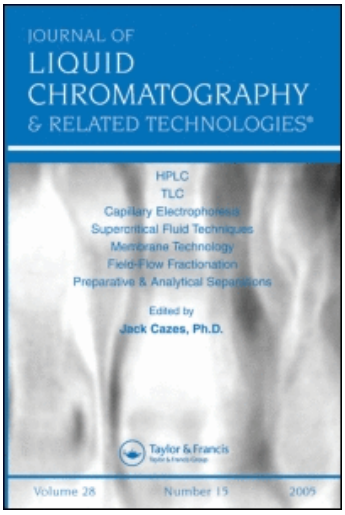

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Analysis of Ferric and Ferrous Ions in Soil Extracts by Ion Chromatography

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ANALYSIS OF FERRIC AND FERROUS IONS IN SOIL EXTRACTS BY ION CHROMATOGRAPHY

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ABSTRACT

A method using ion chromatography (IC) for the analysis of ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in soil extracts has been developed. This method uses an ion exchange column with detection at 520 nm after post-column derivatization. Selectivity is achieved by using an anionic chelating agent, pyridine-2,6-dicarboxylic acid, to form anionic complexes with ferric and ferrous ions. Using this method, both ferric and ferrous ions can be analyzed directly and simultaneously. The soil extractions were carried out with both 0.5 M hydrochloric acid (HCl) and 0.36 M oxalate under anaerobic conditions. Ferric and ferrous ions were stable in either 0.5 M HCl solution or deionized water at pH ~ 1.7 when stored outside of a glove box. Ferrous ion was readily oxidized to ferric ion in aqueous solutions at pH values above 4.0 and in 0.36 M oxalate solutions at all pH values.

In addition, we note that ferric ion in 0.5 M HCl was detectably reduced to ferrous ion when stored for 24 hours in a glove box containing a few percent of hydrogen gas. The study indicated that there was no interference in the HPLC analysis from the common cations Ca^{2+}, Mg^{2+} and Al^{3+}.

INTRODUCTION

The microbial reduction of ferric ion (Fe^{3+}) to ferrous ion (Fe^{2+}) is an important geochemical process which takes place in many aquatic sediments and aquifers.[1,2] This Fe^{3+} reduction is of environmental significance as it can result in the release of trace metals,[3] phosphate,[4] and undesirably high concentrations of iron[2,5] into water supplies. Ferric ion may also be an important oxidant of contaminant organic compounds.[6,7]

Ammonium oxalate and hydrochloric acid solutions have been used to extract ferrous and ferric ion from soils and sediments.[8,9,10] A method using spectrophotometric determination of ferrozine-iron complexes[11] has been widely used for analysis of ferrous concentration in acidic oxalate soil extracts.[12] The total iron concentration is determined by reducing ferric ion to ferrous ion and then analyzing the ferrous ion concentration using this method.

The disadvantages of this method are that ferric ion cannot be directly analyzed, the procedure is time consuming, and high experimental errors can occur during sample preparation, mixing of complexing agent with extracts, and addition of reducing agents.

This work reports an ion chromatographic method that has been developed to analyze ferric and ferrous ions in extracts directly and simultaneously. The objectives of this work were:

1. to study the stability of ferric and ferrous ions under various conditions;

2. to evaluate the stability of ferric and ferrous ions in both 0.36 M oxalate and 0.5 M HCl solutions and;

3. to investigate the extraction yields of ferric and ferrous ions from soil using 0.36 M oxalate and 0.5 M HCl as extraction solutions.

MATERIALS AND METHODS

Chemical and Reagents

Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sodium sulfite and hydrochloric acid (37%) were obtained from J. T. Baker (Phillipsburg, NJ, USA). Sodium phosphate ($NaH_2PO_4 \cdot H_2O$), sodium perchlorate ($NaClO_4$), ammonium oxalate ($(COONH_4)_2 \cdot H_2O$) and oxalic acid ($H_2C_2O_4$) were obtained from Aldrich Co. (Milwaukee, WI, USA). Acetic acid, ammonium hydroxide (20% to 22%) and sodium hydroxide (50%) were obtained from Fisher Scientific (Pittsburgh, PA, USA). O-phenanthroline and pyridine-2,6-dicarboxylic acid were purchased from Fluka (Ronkonkoma, NY, USA). Sodium acetate 4-(2-pyridylazo) resorcinol was obtained from Dionex (Sunnyvale, CA, USA) and methanol was purchased from Burdick and Jackson (Baxter, Muskegon, MI, USA). Water used in this study was 18 mΩ deionized water (DI water) obtained from a Millipore Milli-Q system. (Milford, MA, USA).

Ion Chromatography

The ion chromatography instrumentation included a Dionex HPLC-CS5 column, a Dionex postcolumn reaction unit, a Dionex advanced gradient pump, a Waters (Milford, MA, USA) 486 tunable absorbance detector set at wavelength 520 nm, and a Waters 770 autosampler with a polyetherether ketone (PEEK) sample loop (0.6 mL).

The mobile phase was 6 mM pyridine-2,6-dicarboxylic acid, 50 mM acetic acid, and 50 mM sodium acetate. The postcolumn reagent was 0.3 mM 4-(2-pyridylazo) resorcinol, 1 M acetic acid and 3 M ammonium hydroxide. The flow rates of the mobile phase and the postcolumn reagent were 1.0 and 0.7 mL/min, respectively. The data acquisition time was 16 min.

Ferric and ferrous ions were successfully separated and analyzed using an ion exchange column. Good selectivity was achieved by using the anionic chelating agent, pyridine-2,6-dicarboxylic acid (PDCA). Using this chelating agent, anionic complexes are formed:[13]

$$Fe^{3+} + 2\,PDCA \longrightarrow Fe(PDCA)_2^- \quad (1)$$

$$Fe^{2+} + 2\,PDCA \longrightarrow Fe(PDCA)_2^{2-} \quad (2)$$

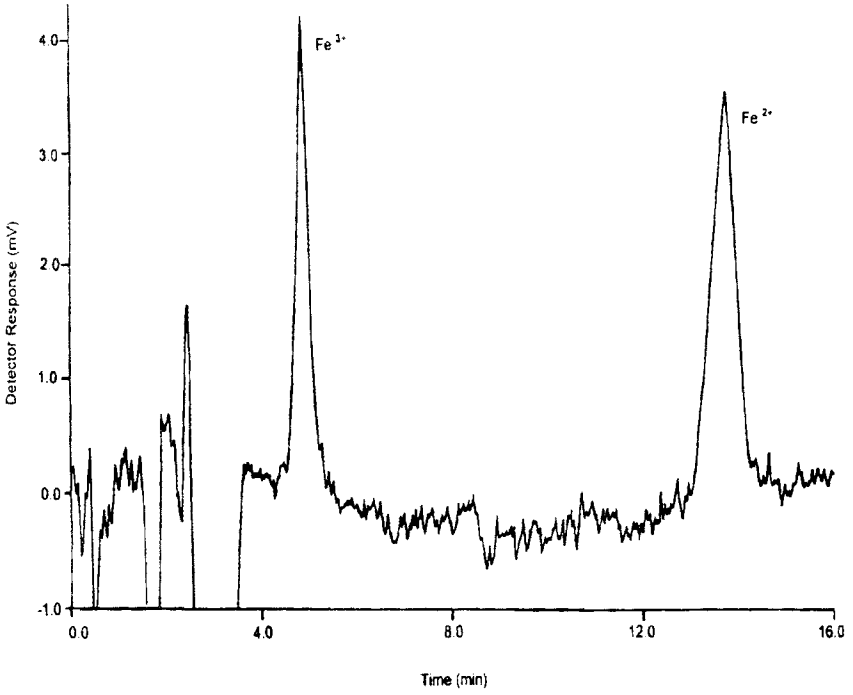

Figure 1. Standard of ferric and ferrous ions (0.5 μM) in DI water at pH 1.7.

The Fe^{3+} complex elutes prior to the Fe^{2+} complex (Figure 1) since the former is a monovalent anionic complex and the later a divalent anionic complex. The elution order is consistent with an anion exchange mechanism. Spectrophotometric detection was at 520 nm after postcolumn derivatization with 4-(2-pyridylazo) resorcinol (PAR). PAR was continually added to the column effluent stream.

Prior to analysis, oxidation agents present in the ion chromatography system were removed by using 0.1 M sodium sulfite (12.6 g/L) sparged with helium (He) and then pumped at 1.0 mL/min through the system for at least one hour before the mobile phase was pumped. The mobile phase was sparged with He before (at least 30 minutes) and during the analysis. Three check standards (40 μM standard of ferric and ferrous ions) were usually analyzed before the analysis of soil extracts. The concentrations of ferrous ion in the first two check standards may be low due to oxidation agents remaining in the ion chromatography system.

Ferric and Ferrous Ions Standard Preparation

500 mL of DI water was adjusted to pH~2.0 with hydrochloric acid, sparged with helium for at least 30 min, then ferric nitrate (0.2020 g, $Fe(NO_3)_3 \cdot 9H_2O$) and ferrous sulfate (0.1390 g, $FeSO_4 \cdot 7H_2O$) were added making 1 mM standard solution of ferric and ferrous ions. This standard solution was determined to be stable for at least two months at room temperature (21°C). The standards used in the calibration curve and check standards were prepared from dilutions of the 1 mM ferric and ferrous ion standard using acidified DI water at pH ~ 2.0, sparged with He. The pH of standard solutions in basic condition were adjusted with sodium hydroxide solution (50%) and determined with a Cole Parmer pH meter model 05669-20.

Soil Sample Collection

Soil samples used in this study were portions of cores collected from the Wurtsmith Air Force Base in Michigan. The cores were collected in plastic core liners and placed in a field glove bag purged with helium. The soils were split into sections, placed into previously sterilized mason jars, shipped on ice back to the laboratory, and then stored in an anaerobic glove box in the dark.

Extraction

Oxalate solution (0.36 M) was prepared using 28 g of ammonium oxalate ($(COONH_4)_2 \cdot H_2O$) and 15 g of oxalic acid ($H_2C_2O_4$) in one liter of DI water. The final solution pH was 3.1. 0.5 M HCl solution was prepared using 42 mL of HCl (36%) in one liter of DI water. The final solution pH was 0.73. These solutions were sparged with helium to remove oxygen and stored in an anaerobic glove box.

All extraction procedures and sample handling were conducted in a glove box containing 6-7% hydrogen in nitrogen. Light-sensitive solutions and extracted soil samples were covered with aluminum foil and stored in the glove box.

Wet sediment (~0.5 g) was placed in pre-weighed and labeled 30 mL septa vials. The bottles were re-weighed to determine the precise weight of wet soil being extracted. 0.5 M HCl or 0.36 M oxalate solution was added to the sediment at the ratio of 1 g wet sediment to 10 mL extraction solution.

Table 1

Analytical Precision and Detection Limits

Injection Vol.[a] /Concentration	Mean Solut. Conc. (μM)[b]		Standard Deviation (SD)		PSD[c]		Detection Limits (μM)	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
100 μL/5 μM	5.12	4.88	0.140	0.213	2.9%	4.4%	0.45	0.64
500 μL/0.5 μM	0.48	0.49	0.012	0.006	2.5%	1.2%	0.03	0.02

[a] 5 μM standard solutions of ferrous and ferric ions were analyzed with injection of 100μL. 0.5 μM standard solutions of ferrous and ferric ions were analyzed with injection of 500 μL. The solution pH was 1.7.

[b] Mean solution concentrations (x) were calculated from the results of three standard solutions analyzed.

[c] PSD: Percent relative standard deviaiton (= 100 x (SD/x)).

Table 2

Standard of Ferric and Terrous Ions at Various pH, and in 0.5 M Hcl and 0.36 M Oxalate Solutions

Solvent	STD (μM)	pH	Fe^{3+} Detected (μM)	pH	Fe^{2+} Detected (μM)
DI Water (after 2 months)	40	1.7	40.8	1.7	39.6
DI Water	40	1.7	40.6	1.7	41.2
	40	3.1	39.8	3.1	40.9
	40	3.9	14.2	4.1	20.9
	40	6.1	16.1	6.0	6.9
	40	11.5	24.1	11.1	2.9
0.5M HCL	40	0.7	39.7	0.7	41.6
0.36M Oxalate	40	3.1	55.6	3.1	1.1
0.5M Hcl (kept in glove box 24 hrs)	100	0.7	50.7	0.7	103.3
0.36M Oxalate (kept) in glove box 24 hrs)	100	3.1	136.5	3.1	1.2

The bottle was foil-wrapped, sealed, placed on a magnetic stirrer, and extracted for 24 hours. After the extraction, the supernatant liquid was filtered using a 0.22 μm syringe filter to remove any solids and recapped. The samples were analyzed as described in the Methods Section.

RESULTS AND DISCUSSION

Analytical Precision and Detection Limits

Ferrous and ferric ions were analyzed quantitatively with a good degree of precision and accuracy (Table 1).

Triplicate analyses of 500 μL injections of 0.5 μM ferrous and ferric ion standard and 100 μL injections of 5.0 μM of ferrous and ferric ion standard were used to determine the detection limits and quantitation limits. The detection limit and the quantitation limit were calculated as three times the standard deviation of the mean and ten times the standard deviation of the mean. Using an injection volume of 500 μL, the detection limits were 0.04 μM and 0.01 μM for ferrous and ferric ions, respectively, and the quantitation limits were 0.13 μM and 0.03 μM for ferrous and ferric ions, respectively. Using an injection volume of 100 μL, the detection limits were 0.45 μM and 0.64 μM for ferrous and ferric ions, respectively, and the quantitation limits were 1.50 μM and 2.13 μM for ferrous and ferric ions, respectively. Figure 1 shows the chromatogram of 0.5 μM standard of ferric and ferrous ions at pH ~ 1.7 using an injection volume of 500 μL.

Stability of Ferric and Ferrous Ions Standards Under Various Conditions

The oxidation and reduction of ferrous and ferric ions were studied independently, using separate standard solutions of ferric and ferrous ions. The pH of each solution was determined. Table 2 shows the analytical results for 40 μM standards of ferric and ferrous ions at pHs ranging from 0.7 to 11.5 in 0.5 M HCl, DI water and 0.36 M oxalate solutions.

Ferric and ferrous ions were stable in DI water at pH values of 1.7 and 3.1 and in 0.5 M HCl (pH 0.7). Ferrous ion standards of 40 μM were detected at lower than expected concentrations at pH values above 3.1. The low concentrations of ferrous ion at pH above 3.1 can be attributed to oxidation by atmospheric O_2.

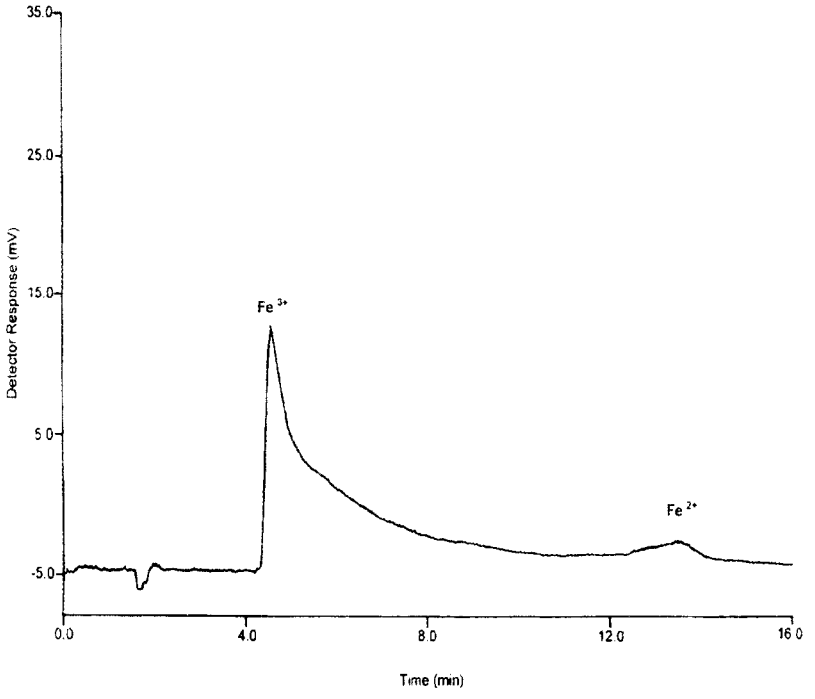

Figure 2. Standard of ferrous ion (40 μM) in DI water at pH 11.1.

The oxidation of ferrous ion to ferric ion is very significant at pH 11.1 as shown in Figure 2. A ferrous ion concentration of only 2.9 μM was detected for 40 μM ferrous ion standard at pH 11.1, while the ferric ion concentration, produced from oxidation of ferrous ion, was detected to be 21.5 μM. As seen in Table 2 the detected concentration of ferric ion in ferric ion standard (40 μM concentration) at pH 3.9 and above is 65% to 40% lower than at pH 1.7 and 3.1. A mixed standard of ferric and ferrous ions in DI water at pH 1.7 and sparged with helium was stable for at least two months. In addition, the apparent ferric ion concentration for the 0.36 M oxalate solution of ferrous iron standard was very high (55.6 μM). The oxalate solution has very low background absorbance and therefore did not contribute to the high absorbance of ferric ion. To calculate the ferric ion concentration accurately in oxalate solutions, a calibration must be performed in the ferric ion standard made with the oxalate solution.

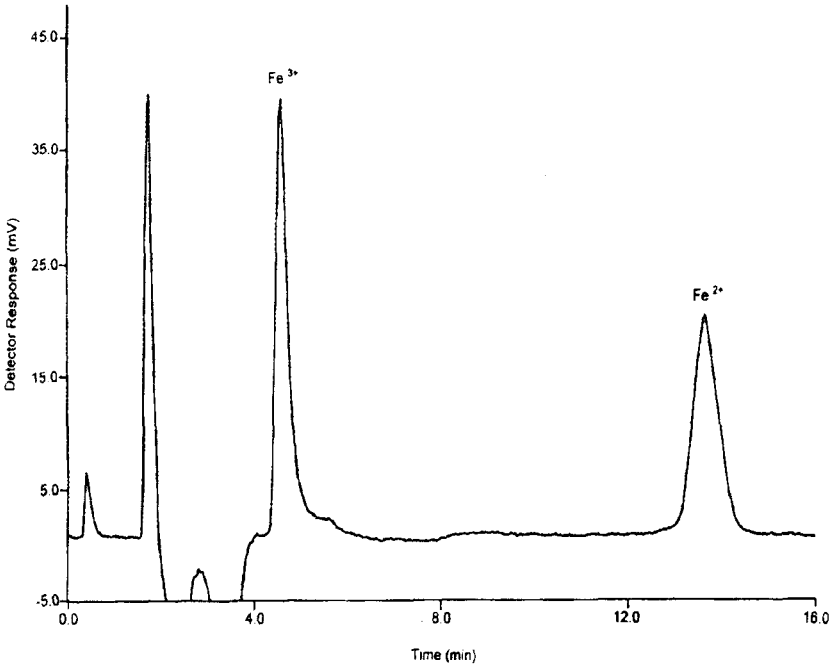

Figure 3. Standard of ferric ion (100 μM) in 0.5 M HCl and stored in a glove box for 24 hours.

Table 3

Standard of Ferrous Ion in Oxalate Extraction Solution

Fe^{2+} Standard (mM)	Detected Fe^{2+} (mM)	Detected Fe^{2+} (mM)
0.250	0.016	0.229
1.000	0.041	0.893
2.000	0.286	1.631
3.000	0.530	2.327

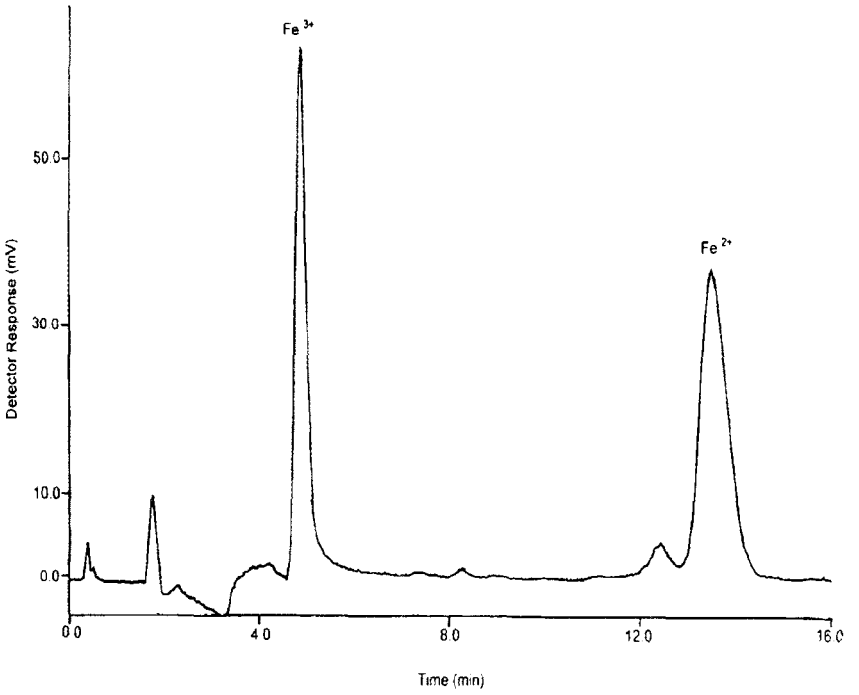

Figure 4. Ferric and ferrous ions extracted from a soil sample with 0.5 M HCl.

Table 2 shows that ferrous ion is detected at lower than expected concentration in oxalate solution (pH 3.1). The low concentration of ferrous ion in the oxalate solution cannot be attributed to solution pH alone because ferrous ion is stable at pH 3.1 in DI water. Oxidation of ferrous ion apparently occurs easily at lower pH in the presence of oxalate. The evidence supporting this suggestion is that the spike of ferrous ion in 0.36 M oxalate solution immediately shows the yellow color, characteristic of ferric ion at pH values above 3.1.

Table 3 shows the detected concentrations of ferric and ferrous ions from the ferrous ion standards, 0.25 mM to 3.0 mM, in the oxalate solution. In each case, ferric ion was formed from the oxidation of ferrous ion. Ferric ion concentration increases as the ferrous ion concentration increases. The total concentrations of ferric and ferrous ions are approximately equal to the ferrous ion concentrations in the standards. The ferric ion concentrations were calculated from the calibration performed in the ferric ion standard made in the oxalate solution.

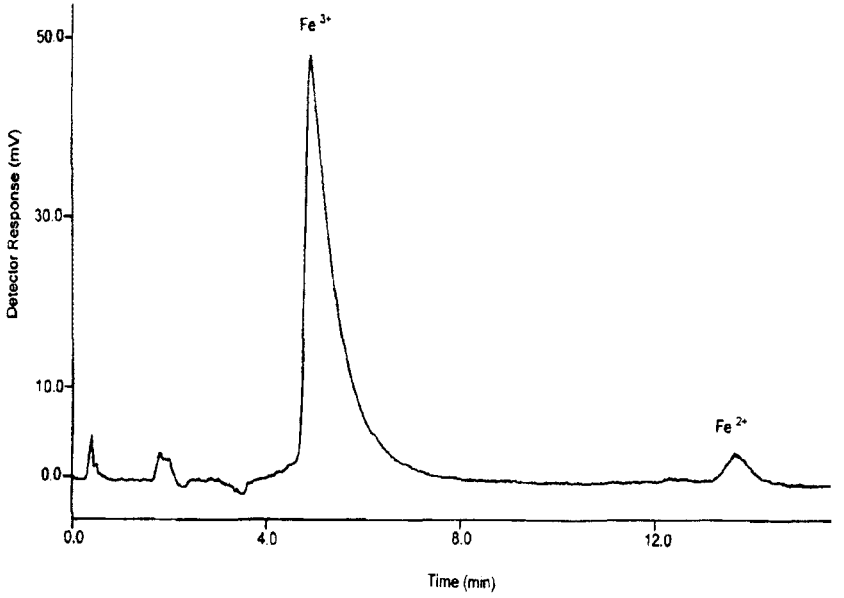

Figure 5. Ferric and ferrous ions extracted from a soil sample with 0.36 M oxalate.

Standard Solutions of Ferrous and Ferric Ions in the Glove Box

Four standards at concentrations of 100 μM ferric and ferrous ions in 0.5 M HCl and 0.36 M oxalate were kept in the glove box for 24 hours. As shown in Figure 3, ferric ion in the 0.5 M HCl was partly reduced to ferrous ion resulting in ferric and ferrous ions concentrations of 50.66 μM and 39.81 μM, respectively. The reduction can be attributed to the 6-7% hydrogen in the hydrogen/nitrogen gas mixture used in the glove box as is typical in glove boxes where anaerobic microbial experimentation is conducted. The ferrous ion concentration in 0.5 M HCl was stable (103.3 μM after 24 hours; Table 2). As expected, the ferrous ion in the oxalate solution showed almost complete conversion of ferrous ion to ferric ion (Table 2). The ferric ion in the oxalate solution showed a high apparent concentration as discussed above, and therefore ferric ion reduction was not observed in oxalate solutions.

Table 4

Ferric and Ferrous Ions in Soil Extractes with O.36M Oxalate and 0.5M HCL

Soil Sample	Oxalate			0.5M HCl		
	Fe^{2+}	Fe^{3+}	Fe^{3+}/Fe^{2+}	Fe^{2+}	Fe^{3+}	Fe^{3+}/Fe^{2+}
		(μM)				(μM)
1	55	12566	228	291	384	1.3
2	56	1203	21	211	253	1.2
3	60	1938	32	157	369	2.4
4	81	3567	44	239	375	1.6
5	67	1270	19	236	208	0.9

Soil Extracts

Ferric and ferrous ions were detected in soil extracts obtained using 0.5 M HCl solution as an extractant. A typical ion chromatogram is shown in Figure 4. Table 4 shows the results of ferric and ferrous ions in five soil extracts using 0.36 M oxalate and 0.5 M HCl solutions. The concentrations of ferric ion in 0.5 M HCl extracts are in the range of 208 μM to 384 μM and ferrous ion 157 μM to 291 TμM. The ratio of ferric ion to ferrous ion ranges from 0.9 to 2.4.

The actual ferric ion concentrations in these samples were probably higher than those detected because ferric ion is being partly reduced by hydrogen in the glove box atmosphere. The actual ferrous ion concentration should therefore be lower than shown.

The ferric ion concentrations are systematically high in the oxalate-extracted samples, with values ranging from 1203 μM to 12566 μM. The ferric ion concentrations were calculated using the calibration performed with the ferric ion standards made in an oxalate solution. The concentrations of ferrous ion in the soil extracts with 0.36 M oxalate are very low, ranging from 55 μM to 81 μM, apparently due to the conversion of ferrous ion to ferric ion in oxalate solution.

Here, the ratios of ferric ion to ferrous ion concentration ranged from 19 to 228. An ion chromatogram of a soil extract prepared using 0.36 M oxalate is shown in Figure 5.

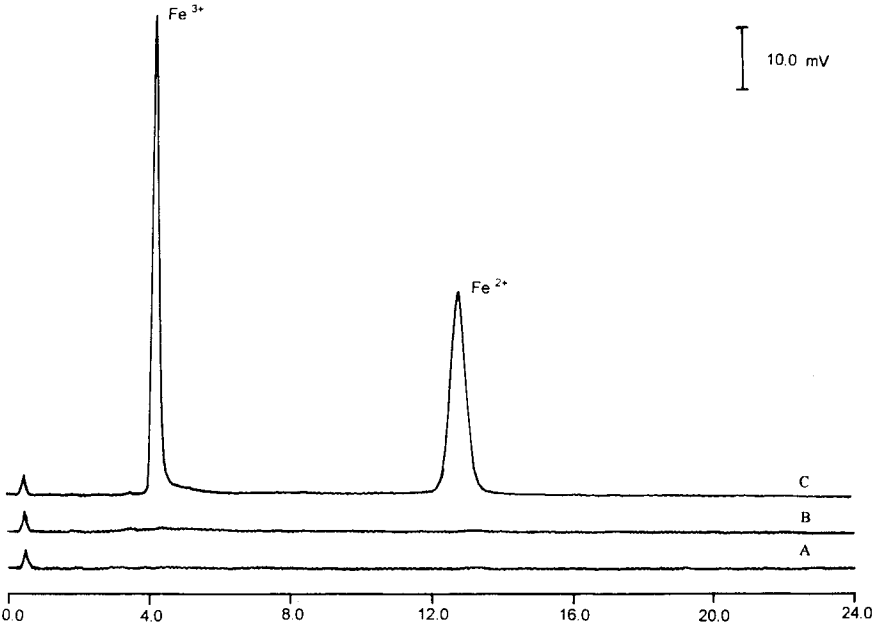

Figure 6. Study of possible interferences from Ca^{2+}, Mg^{2+} and Al^{3+}. Chromatograms of (A) a DI water (pH 2.0) blank; (B) a solution (pH 2.0) containing Ca^{2+} (5.0 mM), Mg^{2+} (2.1 mM) and Al^{3+} (2.6 mM); (C) ferric and ferrous ions (120 μM) with Ca^{2+} (5.0 mM), Mg^{2+} (2.1 mM) and Al^{3+} (2.6 mM) (pH 2.0).

Interference from Ca^{2+}, Mg^{2+} and Al^{3+}

Inorganic ions, such as Ca^{2+}, Mg^{2+} and Al^{3+}, are commonly found in soil extracts. The possibility of interference from these ions was studied. As shown in Figure 6, no peak with meaningful response was found in the chromatogram (B) of a solution containing Ca^{2+} (5.0 mM), Mg^{2+} (2.1 mM) and Al^{3+} (2.6 mM) in comparison with a DI water (pH 2.0) blank (A). The concentrations used were at the high end of those found in the soil extracts for the respective ions.

Figure 6C also shows the chromatogram of 120 μM ferric and ferrous ions spiked into Ca^{2+} (5.0 mM), Mg^{2+} (2.1 mM) and Al^{3+} (2.6 mM). The peak calculation in Figure 6C indicates that the concentrations of ferric and ferrous ions were 123 μM and 127 μM, within experimental error. From this we infer that no interference from Ca^{2+}, Mg^{2+} and Al^{3+} has been demonstrated.

DISCLAIMER

Although the research described in this article has been funded wholly or in part by the U.S. Environmental Protection Agency through Contract #68-C3-0322 to ManTech Environmental Research Service Corporation, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

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