.[11] Recently, IC/ICP-MS has been used for the determination of Co^{2+}, Cu^{2+}, Fe^{3+} and Ni^{2+} complexes.[12] However, ICP-MS is only an element-specific detector and it cannot provide the inherent information required to characterize or confirm specific Fe complexes. In addition, HPLC requires known standards for compound identification via matching of retention times, but many standards for the wide variety of species in environmental samples are not yet available.[5] Furthermore, since metal complexes may partially dissociate during chromatographic separation,[13] kinetic stability is essential for chromatographic separation and identification. ESI mass spectra can be directly acquired from solution samples and the stoichiometry of these species can be determined directly from their *m/z* values.[14,15] For these reasons, the combination of ESI-MS and IC/ICP-MS provides a potential detection technique to identify and quantify trace amounts of metal-speciatied organic complexes in environmental matrices.

In this study, ESI-MS was employed to identify the molecular structure of Fe complexes and their stabilities in solution, which provided a subsequent basis for their ion chromatographic separation. ICP-MS was used for element-specific detection of the trace Fe complexes. Polyatomic interferences, such as $^{40}Ar^{16}O^+$ and $^{40}Ca^{16}O^+$, which are present in large concentrations in the ICP-MS system for environmental samples, and interfere with the detection of ^{56}Fe, can be reduced using an octopole reaction system (ORS) with He or H_2 as either the reaction or the collision gas.[15] The aims of this study were (1) to use ESI-MS for the identification of Fe complexes and to determine whether these complexes were stable in solution, (2) to examine the possibility of removing the polyatomic interference $^{40}Ar^{16}O^+$ using an ORS, and (3) to separate different Fe complexes with reasonable resolution by manipulation of the mobile phase. Finally, the proposed method was used for the detection of Fe-polycarboxylic acid complexes in solutions from soils collected from chelate-enhanced phytoextraction sites.

EXPERIMENTAL

Chemicals and solutions

All chemicals used in this study were analytical grade reagents from Sigma and Aldrich (Shanghai, China). Milli-Q water (18.2 MΩ/cm, Milli-Q Plus system; Millipore, Bedford, MA, USA) was used to prepare all solutions and standards. Fe-polycarboxylic acid complexes were prepared by adding the ligand solution (1 mM, 1 mL), including nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), *N*-(2-hydroxyethyl)ethylene diamine triacetic acid (HEDTA) and diethylenetriaminepentaacetic acid (DTPA), to a $FeCl_3$ solution (1 mM, 1 mL) and were stored in the dark before use to avoid photolysis. Eluents used for IC/ICP-MS were prepared by dissolution of an appropriate amount of ammonium salts in Milli-Q water and were filtered through a disposable 0.45 μm cellulose acetate membrane filter (Millipore). This solution was degassed in an ultrasonic bath prior to use. The eluent pH was adjusted with 0.1 M ammonium hydroxide. Soil solutions were collected directly using a rhizon soil moisture sampler (Eijkelkamp Co., Giesbeek, The Netherlands) 7 days after adding EDTA solution to the phytoextraction sites (Fuzhou, China). The solutions were filtered through a 0.45 μm membrane filter prior to LC/ICP-MS analysis.

FIA-ESI-MS system

Flow injection analysis was carried out using an Agilent 1100 series (Agilent, Waldbronn, Germany) instrument. The carrier solution contained 10 mM ammonium acetate at pH 8.0 and the injection volume was 10 μL. The mass spectrometer was an Agilent 1100 series quadrupole instrument equipped with an ESI source (Agilent, Santa Clara, CA, USA). The instrument was operated in the negative ionization mode. The operating conditions for ESI were nebulizer gas (nitrogen) pressure 40 psi; drying gas (nitrogen) flow rate 12 L min^{-1}; capillary voltage 4000 V and gas temperature 350°C. The fragmentor voltage was set at 80 V.

IC/ICP-MS conditions

An Agilent 1100 liquid chromatography module equipped with a guard column (G3154A/102) and a separation column (G3154A/101, based on porous polymethacrylate resin with 10 μm particle size and an exchange capacity of 50 μeq g^{-1}, Agilent) were used for the separation of the Fe complexes. The samples were injected (50 μL) using an 1100 auto-sampler. The eluent flow rate was 1.0 mL min^{-1}. The outlet of the separation column was connected directly to the Babington nebulizer of an Agilent 7500c ICP-MS instrument (Agilent, Tokyo, Japan) using a 50-cm length of PEEK tubing. The conditions used for ICP-MS were: radio-frequency (RF) power 1450 W, plasma gas (Ar) flow rate 15 L min^{-1}, auxiliary gas (Ar) flow rate 1.0 L min^{-1}, carrier gas (Ar) flow rate 1.15 L min^{-1}, sampling depth 7.5 mm, integration time 1 s, and dwell time 0.5 s. The Fe complexes were detected at *m/z* 56 (^{56}Fe, 91.72% abundance) and the IC/ICP-MS system was controlled and data processed using the Agilent Chemstation software package.

RESULTS AND DISCUSSION

Confirmation of the structures of Fe complexes by ESI-MS

The use of ESI-MS to study metal-ligand solution equilibria[14,15] is of particular value for metal complex analysis, due to the gentle transition from solution to gas phase that to a large extent maintains solution-phase speciation. The ionization process also generally leads to singly charged species, resulting in simple mass spectra with ions that relate directly to the species in solution or adducts of these species. Hence, in this investigation, we used ESI-MS to study the aminopolycarboxylic acids and also their Fe complexes in the negative ion mode to determine whether ESI-MS could be used to confirm the formation of Fe complexes. A solution containing 10 mM ammonium acetate at pH 8.0 was primarily investigated as the carrier solution because it was compatible with ESI-MS. Initially, standards containing 5 mg L^{-1} of each aminopolycarboxylic acid were injected (10 μL) into the ESI-MS system under the optimized ESI conditions (fragmentor voltage: 80 V, capillary voltage:

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4000 V). Figure 1(a) shows the ESI-MS spectrum of these aminocarboxylic acids where the dominant gas-phase ions were of the form $[L–H]^-$, where L represents the aminocarboxylic acid, corresponding to $[NTA–H]^-$ at *m/z* 190.2, $[HEDTA–H]^-$ at *m/z* 277.3, $[EDTA–H]^-$ at *m/z* 291.3 and $[DTPA–H]^-$ at *m/z* 392.3. In addition, subsidiary peaks, corresponding to the gas-phase ions $[L–2H + Na]^-$ and $[L–3H + 2Na]^-$ were also observed: $[NTA–2H + Na]^-$ at *m/z* 212.2, $[HEDTA–2H + Na]^-$ at *m/z* 299.2, $[EDTA–2H + Na]^-$ at *m/z* 313.2, $[DTPA–2H + Na]^-$ at *m/z* 414.2, $[HEDTA–3H + 2Na]^-$ at *m/z* 321.3, $[EDTA–3H + 2Na]^-$ at *m/z* 335.2 and $[DTPA–3H + 2Na]^-$ at *m/z* 436.2. Subsequently, to understand the complexation of these ligands with Fe^{3+}, a mixed solution of Fe^{3+} with these ligands was injected into the FIA-ESI-MS system. The mass spectrum in Fig. 1(b) shows prominent ions at *m/z*, 330.2, 344.2 and 445.1, corresponding to $[HEDTA–4H + Fe]^-$, $[EDTA–4H + Fe]^-$ and $[DTPA–4H + Fe]^-$, respectively. This identifies the formation of mainly 1:1 stoichiometric Fe-aminopolycarboxylic complexes in agreement with the mass spectra recently obtained for these complexes.[16]

The peak at *m/z* 242.1 is not due to $[NTA–4H + Fe]^-$ since the NTA ligand, although tetradentate, can only lose a maximum of three protons. However, the low abundance peak at *m/z* 279.1 could correspond to a 1:1 Fe-NTA complex of the form $[Fe(NTA\text{-}3H)(H_2O)(OH)]^-$. The relatively low abundance peak at *m/z* 289.1 could be attributable to an iron dimer $[Fe_2Cl_5]^-$, highlighting the complexity of the Fe system in the gas phase. This inherent complexity probably gives rise to the many other low abundance peaks in the spectra. In addition, the $[L–H]^-$ ions of the aminopolycarboxylic acids of interest disappeared from the mass spectra in the

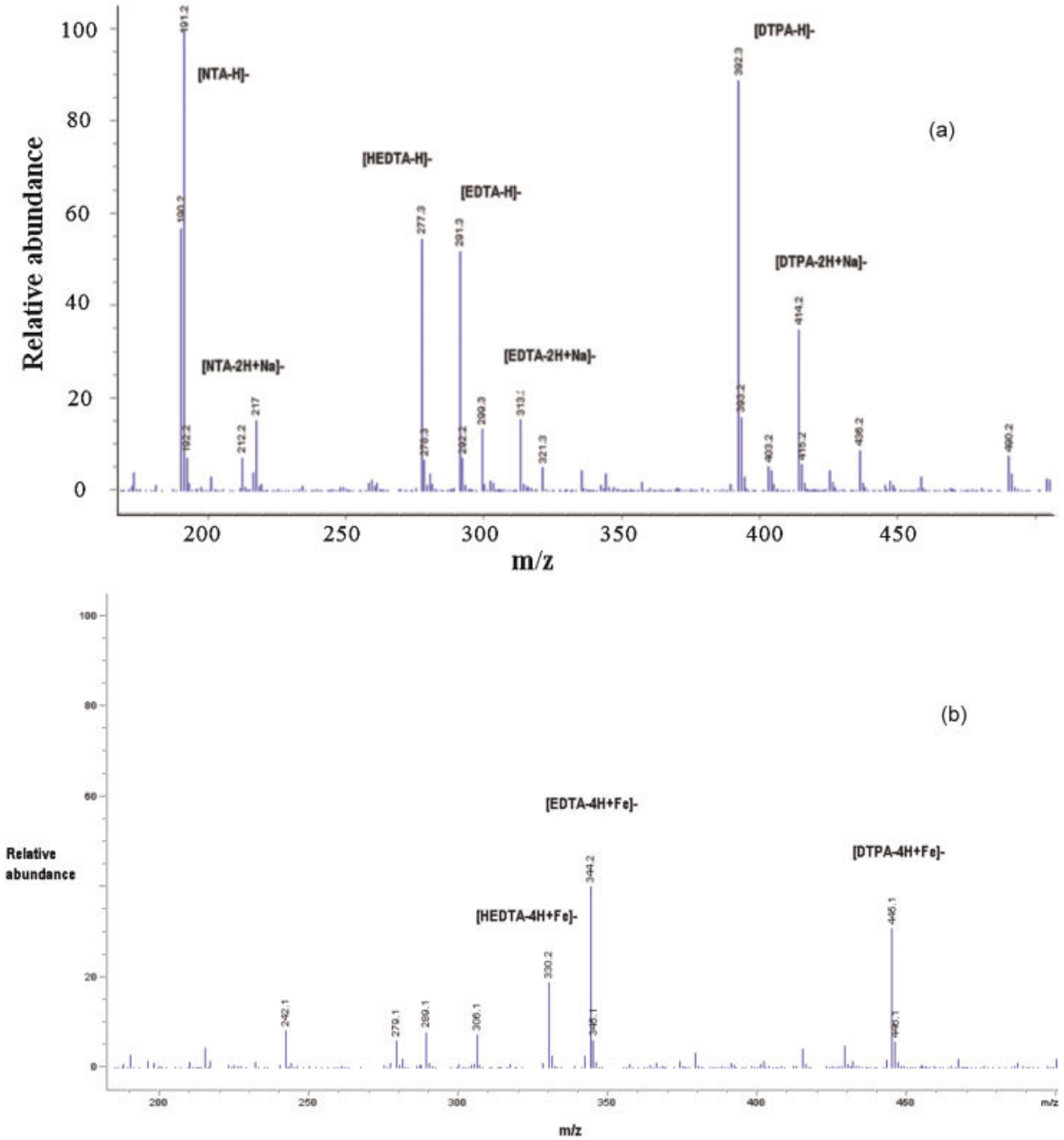

Figure 1. Negative ESI-MS spectra of (a) NTA, HEDTA, EDTA and DTPA and (b) $Fe[HEDTA]^0$, $Fe[EDTA]^{1-}$ and $Fe[DTPA]^{2-}$. Conditions as described in the Experimental section.

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presence of Fe (Fig. 1(b)), indicating that all the amino-polycarboxylic acids were converted into their Fe complexes. Furthermore, the ESI-MS detection of the Fe complexes is specific since Fe has two main stable isotopes with a distinctive Fe isotope pattern (^{54}Fe 6%, ^{56}Fe 92), making it relatively easy to locate unknown compounds which contain Fe, as illustrated by Fig. 1(b). The results obtained from ESI-MS show that all these Fe complexes were stable. On a chromatographic time scale, low stability metal-NTA complexes, including Fe-NTA, using capillary electrophoresis had previously been reported.[17]

Removal of the polyatomic interferences by ORC

Since the RF power and the carrier gas flow rate are usually the most significant parameters affecting the background and the analytical signal, these need to be optimized. A solution spiked with 30 μg L^{-1} Fe[EDTA]$^{1-}$ was directly aspirated into the nebulizer with the eluent [30 mM $(NH_4)_2HPO_4$ at pH 8.0]. The abundance of the blank and spike solution increased with increasing carrier gas flow rate in the range 1.0–1.25 L min^{-1} and with increases of RF power in the range 1300–1500 W. Optimal conditions were obtained with 1450 W power and a carrier gas flow rate of 1.15 L min^{-1}.

The limitation of ICP-MS in the detection of ^{56}Fe is the $^{40}Ar^{16}O^+$ interference generated from argon plasma gas. However, this interference can be reduced using an ORS via the addition of He or H_2 to the reaction cell. Consequently, elimination of the polyatomic ions is accomplished by either collisionally induced dissociation (CID) and kinetic energy discrimination (KED) or chemical reaction.[18] Since the flow rate of He or H_2 is the most significant parameter affecting the background and analytical signals, it also had to be optimized. A solution containing 30 mM $(NH_4)_2HPO_4$ at pH 8.0 and a spiked solution containing 30 μg L^{-1} Fe[EDTA]$^{1-}$ were aspirated into the nebulizer and then into the plasma. The gas flow rates ranged from 0 to 5 mL min^{-1}. The analytical and background signals both decreased with increasing gas flow rate and flow rates of H_2 at 3.0 and He at 3.5 mL min^{-1} were found to give the maximum difference between background and analytical signals and were consequently used as the optimized flow rates.

Figure 2 shows the chromatograms obtained from IC/ICP-MS detection at m/z 56 when either no gas, He or H_2 was added to the reaction cell. The separation of the Fe complexes was performed on an anion-exchange column with an eluent containing 30 mM $(NH_4)_2HPO_4$ at pH 8.0. It can be seen that the background (31 000 counts) and noise level were very high when no gas was added to the cell. However, the background signal and noise level were significantly reduced using either He or H_2, where the background was 800 count and 300 counts, respectively. Compared with the use of no added gas, the background signal was decreased from 100% to 2.58% when He was used as the reaction gas, while the background signal was reduced from 100% to 0.96% using H_2. This indicated that most of the $^{40}Ar^{16}O^+$ interference was reduced or removed when either He or H_2 was added to the reaction cell because either H_2 reacted with $^{40}Ar^{16}O^+$, or He removed $^{40}Ar^{16}O^+$ in favour of analyte ions by means of kinetic energy discrimination.[18]

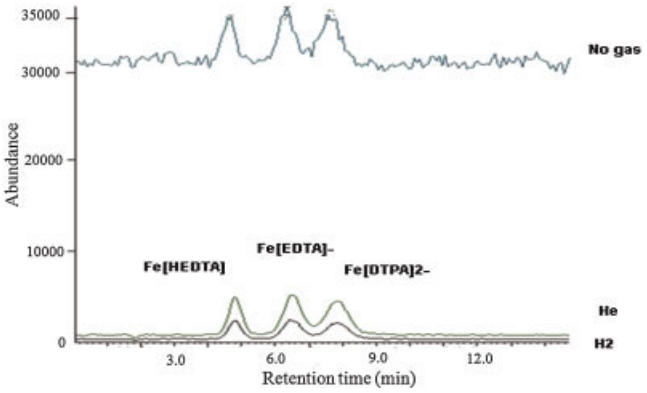

Figure 2. Comparison of the sensitivity and background signal obtained from Fe complexes using the ORS with and without gas: (a) no gas; (b) He at 3.5 mL min^{-1}; and (c) H_2 at 3.0 mL min^{-1}. Mobile phase: 30 mM $(NH_4)_2HPO_4$ at pH 8.0, the concentration for each Fe complex: 200 μg L^{-1}.

However, comparing these two gases, a lower background was obtained when using H_2. Furthermore, the detection limits of Fe were estimated to be 55 μg L^{-1} without adding gas, 10 μg L^{-1} using He, and 5 μg L^{-1} using H_2.

The sensitivity for the detection of ^{56}Fe, as indicated by the counts obtained, decreased in the order of no gas > He > H_2. As shown in Fig. 2, the addition of H_2 or He gas to the cell decreased sensitivity. When normalized to no gas, the relative sensitivity expressed as a percentage was in the order of no gas (Fe[HEDTA], 100%; Fe[EDTA]$^{1-}$, 100%; Fe[DTPA]$^{2-}$, 100%) > He (Fe[HEDTA], 61.82%; Fe[EDTA]$^{1-}$, 83.01%; Fe[DTPA]$^{2-}$, 83.41%] > H_2 (Fe[HEDTA], 34.25%; Fe[EDTA]$^{1-}$, 41.67%; Fe[DTPA]$^{2-}$, 42.87%). Despite the reduction in background signal and noise, the sensitivity for the detection of the Fe complexes decreased when an ORS was used. Compared with He gas, a lower sensitivity and lower background signal were achieved when using H_2 gas. This can be attributed to their different mechanisms: in H_2 mode, H_2 reacted with the Fe complex and consequently reduced the sensitivity.[18] Taking into account the background signal, the detection limit and the sensitivity, a He flow rate of 3.5 mL min^{-1} was recommended.

IC separation of Fe complexes

Since ICP-MS uses only element-specific detection, it is not possible to detect different Fe complexes unless these complexes are well separated by IC prior to detection. Fortunately, during IC the resolution between different Fe complexes can be manipulated by modifying the eluent, e.g., the type and concentration of the competing anion, and the eluent pH.[19,20] As Fe complexes are polyvalent anions they are retained on an anion exchanger. In addition, a buffer salt deposits residue on the sampler and skimmer cones, and it makes the plasma unstable giving considerable signal drift during prolonged use.[15,18] For these reasons, an eluent is required that can achieve reasonable resolution and be compatible with ICP-MS. Since ammonium phosphate and ammonium nitrate are strong competing anions and the ammonium ion readily decomposed on the ICP-MS cones, both ammonium phosphate and ammonium nitrate were considered as suitable eluents.

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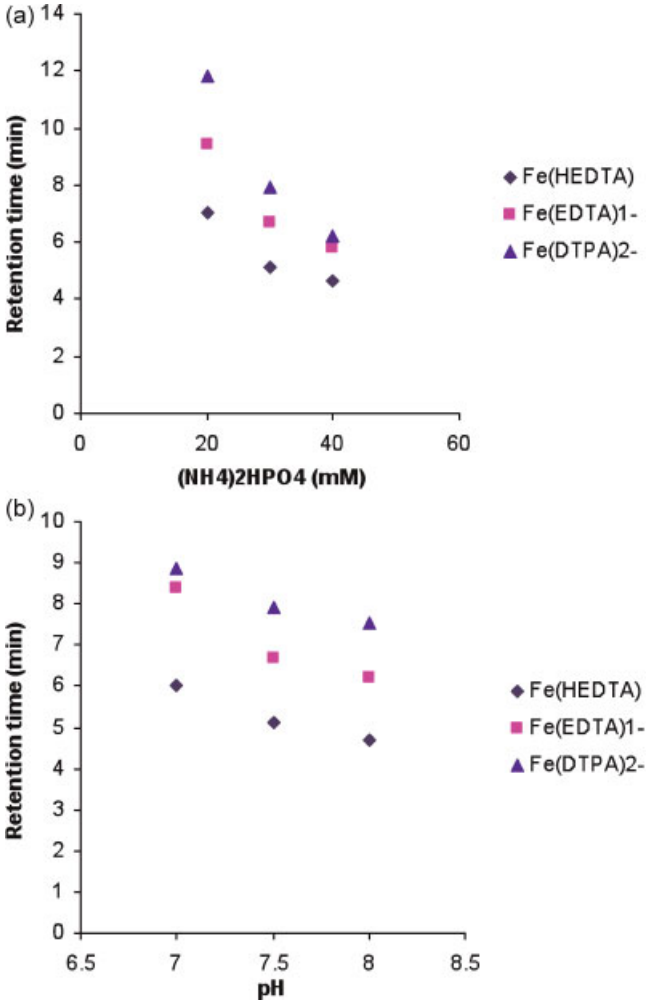

Figure 3. The effect of concentrations of ammonium phosphate (a) and pH (b) on the retention time. Experimental conditions as described in text.

An eluent containing 20 mM ammonium nitrate at pH 6.0 eluted only Fe[HEDTA]^{0} and Fe[EDTA]$^{1-}$ with retention times of 3.71 and 8.42 min, respectively, whereas, when using 20 mM ammonium phosphate at pH 6.0 as the eluent, the retention times for Fe[HEDTA]^{0} and Fe[EDTA]$^{1-}$ were 5.82 and 11.8 min, respectively. In both cases, Fe[NTA] and Fe[DTPA]$^{2-}$ were not observed. This is probably due to the dissociation of Fe[NTA] during chromatographic separation due to its instability, which was previously observed during the separation of Fe[NTA] by capillary electrophoresis,[16] while Fe[DTPA]$^{2-}$ was strongly retained on anion-exchange column because of its high negative charge.[19,20] Comparison of the two competing anions indicated that NO_3^- provided a stronger eluting power than $H_2PO_4^-$. However, since phosphate provides some buffering capacity its eluted power can be manipulated by changes in pH and, consequently, improvement in resolution and retention time is possible. For these reasons, ammonium phosphate was used as the eluent.

Concentration of ammonium phosphate in the eluent in the range 20–40 mM at pH 7.5 were tested As can be observed in Fig. 3(a), the retention time decreased with increasing phosphate anion concentration, and consequently the peak shape improved. Optimal peak shape and resolution were achieved when an eluent containing 30 mM ammonium phosphate was used. The higher the concentration of phosphate anion in the eluent, the more effectively the eluent displaced Fe complexes from the stationary phase and thus the more rapidly the Fe complexes were eluted from the anion-exchange column.[19,20] However, a higher salt concentration in the eluent can result in signal suppression due to increased space-charge effects which defocus the ion beam.[18] Furthermore, the resolution and the peak shape for Fe complexes can be improved by the manipulation of the eluent pH because the mobile phase pH influences the charges both on the competing anions and on the Fe complexes.[19,20] Thus, the eluent pH was tested in the range 7.0–8.0. The retention of the Fe complexes decreased with increasing eluent pH and, as shown in Fig. 3(b), the best peak shape and resolution were observed at pH 8.0.

Analysis of Fe complexes in real samples

Figure 2 shows a typical chromatogram obtained using IC/ICP-MS with a He flow rate of 3.5 mL min^{-1} and an eluent containing 30 mM ammonium phosphate at pH 8.0. The Fe complexes eluted in the order of Fe[HEDTA], Fe[EDTA]$^{1-}$ and Fe[DTPA]$^{2-}$, which depended on their negative charge and consequently their anion-exchange capacity. However, Fe[NTA] was not observed as it was dissociated during IC separation as shown by the weak signal intensity in ESI-MS. This finding was also supported by our recent work on the CE separation of these Fe complexes, as shown in Table 1, where Fe[NTA] was also not observed.[20] Calibration curves for quantification were obtained by plotting peak area versus the concentration of the corresponding Fe complexes. All calibrations were linear over a concentration range of 20–1000 μg L^{-1} with correlation coefficients greater than 0.998. The detection limits (signal/noise 3) ranged from 10 to 13 μg L^{-1}. The reproducibility from the injection of 30 μg L^{-1} (n = 5) from a standard solution containing a mixture of the Fe complexes showed that the relative standard deviation (RSD) was less than 2.9%. In order to test the applicability of the method for the determination of Fe complex species, soil solutions were spiked with a mixed 30 μg L^{-1} Fe complex solution. The recoveries for the Fe complexes ranged from 92.5 to 103.2%. The proposed method was tested to determine if it could be used to monitor Fe complexes in soil

Table 1. Analytical performances for Fe complexes using the proposed method

Species	LDR (μg L^{-1})	Coefficient	DL (μg L^{-1})	RSD (n = 5,%)	Recovery (spiked 30 μgL^{-1}, n = 3, %)
Fe[HEDTA]	20–1000	1.000	10	2.1	103.2 ± 2.5
Fe[EDTA]$^{1-}$	20–1000	0.999	10	2.5	96.6 ± 3.2
Fe[DTPA]$^{2-}$	20–1000	0.998	13	2.9	92.5 ± 3.8

DL = detection limit (signal/noise = 3); LDR = linear dynamic range; RSD = relative standard deviation

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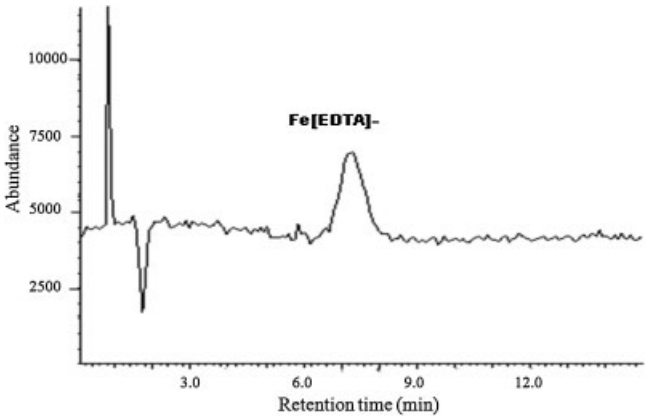

Figure 4. A typical chromatogram obtained from soil solution.

solution. Figure 4 shows a typical chromatogram, where $Fe[EDTA]^{-1}$ was observed with the concentration [$231.2 \pm 2.6\ \mu g\ L^{-1}$ ($n = 3$)]. This indicates that the $Fe[EDTA]^{-}$ was present in the soil solution and phytosiderophores increase the phytoavailability of Fe through the chelation-induced dissolution, or desorption of Fe.

CONCLUSIONS

ESI-MS and IC/ICP-MS are useful complementary techniques for the speciation of Fe-aminopolycaboxylic acid complexes. ESI-MS provides molecular information about the Fe complexes and their stability in aqueous solution, which forms the basis for the IC separation of the Fe complexes. ICP-MS provides highly specific and sensitive detection using an ORS where $^{40}Ar^{16}O$ ion interferences can be significantly reduced by the addition of either He or H_2 to the reaction cell. In this case, He at a flow rate at 3.5 mL min^{-1} was preferred. Fe-aminocarboxylic acid complexes were separated by anion-exchange chromatography using an eluent containing 30 mM ammonium phosphate at pH 8.0, and detected by ICP-MS with an ORS. Potential applications for this technique include the speciation of Fe complexes in soil solutions.

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