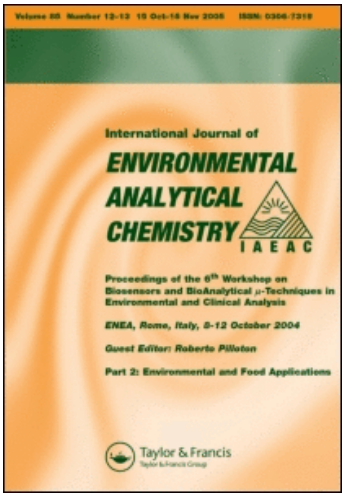

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THE INFLUENCE OF SAMPLE ACIDIFICATION ON THE SPECIATION OF IRON(II) AND IRON(III)

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The influence of sample acidification on the speciation of iron in aqueous solutions has been investigated. When hydrochloric acid is used, iron(II) is transformed into several moieties, believed to be chloro-complexes, whose chromatographic properties are quite different from those of the parent iron(II) species. This process is favored by high (>0.5 M) HCl concentrations.

The determination of iron in acidified samples can be complicated by this transformation, especially if the chromatographic process used cannot separate all the iron species formed. This study points to the necessity to carefully characterize and specify the prevailing sample conditions when iron speciation is done. The strong influence exerted by acidification would suggest that the data obtained be classified as 'conditional', specifying the acid concentration at which measurements were done.

KEY WORDS: Element speciation, ion chromatography, element selective detector, element transformation.

INTRODUCTION

Speciation is a chemical analysis procedure involving the identification and quantification of the various moieties of a chemical entity in a sample. If the chemical entity is an element, the procedure entails the determination of all the different forms of that element present. In this regard, an ideal speciation method is one which can provide analytical information on all the moieties present unambiguously and directly.

Sample processing and the analytical measurement procedure employed are perhaps the most influential factors on the type of speciation data obtained. In sample processing, acidification, filtration, heating, and extraction are common practices. For environmental samples, acidification is necessary for sample preservation and digestion. Unfortunately, this may cause changes in oxidation state and/or conversion of all forms into one form of the analyte. For example, the acidification of iron(III) samples with hydrochloric acid has been found to increase the Fe(II)/Fe(III) ratio as a result of Fe(III) undergoing reduction to Fe(II).[1,2] While such conversions may be desirable for total iron determination, they introduce errors in the information obtained for both Fe(II) and Fe(III).[3]

Numerous methods, combining wet-chemical and spectroscopic procedures, have been developed over the years for the determination of iron in geological, clinical,

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and environmental samples.[4–10] In some of these methods, analyte conversion is done in which the metal ions present are derivatized into complex compounds before or after separation on a chromatographic column.[11–16] Perhaps the oldest and most common method for iron determination is the 1,10-phenanthroline method.[17–19] This is a colorimetric method requiring first the conversion of iron(III) into iron(II) which is then reacted with 1,10-phenanthroline to form a colored complex compound. This is measured spectrophotometrically.

Other ligands have been employed in similar colorimetric methods.[17,18] The common feature of these methods, and their drawback with respect to their use in iron speciation, is the requirement to convert ferric into ferrous iron. Even though the relative concentrations of the individual species present in a sample can be determined ultimately, the procedure is tedious, and prone to errors because of the many steps involved.

The development of ion chromatography (IC) and the large variety of high efficiency ion exchange columns now available have facilitated considerably element speciation. The use of IC with element selective detectors, such as d.c. plasma and inductively coupled plasma atomic emission, allows a direct separation and quantation of free ions, neutral species, and complex ions of a given metal by using a single chromatographic injection.[20–24]

However, even with the availability of more efficient analytical methods, it is essential to know how sample preservation, sample processing, and the analytical protocol employed influence the chemistry of the analyte and the analytical data obtained.

This paper reports the results obtained for the speciation of iron using ion chromatography in combination with d.c. plasma atomic emission spectrometry (IC-DCPAES). The use of DCPAES as an element selective detector (ESD) for ion chromatographic speciation of various elements has previously been reported.[20,21] It has been shown that with this detector, the various species of a given element present in a sample are measured with equal efficiency after separation on the chromatographic column. This approach was employed in this work to study the chemistry of iron(II) and iron(III) in aqueous media, and to investigate how acidification influences their speciation. The study was limited to the investigation of the influence of hydrochloric acid on iron speciation. The maximum concentration of the acid used was 1.0 M.

EXPERIMENTAL SECTION

The objective of the research was to study the influence of sample acidification on the speciation of iron(II) and iron(III), using ion chromatography in combination with d.c. plasma atomic emission spectrometry. An ion chromatograph was used to separate species of Fe(II) and Fe(III) in solution, while the d.c. plasma was used as an element selective detector for the ion chromatograph. The chromatographic effluents were monitored by measuring the atomic emission of iron at 373.4 nm. In this way, chromatographic effluents containing Fe(II) and Fe(III) species were detected with equal efficiency.

Equipment

The chromatographic system used consisted of an ion chromatograph, Dionex Model 2010i (Dionex Corporation, Sunnyvale, California) equipped with cation separator columns Models HPIC-CS2, and HPIC-CS5; each used with corresponding guard columns. HPIC-CS5 is a mixed bed column and has much higher affinity than CS2.

The detector consisted of a three electrode d.c. plasma atomic emission spectrometer, Model Spectraspan IV, Applied Research Instruments. Interfacing of the chromatograph and the d.c. plasma system has been described elsewhere.[20]

Reagents and chemicals

Chemicals and other materials used included ACS certified ferrous ammonium sulfate and ferric nitrate, from Fisher Scientific Company, Fairlawn, New Jersey. Trilithium citrate was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Redistilled hydrochloric acid and double distilled nitric acid were obtained from GSF Chemicals, Columbus, Ohio. A Nanopure II water purification system, Sybron Corporation, Boston Massachusetts, was used in the preparation of deionized (18-M Ω) water. Pyridine-2,6-dicarboxylic acid was obtained from Fluka AG Chemical Company, Switzerland.

General procedure

Characterization of the solution chemistry and the behaviour of Fe(II) and Fe(III) relied on the use of standard solutions. Analytical solutions were prepared by dilution of appropriate volumes of 100 mg/l of Fe(II) (ferrous ammonium sulfate) and Fe(III) (ferric nitrate). In each case, standard solutions were prepared in 0.1 M HCl.

Samples were injected onto the chromatographic column with 1.0 ml-injection loop. The mobile phase flow rate was kept constant at 2.0 ml per minute when CS2 column was used and at 1.0 ml per minute when CS5 column was used. The mobile phase for CS2 consisted of 10 millimolar oxalic acid mixed with 7.5 millimolar trilithium citrate; and for CS5 the mobile phase consisted of a mixture of 6 millimolar pyridine-2,6-dicarboxylic acid (PDCA), 50 millimolar acetic acid and 50 millimolar sodium acetate.

RESULTS AND DISCUSSION

Both Fe(II) and Fe(III) are capable of undergoing a number of chemical reactions including hydrolysis, oxidation (Fe(II)), reduction (Fe(III)), and the formation of complex ions with organic and inorganic ligands. These processes can affect the sample and the analytical standards differently, depending on the respective concentrations and the solution conditions used.

It is important that the analytical protocol employed is able to prevent the occurrence of these processes during the analysis, or changes resulting from them are predictable, and therefore corrected for.

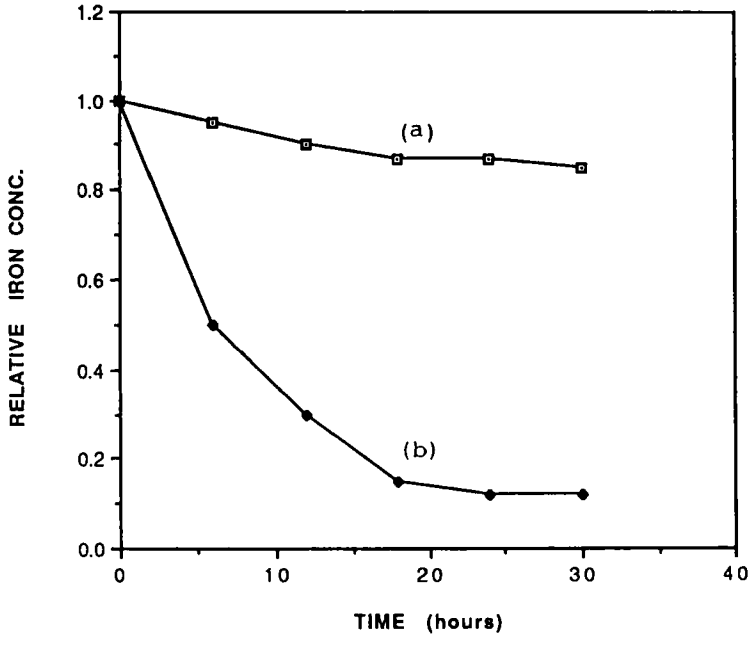

Figure 1 Hydrolysis of iron in deionized water; (a) = Fe(II) ; (b) = Fe(III).

A common practice in metal determination, especially in environmental samples, is sample acidification. This is done to preserve the sample, and to digest the particulate matter that may be present. In iron determination, acidification of the standards used is especially essential in order to prevent hydrolysis and the formation of hydrous oxides which occur readily in water. This is demonstrated in Figure 1 which depicts the disappearance of free iron ions in solution as a result of hydrolysis. A mixture of 1.0 mg/l each of Fe(II) and Fe(III) in deionized water was filtered with 0.2 μm filters after every several minutes. The filtrate was injected on the chromatographic column and the effluent was analyzed for Fe(II) and Fe(III) via d.c. plasma atomic emission measurement at 373.4 nm. Over a period of less than one day, more than 70% of the Fe(III) was removed from solution by hydrolysis. Only about 10% of Fe(II) was transformed.

Such loss of soluble Fe was not observed when the analyte solution was acidified with as low as 0.1 M HCl. Nitric acid is unsuitable because of its tendency to oxidize Fe(II) to Fe(III). While 0.1 M HCl appears to be enough to suppress hydrolysis and related iron transformation processes at low Fe concentration, it was desirable to know how higher acid concentrations would affect the two iron species.

In one experiment, ion chromatograms of 1.0 mg/l Fe(II) and Fe(III) were obtained, separately, in varying concentrations of HCl, starting with 0.1 M. As shown in Figure 2, in HCl medium, as acid concentration increases the Fe(II) which initially eluted at 2.4 min. is converted into a moiety which elutes at 1.3 min. In 1.0 M HCl, vitually all the Fe(II) is converted into the moiety eluting at 1.3 min.. This corresponds to

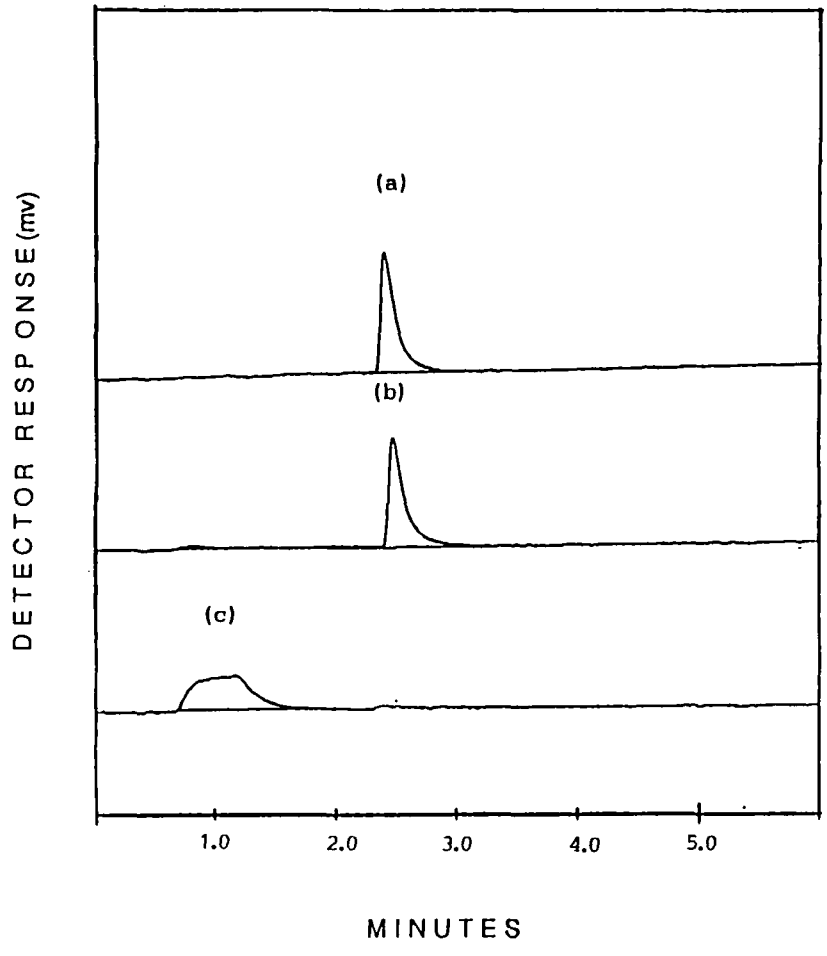

Figure 2 Ion Chromatograms of 1.0 mg/l Fe(II) in (a) 0.1 M HCl; (b) 0.5 M HCl; and (c) 1.0 M HCl, obtained with CS-2 Column; Mobile Phase = 10 mMolar Oxalic Acid + 7.5 mMolar Trilithium Citrate.

the conversion of Fe(II) into some Fe(II) moiety which either interacts very weakly with the cationic exchange resin or is unretained; suggesting that it could be anionic or neutral in nature. The Fe(II) moiety formed is believed to be a chlorocomplex, as has been reported in the literature by others.[3,23,24] As will be demonstrated below, the transformation of Fe(II) is dependent upon the iron(II)/HCl molar ratio. In all cases however, the Fe(II) mass balance can be verified by using the DCPAES detector.

Whereas Fe(III) appears to undergo some transformation in HCl medium, by slight reduction to Fe(II), it was not as pronounced as in the case of Fe(II). Less than 10% of 1.0 mg/l Fe(III) was reduced to Fe(II) in the presence of 1.0 M HCl. However, the speciation of a mixture of Fe(II) and Fe(III) in 1.0 M HCl would present a serious practical problem as the transformed Fe(II) elutes near Fe(III), resulting in seriously overlapping peaks as shown in Figure 3.

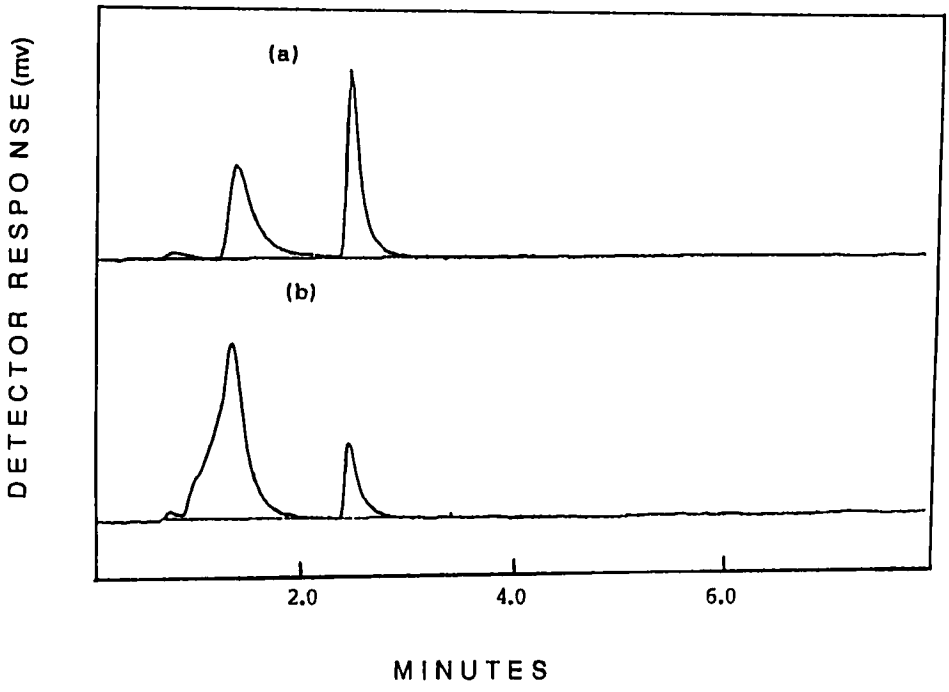

Figure 3 Ion Chromatograms of 1.0 mg/l Fe(II)/1.0 mg/l Fe(III) in (a) 0.1 M HCl; and (b) 1.0 M HCl. Chromatographic conditions were similar to those of Figure 2.

Figure 4 shows the chromatograms obtained when varying concentrations of Fe(II) were acidified with 1.0 M HCl. With increasing Fe(II)/HCl molar ratio, the fraction converted decreases as shown in Table 1. This suggests that when sample acidification is done, a mixture of different Fe(II) species can be produced depending on the Fe(II)/HCl molar ratio. This can further complicate the analysis, leading to erroneous results, especially if Fe speciation is the objective of the analysis.

One requirement of element speciation is that all the moieties containing the targeted element are measured with equal efficiency, requiring only one calibration curve. An element selective detector, such as DCPAES, fulfills this requirement as previously demonstrated.[20,21,25] However, where the analyte transformation occurs as solution conditions change, different calibration curves may be required, depending on the prevailing conditions. From the Fe(II) and Fe(III) chromatograms discussed above, the analytical curves prepared for Fe(II) and Fe(III) in 1.0 M HCl based on the peaks eluting at 2.4 min. and 1.3 min., respectively, are depicted in Figure 5. For comparison purposes, the curves obtained when the two species were in 0.1 M HCl are also shown.

These curves indicate that measurement of Fe(II) would be done with a considerably reduced sensitivity while the sensitivity for the Fe(III) species would be seriously inflated in light of the overlapping peaks of the Fe(III) originally present in the sample and the chlorocomplex formed from the reaction of Fe(II) with HCl.

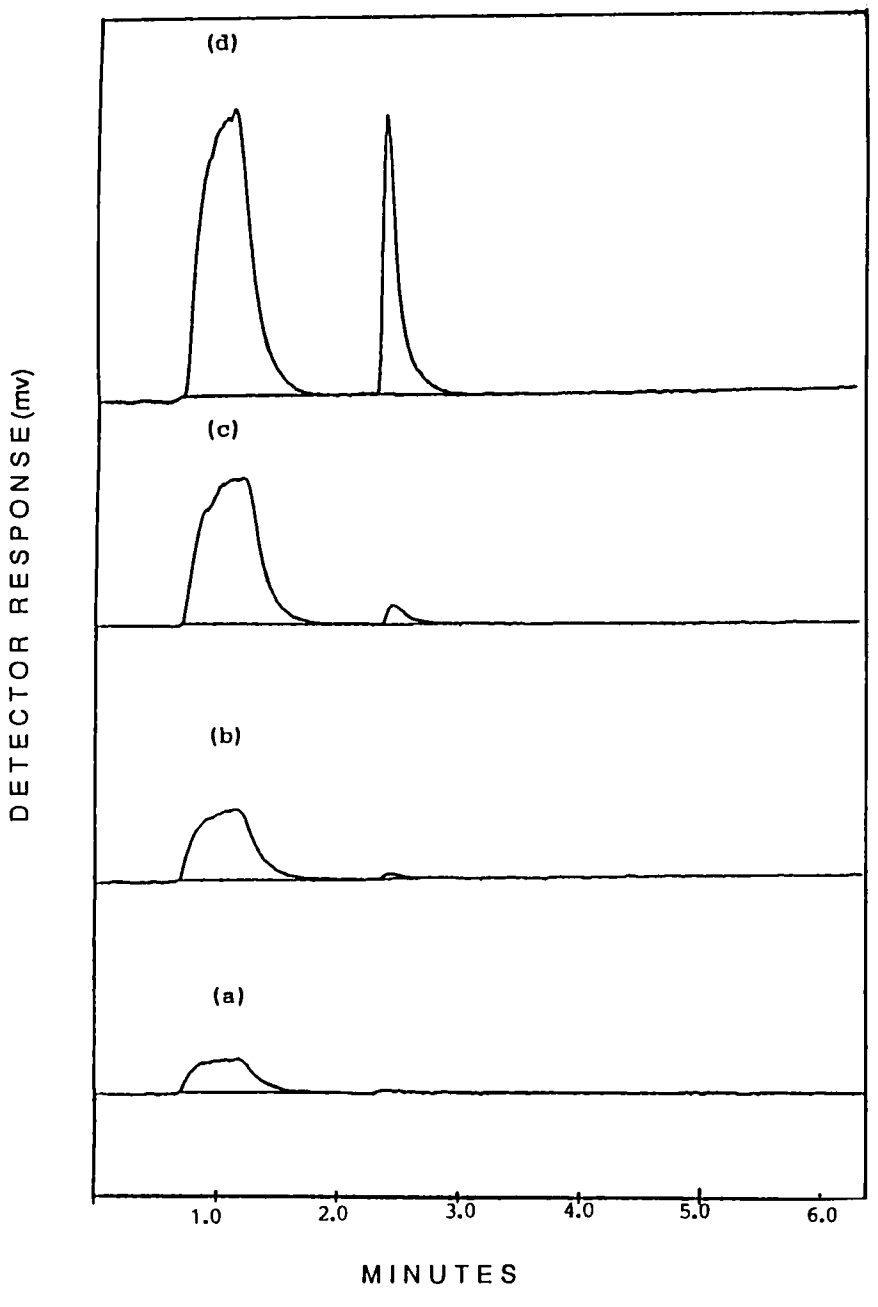

Figure 4 Ion Chromatograms of varying concentrations of Fe(II) in 1.0 M HCl: (a) 1.0 mg/l Fe(II); (b) 2.0 mg/l Fe(II); (c) 5.0 mg/l Fe(II); (d) 10.0 mg/l Fe(II). Chromatographic Conditions were similar to those of Figure 2.

Table 1 Influence of HCl concentration on the fraction of Fe(II) transformed

Fe(II) HCl molar ratio	*Fraction of Fe(II) transformed (%)*
1.78×10^{-5}	100.0
3.56×10^{-5}	97.6
8.90×10^{-5}	95.5
1.78×10^{-4}	76.4

Thus, whereas in 0.1 M HCl the peak areas for both Fe(II) and Fe(III) are fairly linear with concentration, such is not the case when the analytes are in 1.0 M HCl, as depicted in Figure 5.

In light of the observations presented above, the speciation of iron, particularly the determination of Fe(II) and Fe(III) in HCl medium can be done in three possible ways. In the first approach, the determinations can be done by putting into

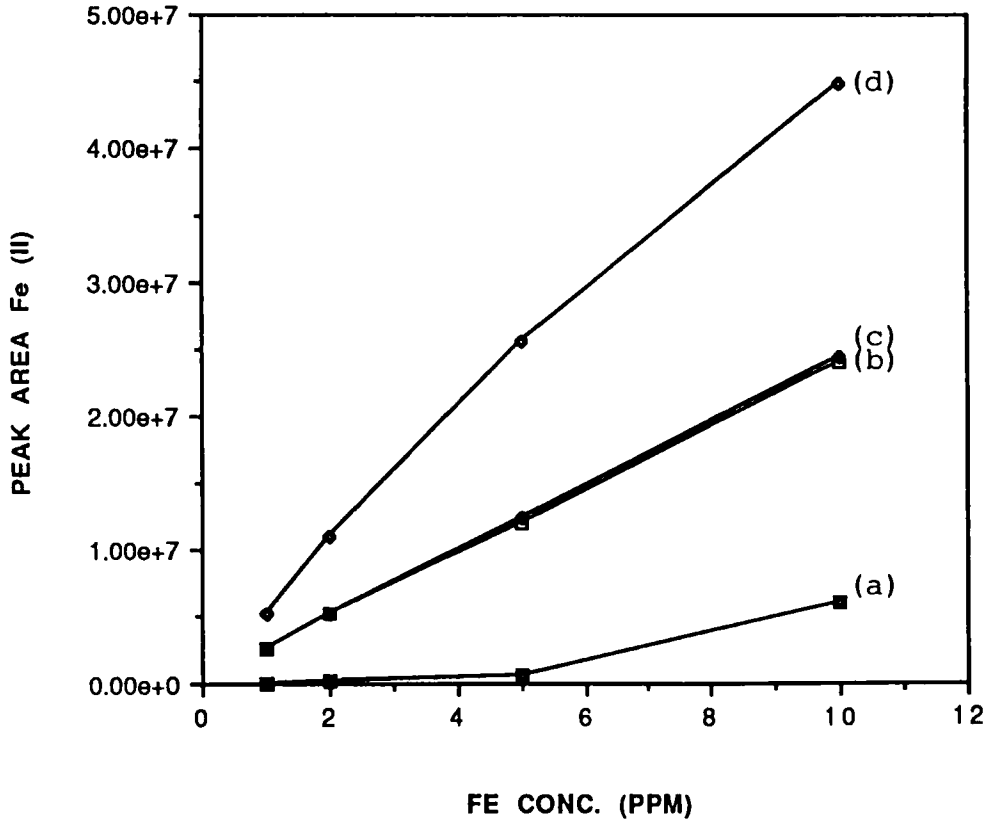

Figure 5 Analytical Curves for Fe(II) and Fe(III) in HCl: Fe(II) in 1.0 M HCl, peak at 2.4 min. (a); Fe(II) in 0.1 M HCl, peak at 2.4 min. (b); Fe(III) in 0.1 M HCl, peak at 1.3 min. (c); Fe(II) + Fe(III) in 1.0 M HCl, peak at 1.3 min. (d). Chromatographic conditions were similar to those of Figure 2.

consideration the fraction of iron(II) converted into the chlorocomplex at a fixed HCl concentration. The Fe(II) concentration measured should then be divided by this fraction to give the concentration originally present. The Fe(III) concentration determined would then have to be corrected accordingly since part of it would be due to the Fe(II) chlorocomplex. Clearly, measurements done via this approach would have a lot of uncertainties especially since the mechanism by which the chlorocomplex is formed is not very well known.

A second approach by which the effects of sample acidification can be accounted for is by doing the analysis such that the results obtained are classified and understood to be 'conditional'. That is, if a decision is made to digest the sample with 0.1 M HCl,

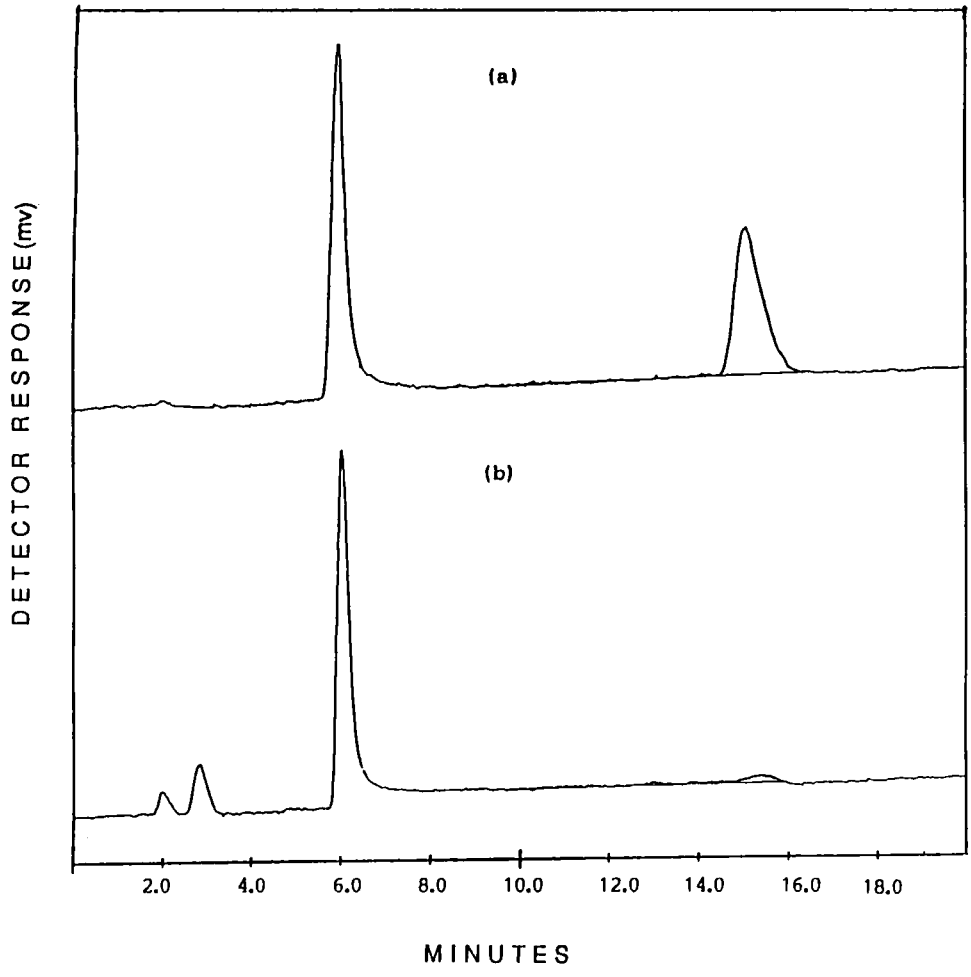

Figure 6 Ion Chromatograms of 1.0 mg/l Fe(II)/1.0 mg/l Fe(III) in (a) 0.1 M HCl; and (b) 1.0 M HCl. Column: CS-5, mobile phase: 6.0 mM pyridine-2,6-dicarboxylic acid + 50 mM acetic acid + 50 mM sodium acetate.

then the data obtained would be labelled as 'specification of Fe in 0.1 M HCl', and likewise for the case where digestion is done with 1.0 M HCl. The data obtained in 0.1 M HCl could be broadly defined as representing soluble Fe(II). The data obtained with 1.0 M HCl would be representing more of total iron since a large fraction of the ferrous species would be co-eluting with Fe(III) and apparently with other forms of iron.

A third approach is by employing a chromatographic process which can separate the Fe(III) from the Fe(II) chlorocomplex. In this way, even if the Fe(II) is converted, the new moiety can be quantitated and added to the Fe(II) peak left untransformed.

This approach was employed by using a 'slower' column than the one employed above. Figure 6(a) shows the chromatograms obtained for a mixture of 1.0 mg/l Fe(II) and 1.0 mg/l Fe(III) in 0.1 M HCl. The small peak at 2.0 min. is believed to represent a small amount of Fe(II) converted into the chlorocomplex in 0.1 M HCl. The major peaks at 6.0 and 15.0 minutes are due to Fe(III), and Fe(II), respectively. As can be seen, the two peaks are well resolved and virtually indentical in peak area.

Figure 6(b) shows the chromatographic peaks obtained for a similar mixture of Fe(II) and Fe(III) in 1.0 M HCl. Two points should be made here: first, the Fe(III) peak at 6.0 min. is completely separated from the chlorocomplexes eluting at 2.0 and 3.0 min.; second, the sum of the areas of the peaks at 2.0, 3.0 and 15.0 min. should be equal to the area of the peak at 6.0 min. This does not appear to be the case from the chromatograms obtained. The discrepancy may be attributed to the Fe(II) species in 1.0 M HCl forming several different moieties, most of which are in such small amounts as to give detectable analytical signal.

Nevertheless, the sum of the residual peaks at 2.0, 3.0, and 15.0 min. appear to be linear with Fe(II) concentration as depicted in Table 2. Therefore, the analytical results obtained in this way should be classified as being 'conditional' to the 1.0 M HCl used.

Figure 7 shows the chromatography obtained for a soil sample, (a) when the sample was acidified with 0.1 M HCl and (b) when it was acidified with 1.0 M HCl. It should be noted that since very little Fe(II) transformation occurs in 0.1 M HCl as demonstrated above, the peak appearing at 15.0 min. in Figure 7(a) should be fairly representative of the fraction of Fe(II) expected in soil samples which have been subjected to atmospheric exposure.

Table 2 Analytical curve data for Fe(II) based on the sums of peak areas of Fe(II) moieties in 1.0 M HCl

Fe(II) conc.	*Peak areas*		*Total peak area*
	at Tr = 3.0 min	*at Tr = 15.0 min*	
0.10	1.05×10^5	(no peak)	1.05×10^5
0.50	4.70×10^5	0.23×10^5	4.93×10^5
1.0	6.17×10^5	2.35×10^5	8.52×10^5
2.0	11.54×10^5	8.01×10^5	19.55×10^5
10.0	26.70×10^5	46.68×10^5	74.38×10^5

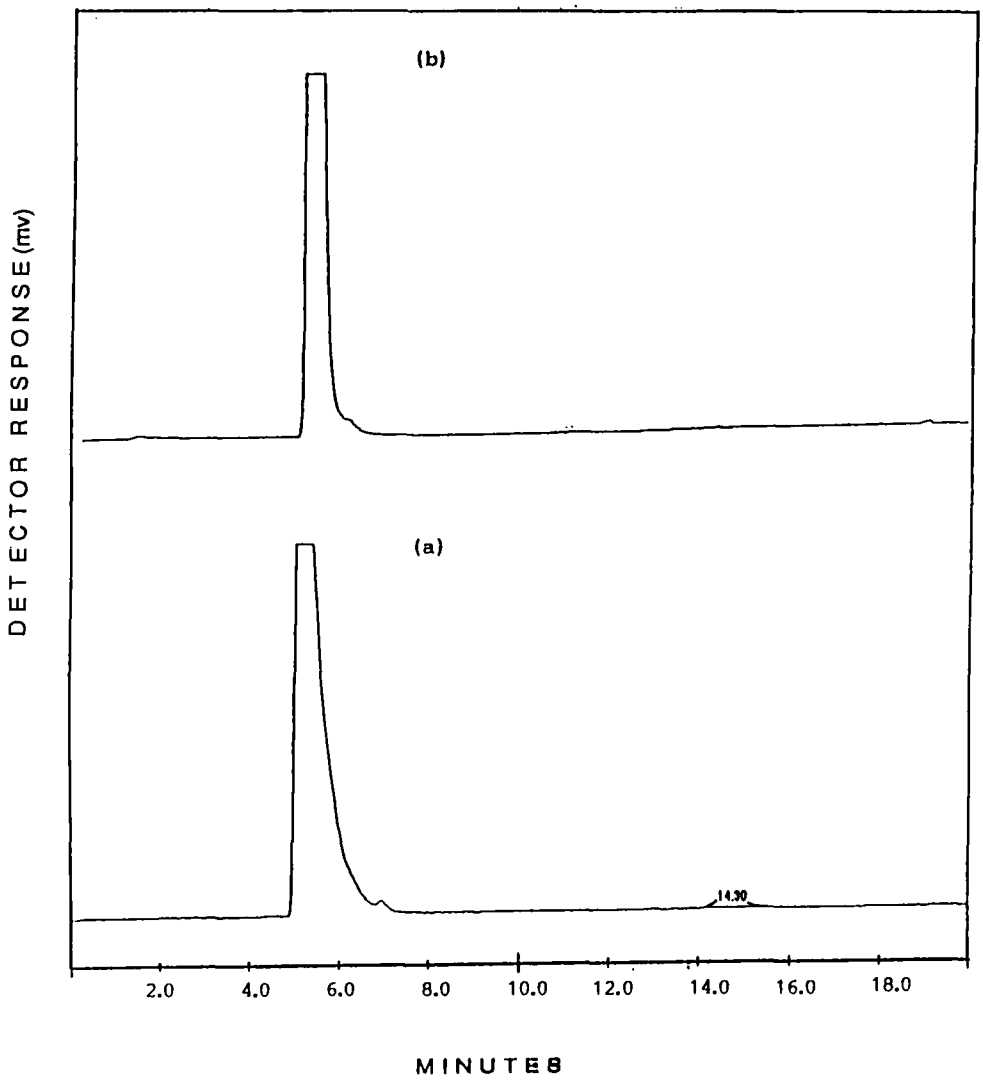

Figure 7 Ion Chromatographic Determination of Fe(II) and Fe(III) in Soil sample; (a) sample was digested with 0.1 M HCl; (b) sample was digested with 1.0 M HCl. Chromatographic conditions were similar to those of Figure 6.

CONCLUSION

The data presented in this paper show that sample acidification can have a profound effect on the speciation of iron. When HCl is used, several Fe(II) species may be present, depending on the acid concentration. Owing to this acid dependence, the analytical data obtained should be regarded as 'conditional', specifying the acid concentration at which the analysis is done.

Most the iron species formed in HCl can be separated on an ion chromatographic column. In this way, even with analyte transformation, quantitative data can easily be done by summing the peak areas corresponding to the moieties formed at the specified acid concentrations.

Acknowledgement

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References

1. C. O. Moses, A. T. Herlihy, J. S. Herman and A. L. Mills. *Talanta*, **35**, 15–22 (1988).
2. J. W. McMahon, *Limnol Oceanog.*, **12**, 437–442 (1967).
3. W. Davidson and E. Rigg, *Analyst.*, **101**, 634–638 (1976).
4. G. R. Carnrick, W. Slavin and D. C. Manning, *Anal. Chem.*, **53**, 1866–1872 (1981).
5. E. Tipping, N. B. Hetherington, J. Hilton, D. W. Thompson, E. Bowles and J. Hamilton Taylor, *Anal. Chem.*, **57**, 1944–1946 (1985).
6. R. E. Sturgeon, S. S. Berman, A. Desaulmiers and D. S. Russell, *Anal. Chem.*, **51**, 2364–2369 (1979).
7. D. A. Segar and J. G. Gonazalez, *Anal. Chim. Acta.*, **58**, 7–14 (1972).
8. G. D. Klinkhammer, *Anal. Chem.*, **52**, 117–120 (1980).
9. J. M. McArthur, *Anal. Chim. Acta.*, **93**, 77–83 (1977).
10. D. J. Hydes, *Anal. Chem.*, **52**, 959–963 (1980).
11. H. M. Kingston, I. L. Barnes, T. J. Brady, T. C. Rains and M. A. Champ, *Anal. Chem.*, **50**, 2064–2070 (1978).
12. K. Ohta, B. W. Smith and J. D. Wineforder, *Anal. Chem.*, **54**, 320–321 (1982).
13. J. R. Jezorek, H. Fraiser, *Anal. Chem.*, **51**, 373–376 (1979).
14. S. Elchuk and R. M. Cassidy, *Anal. Chem.*, **51**, 1434–1438 (1979).
15. J. S. Fritz and J. N. Story, *Anal. Chem.*, **46**, 825–829 (1974).
16. B. P. Dubins, M. R. Strala and G. E. Pacey, *Talanta*, **30**, 841–844 (1983).
17. A. A. Schilt, *Analytical Applications of 1.10-phenanthroline and Related Compounds.* (Pergamon Press: New York, 1969).
18. A. G. Hill, E. Bishop, L. E. Coles, E. J. McLaughlan, D. W. Meddle. J. Pater, C. A. Watson, C. Whalley and P. M. Shallis, *Analyst.*, **103**, 391–396 (1978).
19. Ibid pp. 521–524.
20. I. T. Urasa and F. Ferede, *Anal. Chem.*, **59**, 1563–1568 (1987).
21. I. T. Urases and S. H. Nam, *J. Chromatogr. Sc.*, **27**, 30–37 (1989).
22. G. J. Savenich and J. S. Fritz, *J. Chromatogr.*, **347**, 147–154 (1985).
23. C. L. Stanley and R. F. Kruch, *J. Chem. Phys.*, **34**, 1450–1451 (1961).
24. A. Glasner and P. Avinur, *Talanta*, **11**, 761–773 (1964).