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Ion chromatography of organic-rich natural waters from peatlands V. Fe^{2+} and Fe^{3+}

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Abstract

Pore waters from two peat bogs in the Jura mountains, Switzerland, were analyzed for Fe^{2+} and Fe^{3+} using ion chromatography (IC). In order to prevent oxidation, the samples were collected under N_2 using in situ diffusion-equilibrium pore water samplers (peepers). The metals were separated on a Dionex CS-5 analytical column and detected by visible absorbance at 520 nm after post-column mixing of the pyridine–2,6-dicarboxylic acid eluent with 4-(2-pyridylazo)resorcinol. The concentrations of total Fe determined by IC ranged from 0.1 to 2 μg/g and agreed well with total Fe measured in the same samples with inductively coupled plasma spectroscopy. However, a problem is caused by humic substances present in the samples because they gradually contaminate the column. Contaminated columns show reduced precision, peak tailings and reduction of Fe^{3+} to Fe^{2+} on the column. The relatively high Fe^{3+} concentrations measured in the pore waters are not an oxidation artefact, but instead reflect the stabilization of the trivalent oxidation state by complexation with humic substances.

1. Introduction

The usual approach to determine Fe^{2+} and Fe^{3+} in geological materials is to use a colorimetric method (e.g. Refs. [1] and [2]). Organic-rich natural waters from peatlands, however, may be intensely colored due to high concentrations of dissolved humic materials. For example, peat bog pore waters in the Jura mountains of Switzerland contain dissolved organic carbon (DOC) concentrations on the order of 50–120 mg/l [3]. Their color might interfere with a colorimetric determination of Fe^{2+}. Moreover, a few preliminary tests with bog waters using a colorimetric method showed unstable (drifting) readings upon the addition of the reducing agent.

In contrast to colorimetric methods which necessitate sample preparation and separate determination of Fe^{2+} and total Fe, ion chromatography (IC) offers the possibility to measure both Fe^{2+} and Fe^{3+} simultaneously with a single injection [4]. This approach has recently been used to successfully determine Fe^{2+} and Fe^{3+} in acid digests of rocks [5].

The principle objective of the study presented here is to evaluate the IC method for direct measurement of Fe^{2+} and Fe^{3+} in organic-rich, anaerobic waters from peatlands. The sampling procedure employed peepers and this approach

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has been shown to involve minimal sample alteration [6].

2. Experimental

2.1. Location of sites

The pore waters studied were collected from two continental bogs in the Franches-Montagnes region of the Jura Mountains, Switzerland. The elevation is approximately 1000 m above sea level. One of the bogs, Tourbière de Genevez (TGe), consists of 1.5 m of peat, while at the other site, Étang de la Gruyère (EGr), peat accumulation is more than 6 m. More detailed descriptions of the sites are given elsewhere [3].

2.2. Sampling of peat pore waters

The pore waters analyzed in this study were obtained using peepers [7]. Peepers were originally designed for studying pore waters in lake or sea sediments [8]. They consist of a single housing made up of individual 30-ml Plexiglass chambers that are filled with deionized, deaerated water and covered with a 0.2-μm membrane filter. The chambers were inserted into the bog at different depths and allowed to equilibrate with the pore waters for about five weeks. To prevent oxidation during sample collection and handling, the peepers were pulled directly from the bog into N_2-filled glove bags. Individual chambers were then sampled through the glove bag using syringes. Syringes were assembled with plastic tips instead of stainless-steel needles to prevent sample contamination. The samples were brought to the laboratory in closed syringes which were kept in a cold storage bag and then analyzed immediately. Because a 0.2-μm filter was built into the sampler, there was no need to vacuum-filter the pore waters prior to analysis.

2.3. Ion chromatography

A CS-5 column with a CG-5 guard column was used for most measurements. In addition, a glass-lined column (from SGE, Weiterstadt, Germany) and a PEEK column filled with Nucleosil 5 SA and 10 SA resins (Macherey Nagel, Germany) were also tested.

The eluent used for the CS-5 column was 6 m*M* pyridine–2,6-dicarboxylic acid (PDCA)–90 m*M* acetic acid–40 m*M* NaOH. The eluent was adjusted to pH 4.8 with NH_4OH. Detection was accomplished by mixing the eluent with a 4-(2-pyridylazo)resorcinol (PAR) post-column reagent containing 0.5 m*M* PAR, 1.0 *M* 2-dimethylaminoethanol, 0.5 *M* NH_4OH and 0.3 *M* sodium bicarbonate. The flow-rate of the eluent was 1 ml/min, while the PAR reagent was added at 0.5 ml/min. In contrast to a report by Yan et al. [9] no increase in sensitivity was observed on heating the reaction coil.

The eluent used with the Nucleosil columns was 115 m*M* tartaric acid adjusted to pH 4 with NH_4OH (adapted from Ref. [10] with higher pH to reduce the retention time of Fe^{2+}). The size of the injection loop used was 100 μl.

2.4. Calibration

Iron(III) standards were prepared by diluting a 1000 mg/l Merck standard in dilute (pH 3) HCl solution (prepared with 1 *M* HCl, Merck p.a.). To prevent photoreduction of Fe^{3+} the standards were kept in the dark. Iron(II) standards were prepared by dissolving 702 mg ammonium–iron(II) sulfate in 1 l of deionized water acidified with HCl to pH 3. Ascorbic acid (1 mg/l) was added to reduce all the iron. When Fe^{3+} standards were analyzed after Fe^{2+} standards (containing ascorbic acid), considerable reduction of Fe^{3+} was observed. For this reason the instrument was calibrated for Fe^{2+} after the pore water samples had been measured.

3. Results

3.1. Detection limits, precision and accuracy

Using CS-5/CG-5 columns detection limits initially were 5 ng/g for Fe^{3+} and 10 ng/g for Fe^{2+}. However, due to the presence of humic acids in the samples the column performance

declined with time and did not meet normal IC standards with respect to precision and detection limit.

The following replicate measurements illustrate the precision of the method: The relative standard deviation (R.S.D.) of a 50 ng/g Fe^{3+} standard was 7.7% ($n = 11$). A mixed Fe(II)–Fe(III) standard ($n = 21$) measured alternately with pore water samples gave an R.S.D. of 6.8% for the total iron concentration (200 ng/g total Fe). A mixed standard with 400 ng/g total Fe measured with no samples injected between the standards gave an R.S.D. of 2.5% ($n = 9$). The precision for the samples is slightly poorer because the peaks seen in the sample chromatograms are generally broader.

Accuracy can be estimated by comparing the IC and inductively coupled plasma (ICP) spectroscopy data for these waters. The sum of Fe(II) and Fe(III) measured with the IC are comparable to the concentrations of total dissolved iron measured by ICP (Table 1).

Calibration curves were linear for both Fe^{3+} (50 ng/g to 1 μg/g) and Fe^{2+} (100 ng/g to 2 μg/g). Calibration curves for the low ng/g range are shown in Fig. 1.

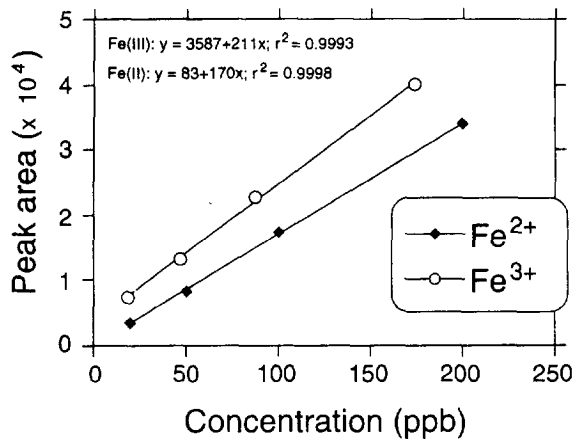

Fig. 1. Calibration curves for Fe(II) and Fe(III) obtained on a CS-5 column contaminated with humic materials. The corresponding Fe(III) peaks were shaped approximately as shown in Fig. 3.

3.2. Effects of organics-removal cartridges

Iron, like other cations, may be complexed by humic substances present in the pore water samples. When the humic substances are removed by using an organics-removal cartridge (Dionex OnGuard-P) this portion of iron may be lost. Ranging from 8 to 74% of total dissolved Fe, on average about 40% of the Fe was lost in this way. Both Fe^{2+} and Fe^{3+} were lost (see Table 1). The difference in the iron concentrations between measurements where humic acids were removed with an OnGuard-P cartridge and measurements without a cartridge might be taken as an estimate for the amount of iron complexed by humic acids. However, the results were variable and the distribution of complexed species (as determined in this way) in

Table 1
Iron(II), iron(III) and total iron concentrations of pore water samples from TGe as determined by IC compared to total dissolved iron measured by ICP

Depth (cm)	Fe^{2+} (IC) (ng/g)	Fe^{3+} (IC) (ng/g)	ΣFe (IC) (ng/g)	Fe total (ICP) (ng/g)	Fe^{2+} retained (%)	Fe^{3+} retained (%)
18	327	112	439	511	35.8	58.2
25	504	139	643	728	38.6	51.4
40	639	214	853	968	44.9	36.1
55	989	353	1342	1460	48.5	34.7
65	1400	509	1909	2005	22.4	34.0

The correlation between IC and ICP is excellent ($r^2 = 0.999$). Apparently, the sum of Fe^{2+} and Fe^{3+} (measured by IC) is less than total dissolved Fe (measured by ICP) by 5 to 14%. A part of this difference may be due to extremely stable organic complexes of Fe which were not measured by IC. The amount of iron retained on the organics-removal cartridges is variable and gives only a rough estimate for the degree of iron complexation by humic material.

a profile was often irregular. This suggests that the amount of iron lost when passing the sample by hand through an OnGuard-P cartridge is variable and gives only a very rough idea of the degree of complexation with humic acids.

In order to liberate iron from the complexes and therefore avoid its retention on the cartridge a few attempts were made to acidify the samples with HCl to pH 1. Those measurements also showed irregular results: sometimes more iron was measured in the treated than in the untreated samples, while at other times considerably less iron was measured in the treated sample. Slow kinetics of complexation reactions of iron and humic substances might be one reason for these findings. Because more humic substances are retained on the cartridges in the acidified samples more iron is also removed when replacement of complexed metals by protons is slow. In the end, it was decided not to use the cartridges despite the possible damage of humic acids to the columns.

3.3. Effects of humic substances present in the samples

On-column redox reactions are a general problem with IC determination of Fe^{3+} and Fe^{2+}. Some authors mention problems with the oxidation of Fe^{2+} on a CS-5 separator column even after the column had been rinsed with 0.1 *M* Na_2SO_3 [11], while other studies with the same column do not report such problems [5,12].

In the present study, a major problem was the reduction of Fe^{3+} due to the accumulation of humic substances on the column. After a number of injections the column was permanently in a slightly 'reducing state'. While iron(III) standards measured on an uncontaminated column yielded sharp Fe^{3+} peaks and showed no Fe^{2+} peak, a poisoned column showed tailing of the Fe^{3+} peak and a discrete Fe^{2+} peak. The Fe^{2+} peak reflects reduction of Fe(III) at the beginning of the column (guard column). Tailings show deterioration of the retention behavior for Fe(III). The decline of the iron(III) peak with time is illustrated in Fig. 2. Rinsing the columns with 0.1 *M* NaOH and exchanging the guard

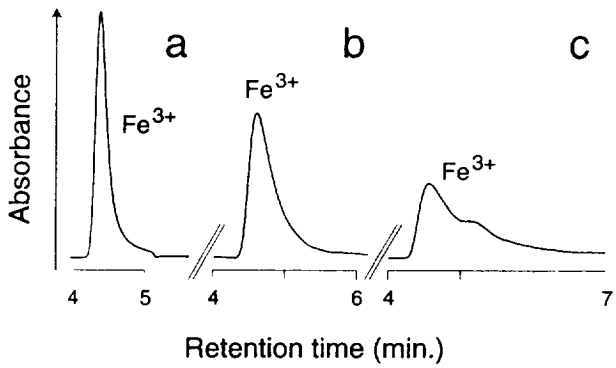

Fig. 2. Effect on the Fe(III) peak of contamination of a CS-5 column by humic materials. While an uncontaminated column gives sharp peaks (a), with increasing contamination peak tailing occurs (b), and finally the peaks become irregular (c). Moreover, some of the Fe^{3+} is reduced to Fe^{3+} on a contaminated column.

column were necessary to regenerate column performance. An example chromatogram of bog pore water obtained with an already contaminated column is shown in Fig. 3.

3.4. Monitoring of possible redox reaction on the column

The extent to which the Fe^{2+}/Fe^{3+} ratio was possibly changed on the column was determined by analyzing a mixed Fe^{2+}–Fe^{3+} standard subsequent to each sample. The appropriate Fe^{2+}–

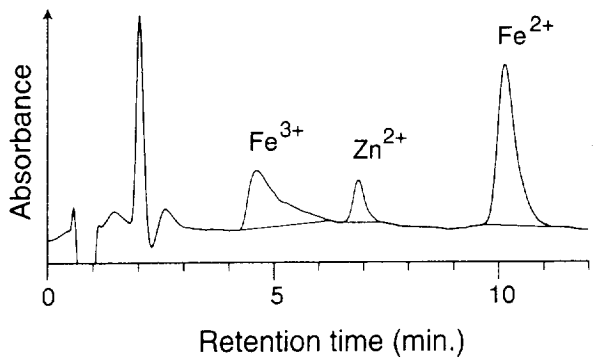

Fig. 3. Chromatogram of a bog pore water sample. Column: CS-5; eluent 6 m*M* PDCA. The column is considerably contaminated with humic material present in the samples as is seen from the tailing of the Fe^{3+} peak. In addition to iron it was possible to measure Zn^{2+}.

Fe^{3+} ratio of the standard had been measured with an uncontaminated column. Measurements on an uncontaminated column also showed that the Fe^{2+}/Fe^{3+} ratio of the mixed iron standard did not change in the course of a day (R.S.D. = 4%, $n = 9$).

Compared to the true Fe^{3+} concentration of the mixed standard, almost all measurements made subsequent to pore water samples showed less Fe^{3+} but more Fe^{2+}. Hence, during the measurements of the samples, the column was in a reducing state. The concentrations of total Fe in the mixed standards, however, was constant (see above). Maximum reduction observed in the control standards ranged from 15% to 20% of Fe^{3+} reduced. Normally it was less, often not more than 5%. However, no significant correlation was found between the extent of reduction in the control standards and the Fe^{2+} content, the total Fe concentration, or the Fe^{2+}/Fe^{3+} ratio of the preceding pore water sample. Due to this non-correlation and due to the conditioning effect of the intermittent mixed standards the samples are not likely to have affected each other.

Analysis of intermittent mixed standards (with Fe^{3+} and Fe^{2+} concentrations similar to the pore water samples) suggests that some of the trivalent iron in the pore waters may have been reduced to Fe^{2+}. The measured Fe^{3+} concentrations in these waters, therefore, represent minimum values. The true Fe^{3+} concentrations of these waters may be 5–15% higher. Samples were probably less affected by the column contaminants (humic acids) than the control standards because the latter conditioned the columns and because the samples had already been in contact with those contaminants previously. Without question, the Fe^{3+} measured in the bog pore waters is not an on-column oxidation artefact.

3.5. Performance of silica-based columns

Silica-based resins (Nucleosil 10 SA) packed in a glass-lined column were successfully used for Fe^{2+} and Fe^{3+} determinations in rainwater [11]. On the other hand, on-column reduction of Fe^{3+} was reported using columns filled with a similar resin (Nucleosil 5 SA) [13].

A few tests were done using silica-based columns. With the methods specified above a PEEK column packed with Nucleosil 5 SA resin showed a sensitivity that was comparable to that of the CS-5 column and higher than that of a glass-lined column filled with Nucleosil 10 SA. Both columns showed a slight reduction of Fe^{3+} after the injection of a Fe^{2+} standard. The main problem, however, was a system peak underlying the Fe^{3+} peak when the pH of the sample was below 4. This made measurements of low Fe^{3+} concentrations impossible.

3.6. Iron content and speciation in peatland pore waters

The concentrations of Fe^{2+} and Fe^{3+} in pore waters from Tourbière de Genevez (TGe) and Étang de la Gruyère (EGr) are given in Table 1 and Fig. 4, respectively. Total dissolved Fe concentrations are up to ten times higher at TGe compared with EGr. This difference may be explained as follows. The amount of mineral matter in the peats is higher at TGe than at EGr, and increases progressively with depth [3]. As a consequence, the Fe concentrations in the peats

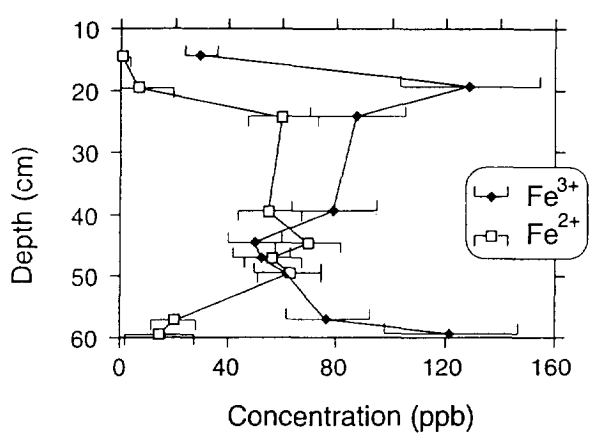

Fig. 4. Iron speciation in bog pore waters from Etang de la Gruyère (EGr). The estimated 95% confidence limits are indicated.

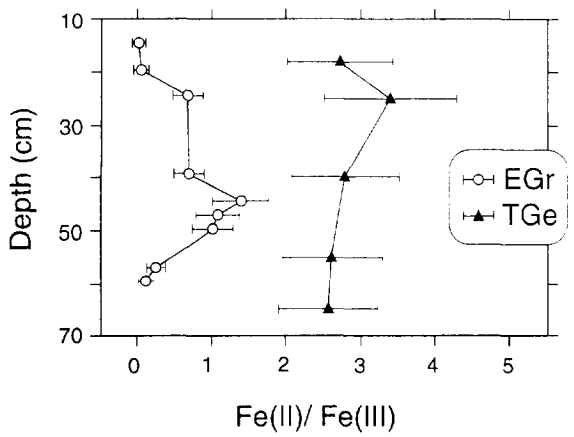

Fig. 5. Ratio of Fe^{2+}/Fe^{3+} measured in two peat bog profiles from the Jura Mountains, Switzerland. The 95% confidence limits are indicated.

at TGe are higher, and these too increase with depth.

A second difference between the two bogs is the Fe^{2+}/Fe^{3+} ratio which is higher at TGe than at EGr (Fig. 5). This may reflect a lower redox potential in the pore waters of TGe. This hypothesis is supported by the occurrence of sulfide at TGe, while at EGr no sulfide was detectable [14]. In both bogs, however, the Fe^{2+}/Fe^{3+} ratio is orders of magnitude lower than would be expected for pore waters which are anoxic and sulfidic. The high concentrations of DOC may have contributed to the relative abundance of Fe^{3+} in both bogs by forming stable Fe^{3+} complexes. For example, if the dissolved organic matter provides enough sites that stabilize Fe(III) relative to Fe(II), then a relatively low $Fe(II)_{total}/Fe(III)_{total}$ ratio may be in equilibrium with a high ratio of (free) Fe^{2+}/Fe^{3+} (see e.g. Ref. [15]).

4. Conclusions

IC can be used to measure Fe^{2+} and Fe^{3+} simultaneously in anaerobic water samples. Pore water samples which were filtered in situ using peepers installed in the bog required no pretreatment prior to injection. If the samples are maintained in an anoxic condition during sample collection and handling (as described in this paper), reliable measurements of Fe^{2+} and Fe^{3+} can be made with the following limitations. First, the abundance of humic acids in organic-rich natural waters —such as those from peatlands— leads to progressive contamination of the CS-5 separator column. This leads to broadening of the Fe^{3+} peak and diminished precision. Second, the humic materials adsorbed to the column also reduce part of the Fe^{3+} present in the samples to Fe^{2+}. Despite this, no more than 20% (and often much less) of the Fe^{3+} was reduced in any sample. The precision of the measurements is approximately ± 10% (R.S.D.) for both Fe^{2+} and Fe^{3+}.

In order to reduce the organic contamination problem the humic materials must be removed from the samples prior to analysis. One possible approach could be to incorporate dialysis membranes in the design of the peepers to allow in situ separation of free, dissolved inorganic anions and cations from large-molecular-weight humic acids. Once such a system had equilibrated, Fe^{2+} and Fe^{3+} could be measured in the dialyzed solutions by IC; this would provide the free metal ion concentrations while minimizing column contamination. Organically bound Fe^{2+} and Fe^{3+} could be measured (from undialyzed samples containing the humic fraction) by acidifying the samples to at least pH 1 and thus liberating metals from complexes. The humic material could then be adsorbed on a suitable resin.

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References

[1] S.F. Fritz and R.K. Popp, *Am. Mineral.*, 70 (1985) 961–968.
[2] P. Komadel and J.W. Stucki, *Clays Clay Miner.*, 36 (1988) 379–381.
[3] W. Shotyk and P. Steinmann, *Chem. Geol.*, 116 (1994) 137–146.
[4] J. Weiss, *Handbook of Ion Chromatography*, Dionex, Sunnyvale, CA, 1986.
[5] Y. Kanai, *Analyst*, 115 (1990) 809–812.
[6] P. Steinmann and W. Shotyk, *J. Chromatogr.*, 706 (1995) 281–286.
[7] P. Steinmann, *Ph.D. Thesis*, University of Bern, Bern, 1995.
[8] R.M. Hesslein, *Limnol. Oceanogr.*, 21 (1976) 912–914.
[9] D. Yan, J. Zhang and G. Schwendt, *Fresenius Z. Anal. Chem.*, 331 (1988) 601–606.
[10] H. Hofmann, P. Hoffman and K.H. Lieser, *Fresenius J. Anal. Chem.*, 340 (1991) 591–597.
[11] T. Sinner, P. Hoffmann and H.M. Ortner, *Spectrochim. Acta*, 48B (1993) 255–261.
[12] C.O. Moses, A.T. Herlihy, J.S. Herman and A.L. Mills, *Talanta*, 35 (1988) 15–22.
[13] A. Seubert and G. Wünsch, *Anal. Chim. Acta*, 256 (1992) 331–348.
[14] P. Steinmann and W. Shotyk, *J. Chromatogr.*, 706 (1995) 287–292.
[15] W. Stumm and B. Sulzberger, *Geochim. Cosmochim. Acta*, 56 (1992) 3233–3257.