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Ion chromatography of organic-rich natural waters from peatlands
IV. Dissolved free sulfide and acid-volatile sulfur

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Abstract

Organic-rich, acidic, anaerobic pore waters from two peat bogs in Switzerland were analyzed for sulfide using ion chromatography (IC) with electrochemical detection. With one Dionex CarboPac PA1-Guard as separator column and another one in front of the 100-μl injection loop, it was possible to separate sulfide and cyanide with detection limits as low as 1 ng/g sulfide. Pore water samples were obtained using in situ diffusion–equilibrium pore water samplers (peepers). Samples were collected under N_2 to prevent sample oxidation. Instead of preserving the dissolved sulfide with zinc acetate, sulfide was preserved by collecting the samples into 5-ml syringes containing 1 ml of concentrated eluent. In this way, the pH of the sample increased to 12 and no volatile H_2S was lost. Measured sulfide concentrations in the pore waters were all below 20 ng/g. Some samples were spiked in the field to contain 5 ng/g sulfide. This amount could be detected using IC, whereas unspiked aliquots of the same samples yielded no sulfide peak. Based on the measurements of total dissolved sulfur, sulfate and sulfide, almost all of the sulfur in the pore waters is organically bound. The IC method presented here is well suited for the measurement of acid-volatile sulfur (AVS), and was applied to AVS measurements of some pore water samples. Trapping the volatilized H_2S in eluent gave low detection limits and allowed rapid analyses without further treatment of the solution. The measured concentrations of AVS were not significantly different from the concentrations of free dissolved sulfide, suggesting that metal–sulfide complexes are relatively unimportant sulfur species in these waters.

1. Introduction

A variety of analytical methods are available for measuring sulfide in natural waters, including colorimetry, ion-selective electrode potentiometry, polarography, gas chromatography, atomic absorption spectroscopy, titrimetry and fluorimetry [1]. Unfortunately, all these methods are either subject to possible interferences and/or lack adequate sensitivity. To avoid the interference of halogens, cyanide, thiocyanate and thiosulfate, Rocklin and Johnson [2] used ion chromatography (IC) with amperometric detection to separate sulfide (HS^-) from the other species and quantify HS^- to concentrations as low as 30 ng/g. At concentrations below approximately 20 ng/g, however, they reported irreproducible peaks which sometimes disappeared entirely.

The lack of success at very low HS^- concentrations (< 20 ng/g) is a significant limitation of the method because dissolved sulfide is a trace

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constituent in most natural waters. The reproducibility problem at these low concentrations was studied in detail by Han and Koch [3] who attributed this to impurities in the eluent and adsorption of sulfide on the separator column. By carefully cleaning the columns, using a second guard column to remove contaminants from the eluent before the injection loop, and minimizing the length of the separator column, Han and Koch [3] achieved detection limits as low as 0.1 ng/g.

Despite the progress which has been made with respect to the IC of HS^- measurements, sample collection and preservation remains a challenge. The usual practice is to preserve the dissolved sulfide by adding zinc acetate, but this leads to severe peak tailing when the sample is directly injected into the chromatograph [1]. Moreover, poor reproducibility, plugged columns and coated electrodes were observed. After only two or three injections, acid cleaning of the columns and detector became necessary [1]. As an alternative to direct injection, Goodwin et al. [1] developed a continuous-flow procedure to separate sulfide from the sample matrix by gas dialysis prior to IC analysis.

The purpose of the study presented here was to measure dissolved sulfide in organic-rich, anaerobic waters from peat bogs by IC using direct injection without adding zinc acetate to preserve the samples. To accomplish this, pore water samples were collected using diffusion–equilibrium pore water samplers (peepers) which filter the waters in situ. This avoids degassing the samples and maintains their existing redox condition [4]. After equilibration the peeper chambers were removed from the bog into plastic glove bags under N_2. The samples were collected from the individual sample chambers of the peepers into syringes containing concentrated eluent. The high pH of this eluent preserves dissolved sulfide and the samples can be injected directly into the ion chromatograph.

A secondary objective of the study was to measure acid-volatile sulfur (AVS) in these waters and to compare these results with the concentrations of free dissolved sulfide.

2. Experimental

2.1. Location of sites

The pore waters studied were collected from two continental bogs in the Franches-Montagne region of the Jura Mountains, Switzerland. One of the bogs, Tourbière de, Genevez (TGe), consisted of 1.5 m of peat, while at the other site, Étang de la Gruyère (EGr), peat accumulation was more than 6 m. More detailed descriptions of the sites are given elsewhere [5].

2.2. Sampling of peat pore waters

The pore waters analyzed in this study were obtained using in situ diffusion–equilibrium pore water samplers (peepers) [6]. Peepers were originally designed for studying pore waters in lake or sea sediments [7]. They consist of a single housing made up of individual 30-ml Plexiglas chambers that are filled with deionized, deaerated water and are 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 directly through the glove bag using syringes. Syringes were assembled with plastic tips instead of stainless-steel needles in order to avoid adsorption of sulfide on the needle. The syringes contained 1 ml of concentrated eluent (five times) to which 4 ml of sample were added. Each sample, therefore, consisted of a slightly diluted pore water aliquot with pH and ethylene diamine (EDA) concentration similar to those of the eluent (see below). This step was needed to prevent losses of volatile H_2S. The samples were brought to the laboratory in the closed syringes — which were kept in a cold-storage bag — and were then analyzed immediately. Because a 0.2-μm filter was built in the sampler, there was no need to vacuum-filter the pore waters prior to analysis.

2.3. Ion chromatography

IC was performed using a Dionex 4500i IC system. Cyanide and sulfide were separated on a Dionex PA1 guard column using 0.5 *M* sodium acetate–0.1 *M* NaOH–0.5% (v/v) EDA as an eluent [8]. Only clear EDA (stored cold) was used to make up the eluent. The eluent flow-rate was 1 ml/min.

All standards were prepared in deaerated 0.1 *M* NaOH solutions made with deionized water (18 MΩ) and 50% NaOH solution (8 g/l). The sulfide stock solution was prepared by dissolving 690 mg/l $Na_2S \cdot 9H_2O$. The cyanide stock solution was made up by dissolving 189 mg/l NaCN. The stock solutions were then diluted in the NaOH solution given above to obtain the working standards.

Metal accumulation on the column degrades its performance [3]. This made periodic rinsing of the columns necessary. Column clean-up was done by first rinsing the columns with deionized water, then for 30 min with 0.1 *M* HCl and again thoroughly with deionized water. Following this the columns were reconnected to the detector and equilibrated with the eluent. In order to trap metals from the eluent an additional guard column was placed between the pump and the injection loop, as suggested by Han and Koch [3]. The resulting back-pressure of the two guard columns used was approximately 700 p.s.i.

The Ag working electrode was polished with toothpaste and the reference electrode filled with eluent. The potential applied at the Ag electrode was 0.00 V. The volume of the injection loop was 100 μl.

In order to minimize column contamination the samples were injected through organics-removal cartridges (Dionex OnGuard-P) which remove humic material present in the sample.

When switching from this sulfide application to another application (e.g. anions or cations detected with suppressed conductivity) on the same ion chromatograph, the whole system must be thoroughly rinsed with deionized water (24 h or longer). Disassembly of the pump heads and rinsing all parts with deionized water helps to shorten the time needed to clean the system.

2.4. Acid-volatile sulfur

A 20-ml volume of pore water was acidified with 10 ml of 1 *M* HCl in a 100-ml three-neck distillation flask assembled with a Liebig condenser and gas tubes. The flask was continually flushed with N_2 gas. The evolved H_2S was collected in a gas trap consisting of a 25-ml glass cylinder filled with 20 ml of eluent. Sample and HCl were allowed to react for 10 min at room temperature and were then heated up and boiled for another 10 min. Similar set-ups (but with a different trap solution and some other analytical technique) have been used to determine AVS in sediments (e.g. Refs. [9] and [10]).

3. Results

3.1. Separation, calibration and precision

With retention times of approximately 1.2 and 2.0 min, sulfide and cyanide were clearly separated. Fig. 1 shows that on a PA-1 guard column the sulfide and cyanide peaks are also well separated from a system peak (occurring when sample matrix is 0.1 *M* NaOH). Other anions that can be detected using amperometry are SO_3^{2-}, $S_2O_3^{2-}$, I^- and Br^- [2]. With the method described here, these ions gave no peaks at concentrations of 1 μg/g. Because all of these species are present in concentrations far below 1 μg/g in the pore waters studied, they cannot interfere with the sulfide measurements.

The sensitivity of the method depends on the condition of the column and the Ag electrode used and can differ considerably between two measuring periods. For example, while it was sometimes possible to calibrate down to 1 ng/g sulfide, at other times concentrations below 10 ng/g could not be detected. One possible reason for the fluctuations of performance between measuring periods might be column contamination due to the build-up of humic substances and

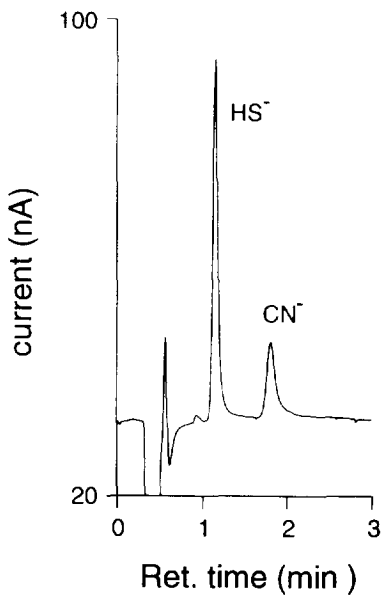

Fig. 1. Chromatogram of a standard (made up in 0.1 *M* NaOH) obtained using a Dionex PA1-Guard column and NaOH–EDA–acetate eluent. Sulfide and cyanide concentrations are 50 and 25 ng/g, respectively. The peak at 0.6 min was always observed when injecting 0.1 *M* NaOH.

metal sulfides [3]. After a column rinse as described earlier it was normally possible to detect 5 ng/g sulfide. During a single measuring period lasting several days, the system was stable. The response for cyanide is similar to that of sulfide but the cyanide peaks are broader. Nevertheless, the detection limit for cyanide is on the order of 5 ng/g or less.

Although Han and Koch [3] achieved good linearity down to concentrations of 1 ng/g HS^-, in this study calibration curves for sulfide typically were non-linear in the low ng/g range but linear at higher concentrations. A typical calibration curve at low concentrations (obtained with standards at 2, 5, 10 and 30 ng/g sulfide) is

$$\text{concentration} = 1.38 + 0.426 \cdot \text{area} - 0.0012 \cdot \text{area}^2 \quad (r^2 = 0.9997)$$

where concentration is the sulfide concentration (ng/g) and area is the peak area (nA s). The reproducibility of the method is good, with relative standard deviations (R.S.D.) for standards $< 5\%$ at the 10 ng/g level. The R.S.D. of pore water samples at this concentration can be as high as 10%. To reduce the R.S.D. for samples and to compensate for anomalous values occasionally recorded (outliers), measurements were usually done in triplicate. The R.S.D. for means of duplicate determinations of samples was 7%. Outliers may be caused by negative peaks occasionally superimposed on the analyte peak (compare baselines in Fig. 2).

As noted by others [2,3] the first few injections each day are used to condition the cell and give either a poor response or no response at all.

3.2. Effect of organics-removal cartridges

The organics-removal cartridges used showed no influence on the sulfide measurements. This is illustrated in Fig. 2 which compares a sample spiked to contain 10 ng/g sulfide and cyanide injected through an OnGuard-P cartridge with a 10 ng/g standard measured without a cartridge.

3.3. Preservation of sulfide in the pore water samples

To evaluate the effectiveness of the measures taken to prevent oxidation of sulfide and loss of

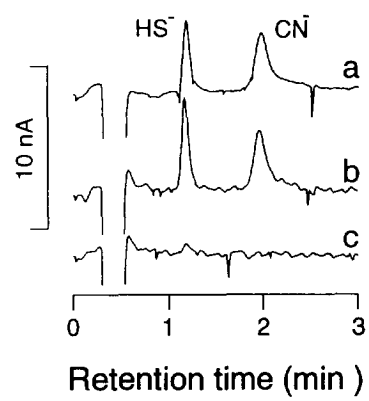

Fig. 2. (a) Chromatogram obtained from a standard containing 10 ng/g sulfide and cyanide. The standard was injected without an organics-removal cartridge. (b) Chromatogram of a pore water spiked with 10 ng/g sulfide and 10 ng/g cyanide. This sample was injected through an organics-removal cartridge. The unspiked pore waters contains only traces of sulfide (c).

volatile H_2S (described above), some samples were spiked in the field. A 4-ml pore water sample was sampled in a syringe containing 1 ml of a 25 ng/g sulfide standard made up in eluent. Therefore, upon mixing, these samples contained an additional 5 ng/g sulfide. On returning to the laboratory the added 5 ng/g sulfide could be measured, whereas no sulfide peak was detected in the unspiked samples of the same pore waters.

3.4. Acid-volatile sulfur

To determine the possible importance of sulfide complexed by metals, AVS was measured in the pore water samples as described above. The acid added during this procedure volatilizes sulfide as H_2S. The method has been shown to volatilize sulfur from (solid) FeS and ZnS but not from organic substances [10,11]. We obtained good recoveries (up to 85%) of standards containing only 1 μg of sodium sulfide using a simple trap (a 25-ml glass cylinder and a 2-ml glass pipette) to remove H_2S from the N_2 gas stream. The absolute detection limit is estimated to be approximately 0.1 μg sulfide. Trapping volatilized sulfide in eluent followed by IC analyses is a rapid and sensitive technique for AVS determinations.

3.5. Simultaneous measurement of sulfide and sulfate

Rocklin and Johnson [2] used a suppressor together with a conductivity detector after the electrochemical detector. This allowed the amperometric detection of sulfide and cyanide together with the conductometric detection of Cl^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} in the same run. An experiment with a similar set-up using an AS4A-SC separator column yielded good results initially. However, after about one day the baseline started to increase and eventually became irregular. This is due to the EDA contained in the eluent. EDA is now known to damage the suppressor [12], and this combined set-up should not be used.

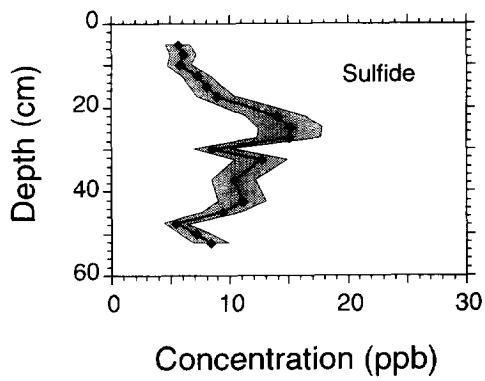

Fig. 3. Sulfide concentration profile measured at Tourbière de Genevez (TGe). The filled rhombs indicate means of duplicate measurements. The 99% confidence limits are indicated.

3.6. Sulfide in bog pore waters

Neither sulfide nor AVS was found in the pore waters of Étang de la Gruyère (EGr). In the other bog studied (Tourbière de Genevez, TGe) free sulfide levels were low (<20 ng/g) but measurable. A typical HS^- profile is given in Fig. 3.

Pore water samples from TGe contained 7–16 ng/g AVS, which is comparable to the concentrations of free sulfide measured by direct injection of the samples. This comparison shows that free, dissolved sulfide measured by direct injection of the samples represents the total sulfide in the bog pore waters.

At both bogs the concentrations of sulfate in the pore waters generally were found to be low (<20 ng/g sulfur in most samples), while total dissolved sulfur and dissolved organic carbon (DOC) were generally high (around 500 ng/g S and 30–70 μg/g DOC). It appears, therefore, that the bulk of the sulfur in these pore waters is organically bound.

No free or acid-volatile cyanide was recorded in any of the samples.

4. Conclusions

IC with amperometric detection allows the determination of sulfide and cyanide at low ng/g

concentrations in organic-rich peat bog pore waters. Samples of 4 ml (mixed with 1 ml of concentrated eluent to avoid loss of volatile H_2S) are sufficient to rinse the organics-removal cartridge and analyze the samples in triplicate; this entire procedure requires 10 min. No other pretreatment and no preservation with zinc acetate is needed when the pore water samples are handled as described above. The comparison with AVS shows that free dissolved sulfide measured by direct injection represents the total dissolved sulfide in those waters.

The combination of the H_2S trap containing eluent and IC to measure sulfide represents an effective, sensitive procedure for measuring AVS. This method is likely to find broad applications for measuring AVS in other kinds of sediments and pore water.

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