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Simultaneous Separation and Quantification of Iron and Transition Species Using LC-ICP-MS

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Abstract

Using liquid chromatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS), this work investigates the simultaneous separation and quantification of seven transition metal species (Fe, Mn, Co, Ni, Cu, Zn, and Cd), based on a separation scheme published by Dionex company that used the spectrophotometric method for quantification. The LC-ICP-MS method overcomes the shortcomings of conventional ferrozine approaches of measuring Fe(II) and total Fe by two separate runs and calculating Fe(III) by the difference of two runs. The advantage is particularly evident in that organo-iron species are found to be the predominant iron species in many natural waters, and the difference method cannot measure the concentration of Fe(III) because ferrozine will not complex with organo-iron species. In the work reported here, the LC-ICP-MS method is successfully applied to the separation of dissolved iron species, as well as six other divalent transition metals in tap water, deionized water, river water, hot springs, and groundwater samples.

Keywords: LC-ICP-MS, Fe(II), Fe(III), Organo-Fe, Transition Metals

1. Introduction

Concentration determination of soluble reactive species is key to understanding biogeochemical processes in aquatic and terrestrial environments. Iron is one of the most reactive elements in aquatic and geological environments, and is involved in the cycling of many major chemicals, as well as trace elements [1]. For example, hydrous ferric oxides (e.g., ferrihydrite) are the most reactive soil components with respect to arsenic sorption and can take up hundreds of mg/kg As, either as As(III) or As(V) [2]. The reduction of Fe oxyhydroxides and release of arsenic has been invoked as a probable mechanism of elevated As concentration in groundwater used for drinking and responsible for the poisoning of millions of people [3,4].

Iron is present in the hydrosphere under two oxidation states, Fe(II) and Fe(III), which are thermodynamically stable under anoxic and oxic conditions, respectively [5]. Measurements of both dissolved Fe(II) and Fe(III) concentration are important in assessing iron's contribution in mediating numerous biogeochemical processes that involves many elements [6]. Most analytical approaches require a separate analysis of dissolved Fe(II) and total dissolved Fe, and the calculation of Fe(III) by the differ-

ence [4]. First proposed by Stookey [7], the ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5, 6-diphenyl-1,2,4-triazine-p, p'-disulfonic acid) method is the most widely-used way of determining Fe(II) and Fe(III). Ferrozine reacts with Fe(II) to form a stable magenta complex species, with a maximum absorbance at 562 nm, which is measured spectrophotometrically. When Fe(III) is also present in the aqueous samples, either as a true dissolved complex or in colloids, a separate reduction step with hydroxylamine ($NH_4OH \cdot HCl$) is performed to measure the total iron, with the difference ascribed to Fe(III) [5,6]. The approach lacks sufficient sensitivity for determining iron concentrations in natural waters at µg/L levels, and therefore a pre-concentration is usually required.

Alternative approaches to the ferrozine method have been proposed [6,8,9]. Yan [6] reported a method of on-line coupling of flow injection separation and pre-concentration with ICP-MS, with a sample volume of 2.5 mL and detection limit of 0.08 µg/L. However, the concentration of Fe(II) was obtained as the difference between the combined Fe(III) and Fe(II), and Fe(III) alone. This was done by controlling the sample acidity range, and detecting the Fe(III) by the Fe(III)-pyrrolidinecarbodithioate (PDC) complex. In summary, relatively little

has been published on the simultaneous measurement of both Fe(II) and Fe(III) in a single run.

Metal ions can exist in several different forms, which are determined by the extent of complexation and the oxidation state. In many aqueous samples, metal ions are present in their hydrated forms. Hydrated metal ions can also be complexed by weak ligands such as organic acids or amino acids. These ligands are generally displaced by the complexing agents used in liquid chromatography eluents, with the total of both hydrated and weakly complexed metal ions determined [10]. Hydrated and weakly complexed transition metals can be separated as cations on a cation exchange column. By adding a carboxylic acid chelating agent to the eluent, the net charge on the metal is reduced, because the carboxylic acids are anionic in solutions above their pKas. The selectivity of the separation is related to the different degrees of association between the metals and the chelating agents producing different net charges on the metal complexes. If strong enough chelating agents are used in high enough concentration, the net charge of the metal complexes can be negative. The resultant anionic metal complexes can be separated by an anion exchange process. The Dionex IonPac® CS-5A column has both cation and anion exchange capacities, allowing metals to be separated as cations or anions on a single column. The 9 µm polymeric pellicular packing of the CS-5A column has an ethylene-vinylbenzene divinylbenzene resin core, 55% cross-linking, consisting of two layers of latex particles, functionalized with both anion exchange alkyl quarternary amine (internal layer) and cation exchange sulfonic acid groups (outer layer), with capacities of 40 and 20 µequivalents, respectively. With pyridine-2, 6-dicarboxylic acid (PDCA) used as the chelating agent in the eluent, the transition metals are separated as anionic complexes in the analytical column of the IonPac CS-5A [10].

The following seven transition metals can be separated and quantified: iron, both ferric (Fe^{3+}) and ferrous (Fe^{2+}), divalent cations of copper, nickel, zinc, cobalt, cadmium, and manganese [10]. The present study was primarily focused on the separation of iron species, as well as the detection and prevalence of organo-Fe species in natural waters. However, the separation of the other six transition metals will also be described in this paper, and some examples of applications in natural waters will be given.

2. Materials and Methods

Except for Fe^{2+} and Fe^{3+}, transition metal standards of 1000 mg/L were obtained from CPI International (Santa Rosa, CA). These stock solutions were purchased in dilute acid (1% - 2% nitric acid) solutions and diluted to different concentrations in deionzied (DI) water for LC-

ICP-MS analyses. Ferrous ammonium sulphate (Mohr's salt, $[NH_4]_2[Fe][SO_4]_2 \cdot 6H_2O$) was purchased from Alfa Aesar (Ward Hill, MA) and ferric chloride hexahydrate (iron III) from Mallinckrodt Baker (Phillipsburg NJ). These chemicals were used to prepare the standard solutions for Fe(II) and Fe(III), respectively. Each individual transition metal was prepared to obtain the retention time from LC separation for peak identification. All solutions were prepared using purified deionzied (DI) water (Milli-Q Ultrapure Water Purification System, Millipore, Billerica, MA).

As reported in Dionex (2011), the eluent for separating the transition metals includes the following mixture: 7.0 mM (PDCA), 66 mM potassium hydroxide, 74 mM formic acid, 5.6 mM potassium sulfate. Dionex carries the MetPac™ PDCA eluent concentrate, which is to be diluted 5 times with 200 mL of the concentrate added with 800 mL DI water to make up 1-L eluent. To adjust the complexing ability of PDCA to optimize the separation time, we also purchased the individual chemicals in making the eluent: PDCA from Alfa Aesar (Ward Hill, MA), potassium hydroxide from EMD Chemicals (Gibbstown, NJ), formic acid from EMD Chemicals, and potassium sulfate from Mallinckrodt Baker (Phillipsburg NJ).

Both ferrous and ferric ions can be separated under the above separation conditions, using PDCA as the chelating agent to form anionic complexes. Because the ferrous ion is easily oxidized to ferric iron, oxygen was removed from the eluent by degassing the eluent solution bottle with helium for half an hour. To remove oxygen from the analytical and guard columns, a solution of 0.1 M sodium sulfite (12.6 g/L Na_2SO_3) was pumped through the columns for 2 hours before the sample analysis [10].

We used an advanced analytical method of LC-ICP-MS for separating and quantifying iron, and the other 6 transition metal species, by modifying the quantification method of Dionex [10], to enable sensitive and simultaneous analyses in aqueous samples. Briefly, the LC system consisted of a PerkinElmer Series 200 Quaternary Pump and a Series 200 Autosampler (PerkinElmer/SCIEX, Sheldon, CT) with an IonPac CS5A analytical and CG5A guard columns from Dionex (Sunnyvale, CA). Separation conditions included the following: mobile phase of MetPac PDCA eluent mixture at pH of 4.2 (adjusted with ammonium hydroxide, with 20% - 22% NH_3), flow rate 1.2 mL/min, and sample injection volume 50 µl.

In the Technical Note of Dionex [10], the metal complexing agent 4-(2-pyridylazo) resorcinol (PAR) is added postcolumn to form a light-absorbing complex with the hydrated and weakly complexed metals. These transition metals are detected by measuring the absorbance at 530 nm of the complex. We used the ICP-MS for sensitive

determination of transition metal species. The effluent from the LC column was directly connected, via 60 cm of trifluoroacetic acid capillary tubing (1.6 mm o.d. × 0.5 mm i.d.), to the nebulizer of a PerkinElmer/SCIEX ELAN DRC II (Sheldon, CT) for the determination of transition metal concentration. The sample introduction system components of the ICP-MS consisted of a cyclonic spray chamber, a Meinhard® type A nebulizer, and platinum cones.

3. Results and Discussion

3.1. Stability of Fe(II) and Fe(III) Solutions

We used the DRC (Dynamic Reaction Cell) capability of ELAN DRC II ICP-MS, with ammonium as the reaction gas at a flow rate of 0.75 L/min and rejection parameter RPq of 0.45, to minimize the polyatomic interference of $^{40}Ar^{16}O$ to ^{56}Fe [11-14]. From the monitored signal intensity results at the atomic mass unit of 56 with only the eluent passing through the column, we observed a baseline level at 22,000 cps (counts per second) under the DRC condition (**Figure 1(a)**), compared to 240,000 cps at the standard mode (*i.e.*, no DRC). A factor of 10 times reduction of baseline level is critical for sensitive measurements of ^{56}Fe.

We next focused on the standards of both Fe(III) and Fe(II) prepared from $FeCl_3$ and $[NH_4]_2[Fe][SO_4]_2 \cdot 6H_2O$. Fe(III) standards from $FeCl_3$ chemicals exhibited only an Fe(III) peak, as shown in **Figure 1(b)**, where the chromatogram for 1000 mg/L solution of Fe(III) was accompanied by only a very small peak at the retention time of Fe(II). However, Fe(II) standard prepared from ammonium iron(II) sulfate ($[NH_4]_2[Fe][SO_4]_2 \cdot 6H_2O$, Mohr's salt) chemicals essentially only shown an Fe(III) peak (**Figure 2(a)**), indicating the oxidation of Fe(II) chemicals over time. Supposedly, Mohr's salt is preferred over iron(II) sulfate as it is much less affected by oxygen in the air than iron(II) sulfate, solutions of which tend to oxidize to iron(III). The oxidation of solutions of iron(II) is very pH dependent, occurring much more readily at high pH. The ammonium ions make solutions of Mohr's salt slightly acidic, which prevents this oxidation from occurring.

We used a reducing agent, 0.1 M $NH_2OH \cdot HCl$, and boiling condition [15] to treat the solution prepared from Mohr's salt, and stored the resultant standard of 1000 mg/L in an autoclaved amber glass bottle.

Standards of Fe(II) with different concentrations were prepared from a working standard of 100 mg/L Fe(II) for LC-ICP-MS studies. **Figure 2(b)** shows the Fe(II) peak, with a negligible Fe(III) peak which likely is caused by the DI water used in standard preparation (to be dis-
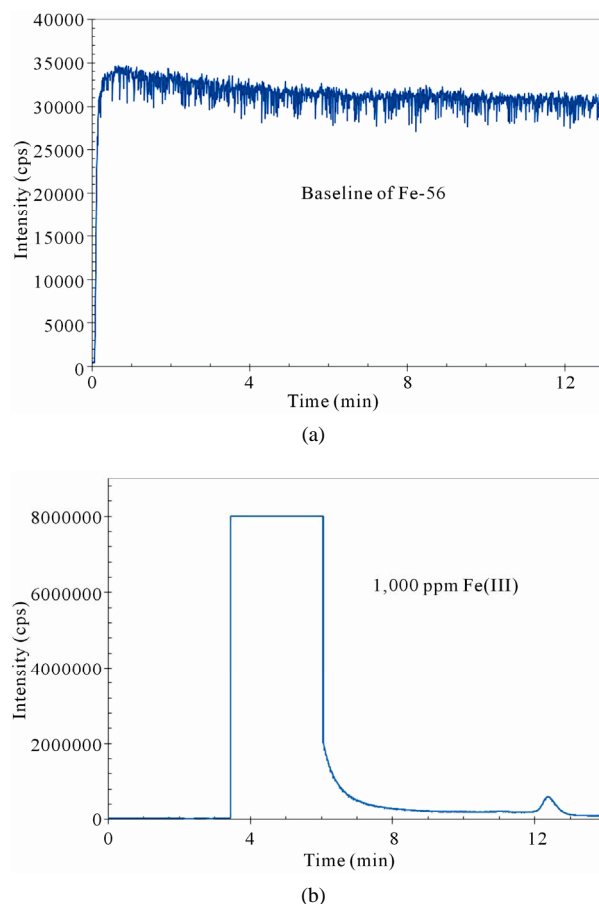

(a)

(b)

Figure 1. (a) LC-ICP-MS ^{56}Fe signal intensity baseline of the eluent solution; (b) Signal intensity of Fe(III), at the retention time around 4 min, prepared from $FeCl_3$ chemicals indicating minimal presence of Fe(II) with a retention time of 12.5 min.

cussed later), of the 100 mg/L Fe(II) working standard.

Figure 3 shows the chromatograms of mixed standards of Fe(II) and Mn(II) at different concentrations. Compared with 24,000 cps background level for ^{56}Fe, the background for ^{55}Mn is only at about 800 cps, indicating much lower polyatomic interference for Mn detection. Multiple measurements of 0.5 µg/L Fe(II) exhibit somewhat different peak height (and area), indicating that the detection limit for Fe(II) by the LC-ICP-MS method is slightly higher than 0.5 µg/L (**Figure 3(a)**). However, this is still a simple and versatile method to measure simultaneously both Fe(II) and Fe(III) at low µg/L concentration levels. In addition, all chromatograms show sharp peaks with reproducible retention times for Fe(II), Fe(III), and Mn(II) species (**Figure 3**). Furthermore, there are Fe(III) peaks reaching 120,000 cps levels from all standards of Fe(II) and Mn(II); this level of Fe(III) probably originates from the DI water used for standard preparation.

3.2. Prevalence of Organic-Fe Species in Natural Samples

The Technical Note of Dionex [10] describes the use of 7 mM PDCA as the complexing agent for seven transition metals, with Fe(III) appearing first and Fe(II) last in the chromatograms. We tested the effect of PDCA concentration on the retention time of Fe, as well as that of other transition metal species; the results are shown in **Table 1**.
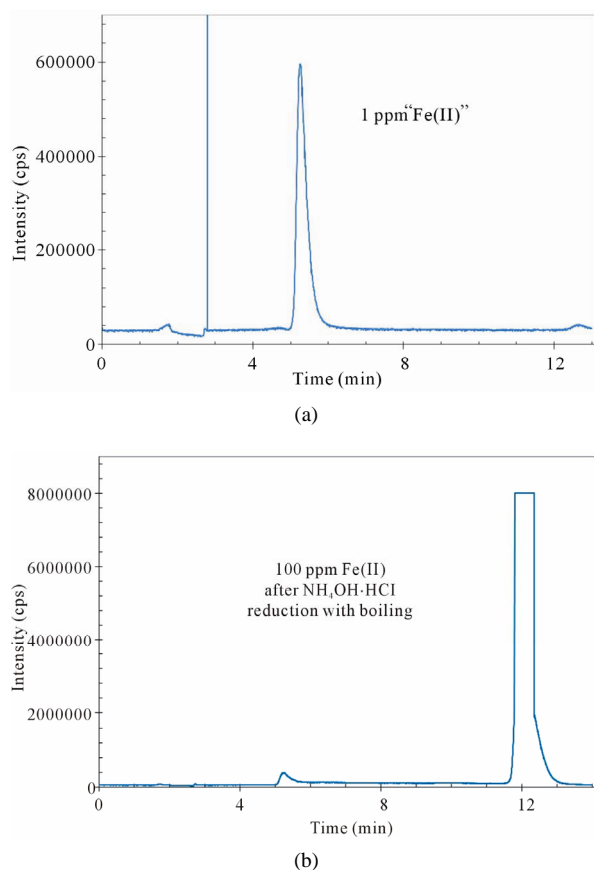

(a)

(b)

Figure 2. (a) Fe(II) standard prepared from untreated [NH$_4$]$_2$[Fe][SO$_4$]$_2$·6H$_2$O chemical indicating its oxidation to Fe(III); (b) Fe(II) standard solution obtained from reductant NH$_4$OH·HCl under boiling condition.

Table 1. PDCA concentration and associated retention of iron species.

PDCA	Species and retention time (min)	Note
3.5 mM	Fe^{3+} (7.0)	Too long separation time
7.0 mM	organo-Fe (2.8); Fe^{3+} (5.0); Fe^{2+} (11.2)	Reasonable separation time
14 mM@	organo-Fe (2.1); Fe^{3+} (3.8); Fe^{2+} (6.5)	Best scheme for separating all 7 transition metals in 8 min

@Preparation of 14 mM pyridine-2, 6-dicarboxylic acid (PDCA), 66 mM potassium hydroxide, 74 mM formic acid, and 5.6 mM potassium sulfate: warm the solution to fully dissolve PDCA; the measured pH is 3.58; add about 10 mL concentrated NH$_4$OH into 4 L eluent solution to adjust pH to 4.22; otherwise, the baseline is not stable in LC-ICP-MS runs.
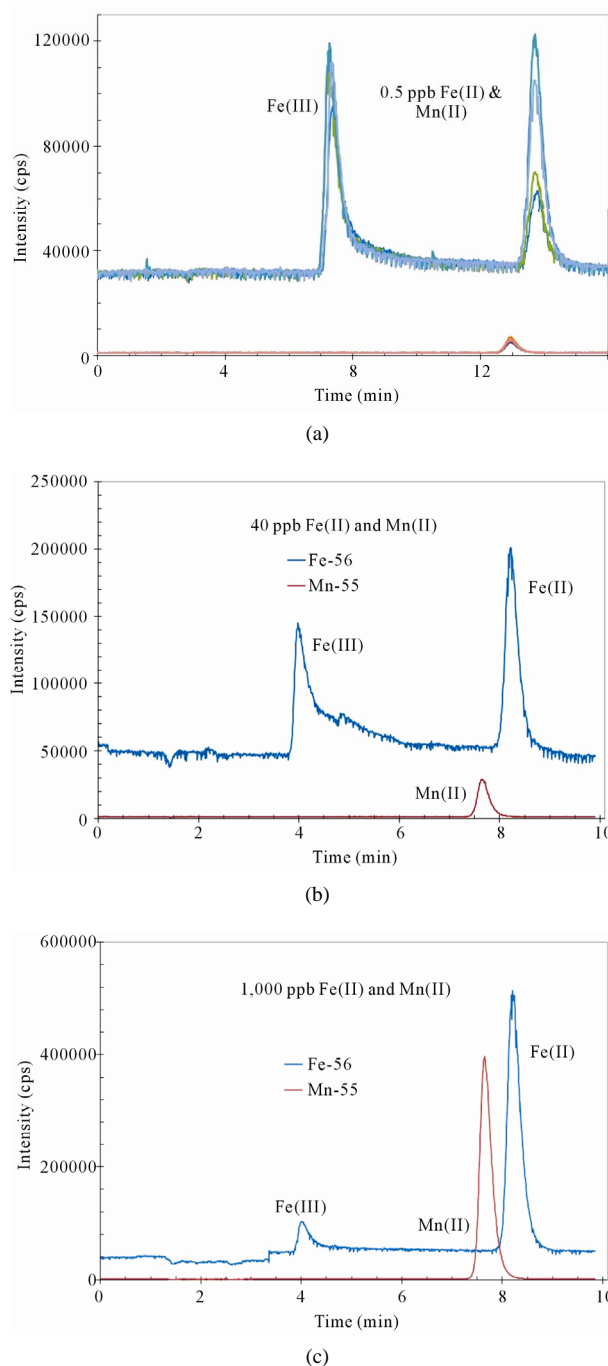

(a)

(b)

(c)

Figure 3. Signal responses of Fe(II) and Mn(II) standard solutions at the concentration of (a) 0.5 μg/L (four duplicate injections are presented); (b) 40 μg/L; and (c) 1000 μg/L. Slightly different PDCA concentrations (Table 1) were used to produce different retention times.

It was observed that a lower PDCA concentration will lead to a longer retention time in the separation condition. We suggest the use of a concentration of 14 mM PDCA to reduce the run time to less than eight minutes for the separation of all 7 transition metal species; note that

some figures shown in this work were obtained at a lower PDCA concentration; this had no effect on the interpretation of results, although the chromatograms show a longer run time (e.g., 12 min). An adjustment of pH to 4.22 is necessary to produce a stable baseline in the eluent mixture of 14 mM PDCA, since PDCA is slightly acidic, with a measured pH of 2.38 for the 14 mM PDCA solution.

Figure 4 shows example chromatograms for groundwater and river water samples collected in Texas; the samples were filtered through a 0.25 µm membrane filer with no other preservation step (e.g., acidification), and stored at 4˚C in a refrigerator. Both samples show a small Fe(III) peak and no Fe(II), while the groundwater shows Mn(II) presence. In addition, both samples show a large ^{56}Fe peak before the ^{56}Fe(III) peak; this is likely related to an organic-Fe species, such as an Fe-complex with natural organic matter （NOM）. Typically, NOM is a complex mixture of organic substances containing a variety of functional groups, such as carboxyls, phenols, thiols and amines, many of which interact strongly with Fe(II) and/or Fe(III). It has been reported that Fe(III) forms
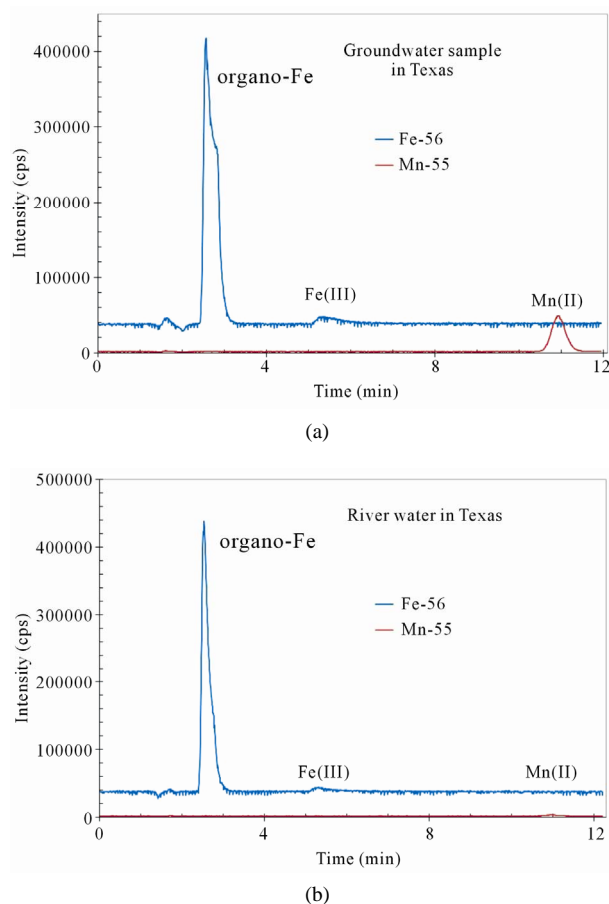
complexes with organic acids. At low Fe concentrations and pH 3.0 - 7.2, mononuclear Fe(III)-NOM complexes completely dominate the speciation, and a substantial amount of the total Fe (>50%) is in the form of organic complexes [16].

We further measured the Fe chromatograms of several solutions of organic materials containing 10 mg/L carbon; these solutions were prepared from the standard reference materials including Suwannee River natural organic matter, Suwannee River fulvic acid, Pahokee Peat humic acid, and Summit Hill soil humic acid (all from the International Humic Substances Society, Denver, CO). We consistently observed the organic-Fe peak for these four materials; the chromatograms of Suwannee River natural organic matter and Summit Hill soil humic acid are shown in **Figure 5**. The iron species in these solutions are predominantly organo-Fe.

In addition, we analyzed the effluent samples from columns packed with sediment samples, where we studied the transport behavior of arsenic species in different sediments [17]. We consistently observed the predominant organo-Fe peaks in the column effluents from both Hanford and Datong basin sediments (**Figure 6**). In a report on determination of the structures and reactivities of Fe associated with NOM (considering that these interactions influence the redox, hydrolysis and solubility of Fe[18]), Rue and Bruland [18] reported that 99.97% of the dissolved Fe(III) in central North Pacific surface waters is chelated by natural organic ligands. We are not aware of the direct detection, or of the prevalence and predominance, of organo-Fe species in natural water. It is important to note that the conventional ferrozine method of analyzing for Fe(III) is based on the difference of measured total Fe and Fe(II), and that the presence of organo-Fe species will affect the measurement of inorganic Fe species. As discussed above, iron forms complexes with dissolved organic matter; where this occurs

(a)

(b)

Figure 4. Detection of iron species and Mn(II) in (a) groundwater; and (b) river water samples in Texas.
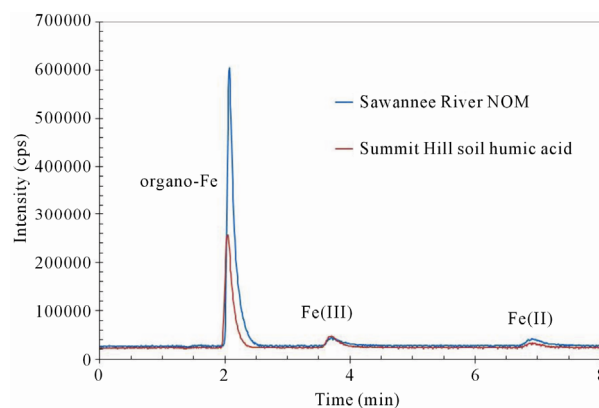

Figure 5. Detection of iron species in (A) Suwannee River natural organic matter; and (B) Summit Hill soil humic acid; both at the concentration of 10 mg/L carbon.
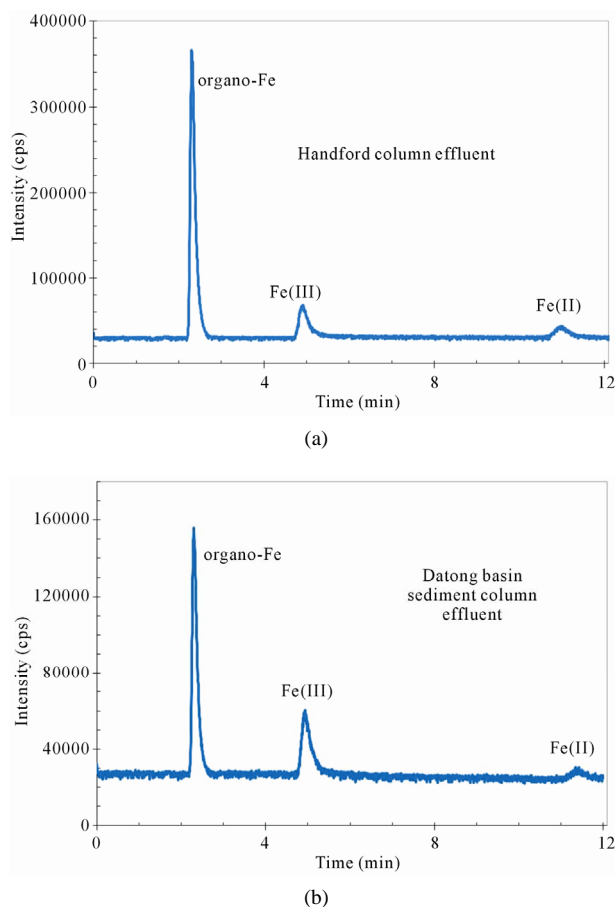
(a)

(b)

Figure 6. Detection of iron species and Mn(II) in the effluent samples collected from a column packed with (a) Hanford sediment in the State of Washington; and (b) Datong Basin in Shanxi province, China.

in seawater, the color development of ferrozine chelates is hindered. To eliminate this factor, samples were heated and exposed to UV irradiation to decompose the organo-iron complex in the work of Kononets *et al.* [19].

3.3. Simultaneous Separation of Seven Transition Metals

The separation scheme can detect seven transition metal species in a single run. Using individual standards, we obtained the retention times of these species in the eluent with 14 mM PDCA concentration (**Figure 7**, **Table 2**). **Table 2** also presents the isotopes monitored for these seven transition metals, the baseline levels, and the intensity responses for these isotopes. Other than Fe-56 and Cu-63, the isotopes for monitored transition metals have low mass interference. After normalizing the natural abundance for these isotopes, the signal intensities for all of these elements are fairly close (**Table 2**), which is expected from their closeness in atomic mass units

Using the separation method for seven transition metals, we further analyzed both the tap water and the DI water in a research lab; the DI water was produced by passing the tap water through the water purification system, which consisted of reverse osmosis and a 254-nm UV lamp for organic molecule oxidation and bacteria destruction. We observed a peak of organo-Fe in the tap water, and this peak was removed in the DI water, possibly from the UV oxidation (**Figure 8**). On the other hand, the heights of Fe(III) and Fe(II) peaks are similar for both tap and DI waters, indicating the inefficiency of the water purification system to remove very low (below about 0.2 µg/L) concentrations of these Fe species. The tap water also has higher concentrations of Cu and Zn than the DI water, probably from the piping system (**Figure 8**).

Water samples from the Gallinas River and the Montezuma Hot Springs in New Mexico also indicate the presence of organo-Fe, as well as Fe(III) and Fe(II), species (**Figure 9**). In addition, there is a detectable amount of divalent Cu, Ni, Zn, and Mn species in these waters.

4. Conclusions

Using advanced analytical tools of LC-ICP-MS and modification of a separation scheme for seven transition metals published by Dionex, we present a versatile method of simultaneous analysis for iron species, with micro-liter injection volumes. The method is assisted by the use of the Dynamic Reaction Cell technique to reduce the detection of ^{56}Fe, and the species check of

Table 2. Retention time and signal intensity of 7 transition metals simultaneously separated and quantified by LC-ICP-MS.

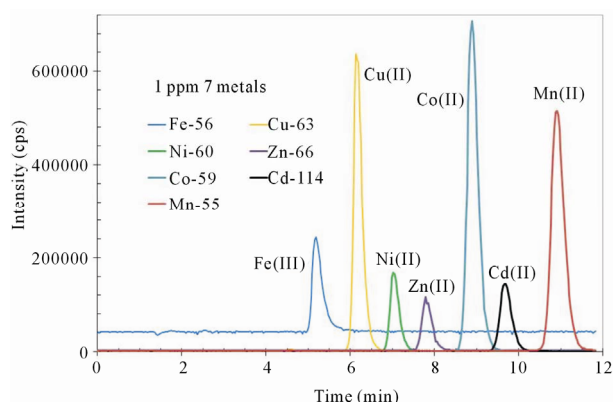|	Cu-63	Ni-60	Zn-66	Co-59	Cd-114	Mn-55	Fe(II)-56
Retention time (min)	3.9	4.3	4.7	5.2	5.8	6.6	6.9
Natural abundance (%)	69.09	26.33	27.81	100	28.86	100	91.66
Baseline level (cps)	25,000	2,600	1,100	140	110	800	25,000
LC-ICP-MS intensity of 1 ppm standard (cps)	7,443,737	2,753,464	1,859,578	10,385,828	3,383,030	14,665,378	7,338,520
Abundance normalized cps/ppb	10,773	10,457	6,687	10,386	11,722	14,665	8,006

Figure 7. Retention times and signal intensities of 7 transition metals in a single run.
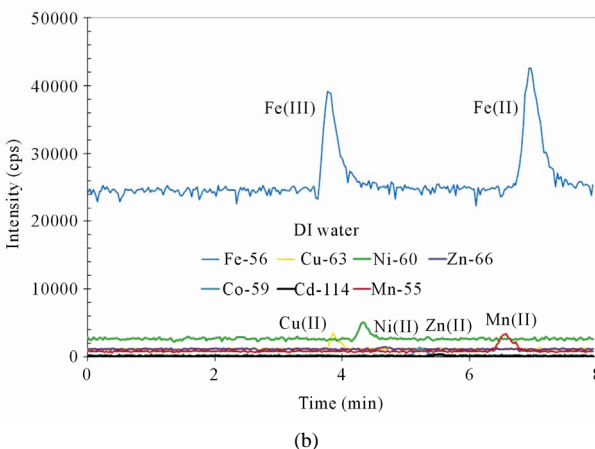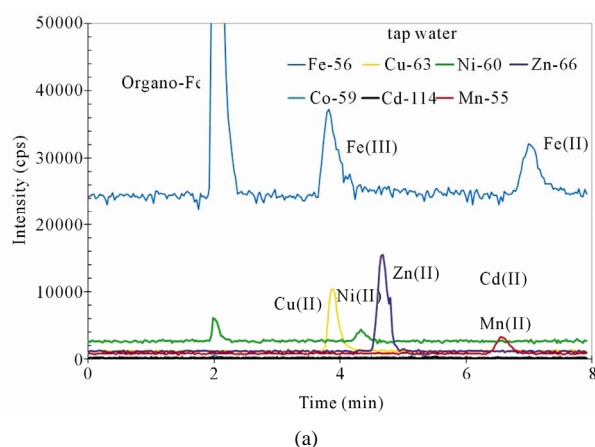

(a)

(b)

Figure 8. Presence of 7 transition metal species in the (a) tap water; and (b) DI water.

Fe(III) and Fe(II) increases the confidence of iron species determination. In particular, we found that most of the iron species in natural waters and geological samples could exist in complexation with natural organic matter. Attention should be paid to the prevalence of organo-Fe species in speciation studies of iron, and to its role in
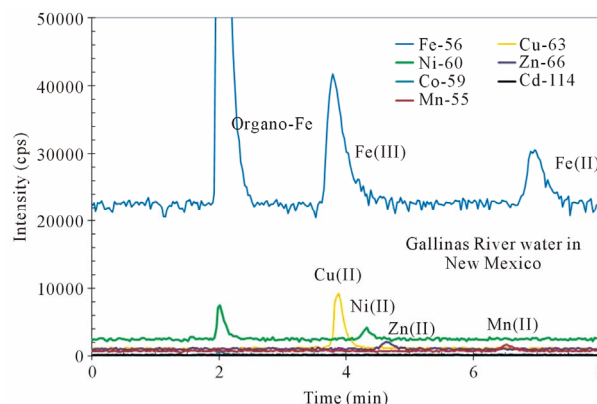
(a)
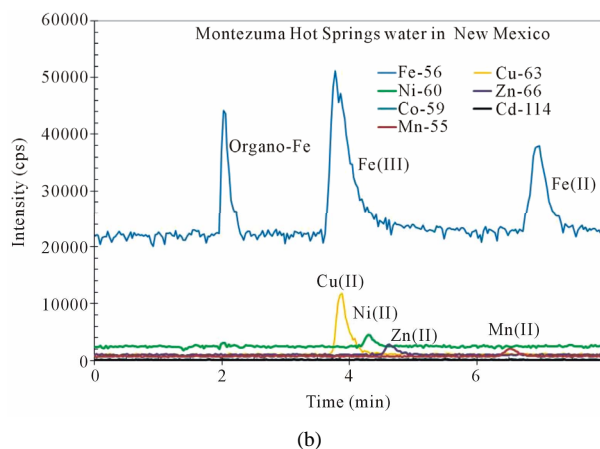
(b)

Figure 9. Presence of 7 transition metal species in (a) Gallinas River; and (b) Montezuma Hot Springs water samples in New Mexico.

modifying the biogeochemical cycling of elements in aquatic and terrestrial environments.

5. Acknowledgments

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