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# Simultaneous determination of small organic and inorganic anions in environmental water samples by ion-exchange chromatography

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## Abstract

Anion-exchange chromatography at elevated pH values is the method of choice for the simultaneous determination of weak and strong low-molecular-mass organic and inorganic acids. These are important species found in the environment where most of them are formed and further degraded, particularly if microbial activities are involved. A step gradient procedure with a weak eluent such as borate on a low-capacity column was developed for the simultaneous one-run one-column determination of most of these types of components in environmental water samples. High selectivity and detection limits below  $1 \mu\text{M}$  were achieved. Other yet unknown coelutions of 3-hydroxybutyrate with fluoride and 2-hydroxybutyrate with propionate were found. The different retention characteristics of a high-capacity column was used to obtain additional evidence to identify interfering components. These separation procedures were used to investigate fog, lake sediment pore water and rain after roof run-offs.

## 1. Introduction

Research on distribution and transformations of chemical species in the environment has led to an increased demand for analytical methods that quantify most of the species of the same kind in one run. This is an ultimate condition in the case of low amounts of available samples.

High-performance liquid chromatography (HPLC) in the ion-suppression mode or ion-exclusion chromatography [1] has been applied to separate organic acids. Acidic eluents that keep weak organic acids protonated are used. In

this neutral molecular form they can be separated by hydrophobic interaction chromatography. Stronger organic and inorganic acids that remain in the ionic form are excluded and discarded. In addition, because of a very weak chromophore, ultraviolet detection has to be performed at very short wavelengths where solvents absorb. This leads to high detection limits (ppm). After organic acids are extracted from water by an organic solvent they can be separated by gas chromatography (GC) with high selectivity. This extraction step allows the concentration of the acids and lowers the detection limits (ppb). However, these methods provide only a restricted section of the whole anion

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profile of an environmental sample. A much broader insight is given by anion-exchange chromatography at elevated pH values, which is very suitable for the analysis of weak and strong organic and inorganic acids. It is often the preferred method for the analysis [2] of these compounds, which are involved in environmental transformation processes where most are formed and further degraded particularly in association with microbial activity [3]. Therefore simultaneous monitoring for organic and inorganic nutrients is essential [4].

For anionic species, anion-exchange chromatography became a powerful tool when high-capacity suppressors [5] and hydroxide-selective anion separator columns were introduced. This combination allows gradient elution which is the most efficient technique for selectivity management to be applied in conjunction with conductivity detection, the most common direct and sensitive technique for the detection of ionic species. Because of the dynamic range of the suppressor capacity, an increasing eluent concentration (e.g. hydroxide up to 150 mM) results in a minimal increase of background conductivity.

Singly charged low-molecular-mass aliphatic organic anions ( $C_{n<6}$ ) exhibit a very low affinity (capacity factors,  $k'$ ) to the anion separator columns so that only a weak eluent strength can provide sufficient selectivity to separate those acids. However, weak eluents do not virtually elute doubly charged low-molecular-mass organic and inorganic anions. Usually, anion chromatographic procedures focus on the latter ones by applying a medium or high eluent strength such as hydroxide at the expense of selectivity of low-molecular-mass organic acids that can be expected to be present in environmental samples. Different strategies involving more than one column have been applied, e.g. samples were automatically injected several times for separation under isocratic (AS4A–carbonate [6]) and gradient (AS5A–OH<sup>-</sup>) conditions [7]. An alternative for gradient separation is a column-switching procedure between two columns with different capacities that are isocratically eluted [8]. Gradient elution has been applied to quan-

tify low-concentrated inorganic and organic anions in Greenland ice. The insufficient separation between acetate and glycolate and between sulphate and oxalate has not been improved significantly using a hydroxide gradient on a multiphase column [9]. A weak eluent such as borate (1.3 mM) on an AS4A column provided a better resolution in the isocratic mode for low-affinity anions [10] and in a gradient mode (7–21 mM) for higher-affinity anions [11]. However, none of these procedures have been shown to separate acetate from lactate, propionate and glycolate.

As we and others [11] have encountered these problems in environmental water samples, an investigation started, aimed to separate environmentally relevant low-molecular-mass aliphatic organic acids including some of their hydroxy analogues in the same run on one column that separates inorganic anions (see Table 1). A varying selection of these species can be found in environmental water samples depending on the emitting sources and the ongoing biological and chemical activity. For example, glycolate is formed by photosynthesis since the same enzyme that catalyses the fixation of CO<sub>2</sub> has also an oxygenase activity which produces glycolate [12]. Its formation and disappearance in algae blooming during day time has been monitored by GC [13]. Under anaerobic conditions biopolymers are degraded in water by fermentative processes to, e.g., acetate, lactate, propionate, butyrate and formate. Since low-molecular-mass organic acids are readily taken up by microorganism, these compounds serve as nutrients and are further oxidized [14]. In atmospheric waters such as fog water and aerosols these acids can be present. They are formed in the aquatic phase from photochemically induced gas-phase precursors [15].

A better separation of low-molecular-mass organic acids allows the identification of these chemical species. This is important in order to correctly diagnose a water body and assign the nature of degradation path (e.g., biological or photochemical) and its mechanism [16] as well as an accurate determination of carbonate by titration (alkalinity), often the main anion in environmental water samples.

Table 1  
Retention times ( $t_R$ ) of environmental relevant low-molecular-mass organic and inorganic components on two different columns

Component		AS11 gradient $t_R$ (min)	AS10 borate isocratic	
Name (abbreviation)	Composition		7 mM $t_R$ (min)	5 mM $t_R$ (min)
3-Hydroxybutyrate (3-OHBU)	H <sub>3</sub> CHOHCH <sub>2</sub> CCOO	5.0	7.2	
Fluoride	F <sup>-</sup>	5.1	6.5	8.1
Lactate (La)	H <sub>3</sub> CHOHCCOO	5.6	7.9	10.1
Acetate (Ac)	H <sub>3</sub> CCOO	5.8	7.9	10.1
Glycolate (Gl)	HOH <sub>2</sub> CCOO	6.2	8.6	
Propionate (Pr)	H <sub>3</sub> CH <sub>2</sub> CCOO <sup>-</sup>	7.0	8.6	
2-Hydroxybutyrate (2-OHBU)	H <sub>3</sub> CH <sub>2</sub> CHOHCCOO	7.0	8.8	
Formate (Fo)	HCOO <sup>-</sup>	8.0	12.0	16
Butyrate (Bu)	H <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CCOO	8.6	9.6	12.5
Methanesulfonate (MSA)	H <sub>3</sub> C SO <sub>3</sub>	9.0	-	
Pyruvate (Pu)	H <sub>3</sub> COCCOO	10.0	16.0	
Valerate (Va)	H <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CCOO	10.8	12.6	
Chloride	Cl	13.0	45	
Nitrite	NO <sub>2</sub>	14.0		
Carbonate	CO <sub>3</sub> <sup>2-</sup>	14 ± 0.4		
Phosphate	PO <sub>4</sub> <sup>3-</sup>	16.2	∞	
Bromide	Br	16.6		
Nitrate	NO <sub>3</sub>	17.1	∞	
Sulfite	SO <sub>3</sub> <sup>2-</sup>	17.8	∞	
Sulfate	SO <sub>4</sub> <sup>2-</sup>	19.0	∞	
Oxalate (Ox)	OOCOO	21.0	∞	

## 2. Experimental

### 2.1. Instrumentation

A DX-300 chromatographic system (Dionex) was used with a standard AGP pump, a PED in the conductivity detection mode, and AI-450 software 3.31. The anion separator columns (200 × 4 mm) IonPac AS10 and AS11 and their corresponding guard columns (50 × 4 mm) AG10 and AG11 were used. The eluent (1 ml/min) conductivity was chemically suppressed by a micromembrane suppressor (AMMS II) regenerated by 25 mM H<sub>2</sub>SO<sub>4</sub> (10 ml/min) or a self-regenerating suppressor (ASRS, current setting 3) that uses the column effluent to supply the proton generated by water electrolysis. An anion trap column (ATC-1, 9 × 24 mm) was installed in front of the injection valve to minimise interferences from anionic impurities in the eluent during gradient elution.

### 2.2. Chemicals

The chemicals used were of highest purity available from Fluka and Merck. Borate eluents were prepared from Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O in 18-MΩ (Nanopure) water and kept under helium pressure.

Stock solutions (1000 ppm) of organic acids were prepared by dissolution of the sodium salts of the acids with freshly purified and 0.2-μm filtered, deionized water (18 MΩ) in carefully rinsed glass volumetric flasks. Stored at 4°C these stocks could be used for a few months. Calibration was obtained from freshly prepared standard solutions. Depending on concentration, storage and handling condition they could be used for a few days.

Turbid samples were filtered through pre-washed (2 h at 80–100°, 18-MΩ deionized water) filters (0.45 μm). Depending on the concentration, 10-, 25- or 50-μl samples were injected.

### 3. Results and discussion

#### 3.1. Chromatographic procedures

A preliminary comparison of borate and hydroxide as eluents for the separation of low-molecular-mass organic components in fog samples revealed that borate provides a better resolution on the more hydrophilic columns AS11 and AS10. Therefore, the separation was investigated with borate as eluent. Its background conductivity was chemically suppressed. For the low-capacity AS11-AG11 (55  $\mu$ equiv.) and the high-capacity AS10-AG10 (210  $\mu$ equiv.) columns a different procedure was established.

#### 3.2. Step gradient procedure on a low-capacity separator (AS11)

The chemical suppression allows a gradient to be applied, and only a gradient provides the selectivity necessary to separate several low-affinity ( $F^-$ , organics) as well as high-affinity (doubly charged organics and inorganics) anions. In the same run for gradient elution the low-capacity column is preferred: it needs a lower eluent strength which gives shorter retention times and a smaller increase in background conductivity during the gradient allowing lower concentrations to be determined. A step gradient (see Table 2) with its almost flat baseline during the important sequence of the chromatogram

turned out to be optimal for short retention times, consistent peak integration and low detection limits. The large affinity range of the anions we are interested in can be divided in three affinity classes. Each of them corresponds to a borate concentration level needed for elution. Low-affinity species ( $F^-$ , all single-charged organics) are best separated in the initial part (see Fig. 1) by a slightly linear gradient of 1–6 mM borate. The duration and concentration of this initial step can be adjusted to the number and types of low-molecular-mass organic acids. This, of course, affects the retention times of anions that elute later. A second medium-affinity group is envisaged by an increase to 20 mM borate for a short time to detect chloride and nitrite. Carbonate eluted at varying retention times around nitrite. Disturbed nitrite peaks have been observed for carbonate concentrations higher than 40 mg/l. All other anions (e.g.  $PO_4^{3-}$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_3^{2-}$ ,  $SO_4^{2-}$  and oxalate) are eluted during a third step of 45 mM borate. Detection limits were determined to be 0.5–1  $\mu$ M depending on the species. In 25 min this procedure achieved the best selectivity so far known for low-molecular-mass organic acids as well as separation and quantification of common inorganic anions in the same run. For a similar purpose on the same column it was proposed [17] to use a hydroxide gradient that starts at a very low concentration (0.5 mM) containing 10% methanol. Every time we used hydroxide at

Table 2  
Borate step gradient for the simultaneous separation of organic and inorganic anions on a low-capacity anion separator column

Time (min)	Flow (ml)	% E1 1 mM borate	% E2 50 mM borate	$E_{mix}$ borate (mM)	Comment
0	1	100	0	1	Injection
8.0	1	90	10	6	start gradient
8.1	1	40	60	30	end first step
10.6	1	40	60	30	start second step
10.7	1	10	90	45	end second step
19.7	1	10	90	45	start third step
19.8	1	100	0	1	end third step
23.8	2	100	0	1	Start initial condition
25.8	1	100	0	1	Speed up reconditioning
27.5	1	100	0	1	Release
					Initial conditions

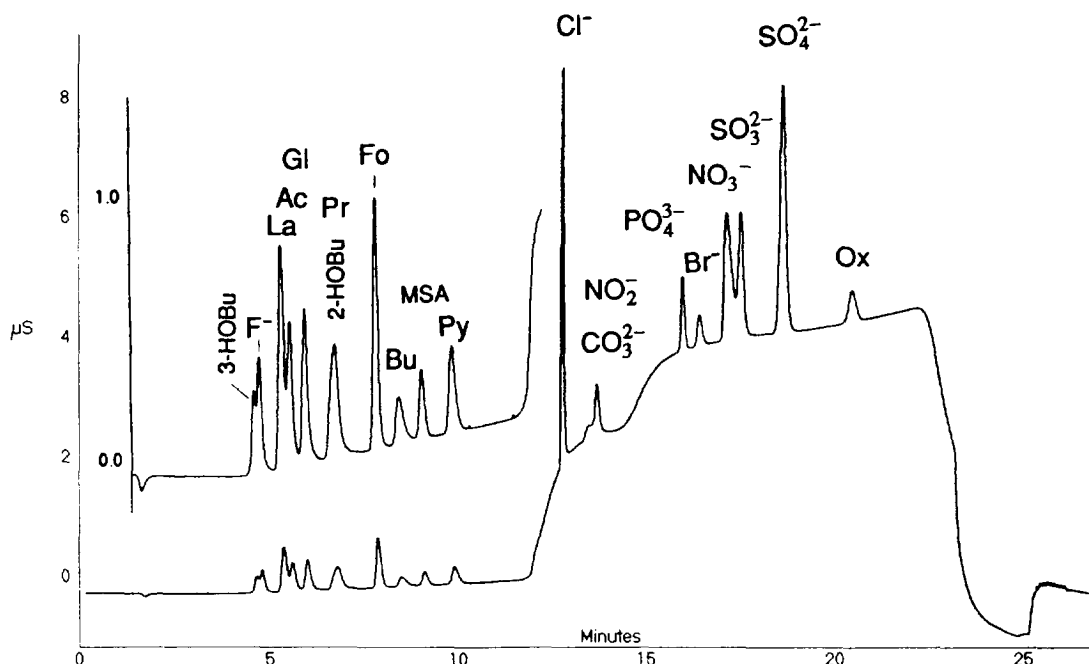


Fig. 1. Chromatogram obtained by the step gradient procedure (Table 2) from a standard solution (25  $\mu$ l injected) containing  $F^-$  (0.25 mg/l), 3-OHBU, La, Ac, Gl, Pr, 2-OHBU, Fo, Bu, MSA, Py, Ox (all 1.0 mg/l),  $Cl^-$  (2.0 mg/l),  $NO_2^-$  (0.65 mg/l),  $CO_3^{2-}$  (40 mg/l),  $PO_4^{3-}$  (1.2 mg/l),  $Br^-$  (0.8 mg/l),  $NO_3^-$  (4.4 mg/l),  $SO_3^{2-}$  (4.0 mg/l),  $SO_4^{2-}$  (4.0 mg/l). For abbreviations, see Table 1. The inset has an expanded response for the same time scale.

the same concentration and methanol at varying percentages (5, 10, 20%) a decrease of selectivity compared to the borate eluent was observed for low-affinity species. There is evidence from the changes in the elution sequence between the two different anion separators (Table 1) and the increasing affinity with increasing carbon chain of unsubstituted aliphatic monocarboxylic acids that the separation mechanism involves hydrophobic attraction which is reduced by methanol. Such an eluent is the best choice to reduce the retention times of organic anions with a high hydrophobic attraction for which a borate eluent is not ideal.

We used this procedure to investigate separation problems associated with the low affinity of low-molecular-mass organic acids. As depicted in Fig. 1, several of these acids have been separated, which were up to now not or poorly resolved, such as acetate from lactate and glycolate from propionate. However, on this column other yet unknown interferences were

found: 3-hydroxybutyrate (3-OHBU) almost co-eluted (shoulder) with  $F^-$  and 2-OHBU perfectly coeluted with propionate. On an AS10 column 3-OHBU was perfectly baseline-separated whereas the occurrence of 2-OHBU was only indicated by a shoulder in the propionate and glycolate (coeluting) peak, respectively.

### 3.3. Isocratic separation on the high-capacity anion separator AS10

A high-capacity column is not recommended for the simultaneous separation of low- and high-affinity anions because of the previously mentioned reasons. Nevertheless, such a column can provide an excellent resolution for low-affinity species. Borate (7 mM, isocratic) was used to separate these species (Fig. 2). For example, fluoride and formate were separated by 6 min. This is twice the resolution compared to the step gradient procedure (Fig. 1) on the low-capacity column. The more polar species (3-OHBU, lac-

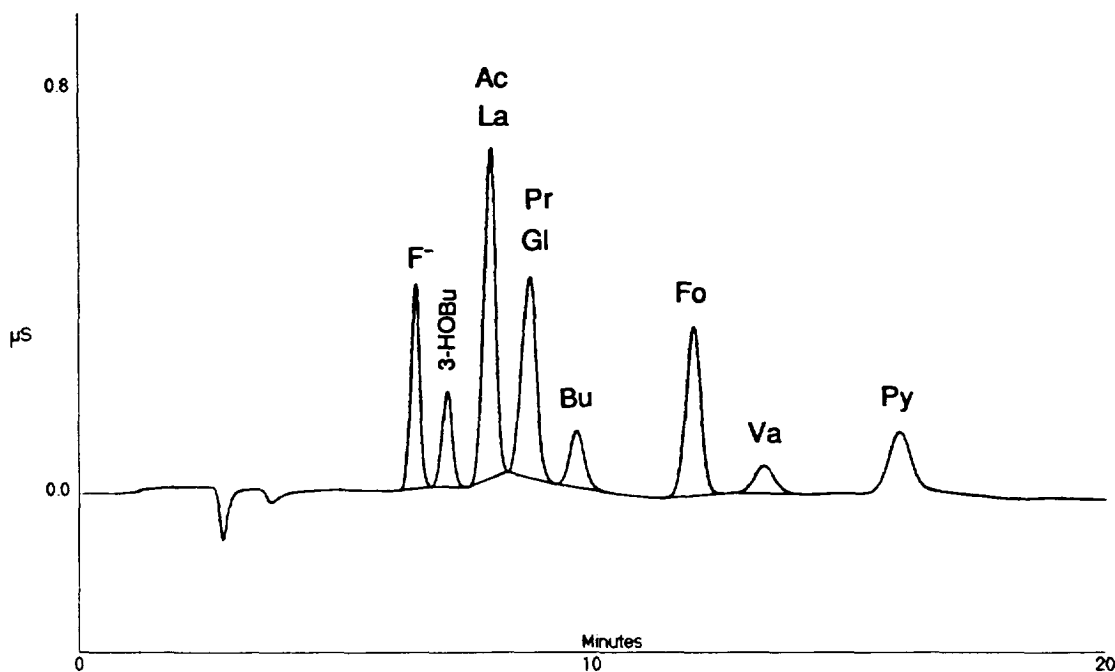


Fig. 2. Chromatogram obtained on the high-capacity column AS10 by isocratic (7 mM borate) elution of a standard solution (25  $\mu$ l injected) containing F<sup>-</sup> (0.25 mg/l), 3-OHBU, La, Ac, Gl, Pr, Fo, Bu, Va, Py (all 1 mg/l). For abbreviations, see Table 1.

tate, glycolate, 2-OHBU, formate and pyruvate) are better retained on this higher-capacity column. This different retention characteristic may help to identify some components in samples. Unfortunately two other  $\alpha$ -hydroxy compounds, lactate and glycolate, coelute with acetate and propionate, respectively (Table 1). A linear borate gradient (5–15 mM) was applied instead of isocratic conditions but no indication was observed that the two compounds coeluted.

The combination of this weak eluent strength on a high-capacity column drastically increased the retention times of strong organic and inorganic acids. Chloride, for example, was eluted after 45 min and others were not eluted at all or at much longer retention times, probably as such broad peaks that they could no longer be detected. In this way the column acted on line as a sample preparation column as well as a separator for low-affinity anions. The long retention time

of chloride allowed the ending of a run after the low-affinity anions had been separated (around 20 min) and the injection of another sample so that chloride from the previous run appeared at the end of the following chromatogram, keeping each analysis interference free of chloride from the former injected sample as shown in Fig. 3. The the column capacity for the accumulation of high-affinity species is sufficient to provide separations without a disturbed peak shape for up to fifteen to twenty fog sample injections (25  $\mu$ l). Obviously this depends on the sample concentrations of the species accumulating on the column. After around thirty injections the loading of the column resulted in clearly disturbed peaks with a shoulder in the onset of the peak as shown in Fig. 4 and asymmetry factors  $< 0.7$ . After rinsing with 200 mM NaOH and reequilibration with 7 mM borate the column had the original performance.

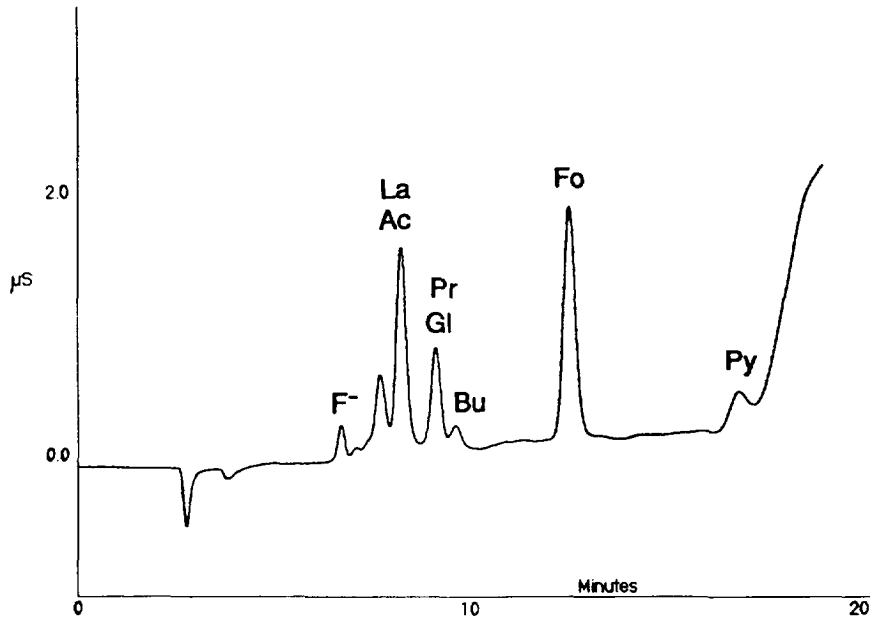


Fig. 3. Chromatogram of a fog sample (25  $\mu\text{l}$  injected) on the high-capacity column AS10 by isocratic elution (7 mM borate).

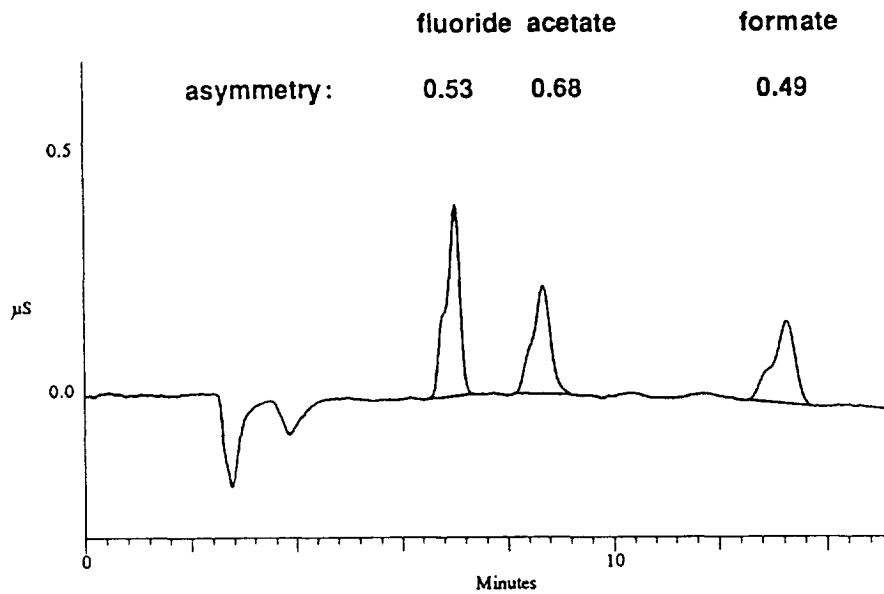


Fig. 4. Chromatogram of a standard solution containing fluoride, acetate and formate (0.1, 0.5 and 0.5 mg/l, respectively, 50  $\mu\text{l}$  injected) obtained on the high-capacity column AS10 after more than twenty consecutive fog sample injections without column wash.

### 3.4. IC analysis of anions in environmental water samples

#### *Fog water*

The composition and concentrations found in fog water [18] strongly depend on emitting sources (e.g. traffic, heating, incinerators) and their variations and meteorological conditions. In our recent IC work we focused on low-molecular-mass organic acids because of their role as iron ligands in iron cycling [16,19]. Biological transformations are of less importance and, since combustion is the main source chemical [20] and photochemical [21] transformations take place in an oxidative environment, we can expect higher concentrations of oxidised forms of low-molecular-mass organic acids. Fog samples were collected as described [16] and subjected to IC analysis within hours. In separate aliquots of stored samples  $\text{SO}_3^{2-}$  was preserved with glycerol and organic acids with chloroform. As depicted in Fig. 3, fog can contain a variety of low-molecular-mass organic acids. Among them acetate (10–400  $\mu\text{M}$ ) and formate (10–150  $\mu\text{M}$ ) were always found in highest concentrations. Together they accounted for 3–10% of dissolved organic carbon. Propionate, butyrate, pyruvate and oxalate ranged from below detection limits (0.5–1  $\mu\text{M}$ ) to 10  $\mu\text{M}$ . The identification of components eluting between  $\text{F}^-$  and acetate (see Fig. 3) and the separation of acetate from possibly present lactate as well as propionate from glycolate by the step gradient procedure remain to be done in an appropriate fog event.

#### *Lake sediment pore water*

Sediments are an important factor in the cycling of the elements in a lake. Biological and chemical reactions at the water sediment boundary decide whether elements are incorporated into the sediment or kept dissolved in the water. These processes occur in a layer of a few centimetre thick or less. The sampling device for sediment pore water, a dialysis chamber [22], delivers around 10-ml samples for one depth. Many or, if possible, all dissolved species have to be determined in such low-volume samples in order to investigate the complicated transforma-

tions. Usually, less than 4 ml are available for an analysis of the anion profile. Since these oxygen-free water samples contain dissolved Fe(II) and Mn(II) that are readily oxidised and precipitated in contact with oxygen at elevated pH we checked a possible coprecipitation of low-molecular-mass organic acids. A solution of 200  $\mu\text{M}$  Mn(II) and 300  $\mu\text{M}$  Fe(II) dissolved in a standard solution containing acetate (8.4  $\mu\text{M}$ ), propionate (2.7  $\mu\text{M}$ ) and formate (4.4  $\mu\text{M}$ ) was aired and brought to pH 12 by NaOH. An intense dark precipitation formed but no decrease of the organic acids compared to the untreated standard solution was found. From this we conclude that no coprecipitation under the chromatographic conditions occurred.

The sediment pore water sampled in lake Sempach during summer (June) and winter (January) contained very low amounts (usual < 2  $\mu\text{M}$ , maximum 6  $\mu\text{M}$ ) of acetate. Since both the formation and degradation of low-molecular-mass organic acids are controlled by different communities of microorganisms only a low intermediate concentration during balanced rates can be observed. So far only once in the summer (June, lake Baldegg) high acetate concentrations up to 90  $\mu\text{M}$  and elevated levels of other organic acids were detected (Fig. 5). This is considered as an exceptional case due to an increase in sedimentation of particulate organic matter that resulted probably during a short period in an overproduction of low-molecular-mass organic acids.

#### *Rain water from roof run-offs*

In extended dense populated areas ground water supply by direct infiltration of rain water became minimal. The water is collected on roofs and roads and drained to the sewage treatment plants. Ground water levels decrease and during storms sewage treatment plants are overloaded and lose their efficiency. Therefore rain from roof run-offs is under investigation for a direct infiltration into the ground. We determined anion profiles in rain water after passage over different roofs. The samples contain species characteristic of the dry deposition before rainfall and chemical and biological transformations



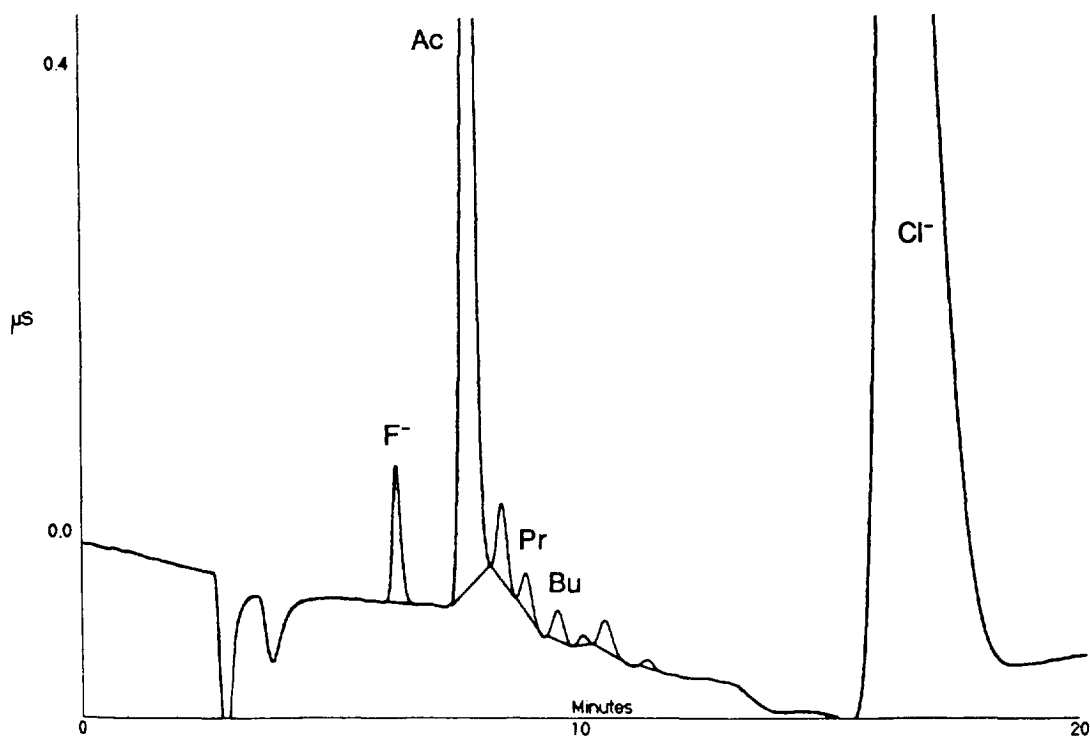


Fig. 5. Chromatogram of a sediment pore water sample ( $50 \mu\text{l}$  injected) on the high-capacity column AS10 using  $7 \text{ mM}$  borate isocratic as eluent. For abbreviations, see Table 1.

occurring in the microenvironment of the roof. An example is given in Fig. 6. The sample from a glass fibre plastic roof has a quite similar composition to fog water. In this case the degradation of plastic is suspected to be the main source of organic acids.

#### 4. Conclusions

The step gradient procedure presented allows the determination of low-molecular-mass organic and inorganic acids in the same run on one column in a reasonably short time. This makes it a unique method to simultaneously obtain a large section of an anion profile in environmental samples. For complex mixtures of low-molecular-mass organic acids a second column with a different retention characteristic helps to identify the components. However, the final proof that

no coelution occurred can only be provided by a detection that gives structural information, such as mass spectrometry.

The occurrence of low-molecular-mass organic acids in environmental samples points to the decisive role of microbial activities. Only when these are unimportant (in atmosphere) or temporarily imbalanced, low-molecular-mass organic acid concentrations higher than a few micromoles can be found.

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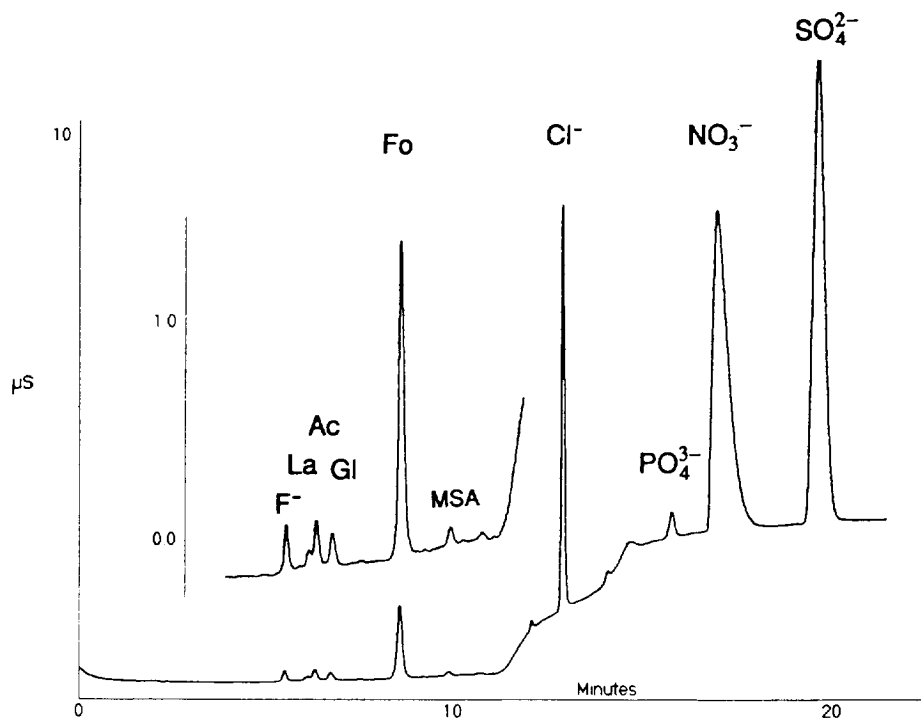


Fig. 6. Chromatogram of rain water sampled after running down a glass fibre plastic roof. Separation (25  $\mu\text{l}$  injected) was performed by step gradient (see Table 2) on a low-capacity column AS11. For abbreviations, see Table 1. The inset has an expanded response for the same time scale.

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