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Ion chromatographic determination of anions and cations at ultra-low concentrations in Alpine snow

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Abstract

As part of the international project ALPTRAC the acid deposition at high Alpine sites was investigated. This paper reports on experiences with ion chromatography in the $\mu\text{g}/\text{kg}$ range that was characteristic for the samples, and on the sample contamination and its sources. Particular emphasis is given to a drop of ionic concentration from the first to the second injection drawn from the vials of the automated sampler. This drop was observed at detection ranges of $3 \mu\text{S}/\text{cm}$ and less and amounted to $17 \mu\text{g}/\text{kg}$ for sodium, $14 \mu\text{g}/\text{kg}$ for chloride and 1 to $4 \mu\text{g}/\text{kg}$ for magnesium, calcium and sulphate.

1. Introduction

Various studies have shown ecosystems in the Alpine region to be very sensitive to the impact of pollutants. The amount of pollutants accumulated in the Alpine snowpack during the winter half year is of special importance for the acidification of mountain lakes and runoff. The rapid release of pollutants occurring with the onset of snowmelt—up to 80% of the bulk solute is released with the first third of the meltwater—can be very harmful to such ecosystems.

To investigate, among other topics, the amount of substances deposited in wet and dry form at heights of 3000 m above sea level and more, an international project (ALPTRAC) was started in 1990. Measurements performed on glaciers in the Tyrolean Alps show that ionic loads there are as high as or even exceed the

amounts measured at valley stations in Tyrol (due to the general increase of precipitation with height). Mean concentrations of ions dissolved in the snowpack, on the contrary, amount to only 25 to 50% of the ionic concentrations found in precipitation of low lying stations [1,2] indicating background conditions in the $\mu\text{g}/\text{kg}$ range, comparable to those in polar regions [3–5]. These low concentrations are mainly observed in snow layers of December to February precipitation, when glaciers lie well above the height of the atmospheric mixing layer and again after the onset of snowmelt in May or June (see Table 3).

While the meteorological and glaciological implications of the investigation will be reported elsewhere, this paper will focus on the methods of detection of ultra-low ionic concentrations. We report on the precautions taken to keep sample contamination from collecting to analysis as small as possible, on experiences with ion chromatography in the ppb range and on one

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aspect we did not find mentioned in the literature before, that is the difference in ionic concentration between two subsequent injections made from one vial using the automated sampler.

2. Experimental

2.1. Sampling and sample preparation

Samples are taken from snow pits dug on glaciers at heights of 3000 m above sea level. In vertical profiles snow layers of 10 cm thick is cut off with a plexiglas tube and filled into air-tight screw bottles made of polyethylene.

Bottles and anything that may come into contact with the samples, are mechanically cleaned in the laboratory, rinsed with diluted HCl, and then carefully soaked and rinsed several times with ultrapure water, so that no residues can be detected. For the transport between laboratory and sampling site all material is packed into clean plastic bags. As additional precaution against contamination overall clothing of polyamide cleaned rubber gloves, and breathing masks are worn during sampling procedure. Samples are transported in frozen state into the laboratory. Until analysis they are kept in the deep freezer at a temperature of -18°C . Just before analysis with the ion chromatograph they are thawed at room temperature. Vials used

for the automated sampler are well rinsed with the sample before being filled and closed with a filter cap.

2.2. Ion chromatography

All ions of interest are analysed with a Dionex DX-100 instrument. We use a two-column set system with suppressed conductivity detection. The conductivity cell is at constant temperature, so that no noise or baseline drift is normally observed down to the $0.3\ \mu\text{S}/\text{cm}$ range.

System control as well as data collection and processing is done by the Dionex AI-450 chromatography software (version 3.32).

Mono- and divalent anions and cations are separated in single, isocratic runs, respectively. Further details of the analysis are summarised in Table 1.

A Dionex automated sampler with 5-ml vials is used to deliver the sample to the sample loop. A volume of $200\ \mu\text{l}$ for the sample loop has proved to be very practicable for this application.

Eluents, anion regenerant and all standard solutions are prepared with ultrapure water of resistivity $> 18\ \text{M}\Omega\ \text{cm}$ at 25°C . Individual stock solutions of $1000\ \text{mg}/\text{kg}$ (ppm) are diluted to mixed standard solutions of concentrations varying from the mg/kg to the $\mu\text{g}/\text{kg}$ (ppb) range. Standard solutions are always prepared just before calibration.

Table 1
Experimental conditions for ion chromatographic analysis

Parameter	Anions	Cations
Ions determined	Cl^- , NO_3^- , SO_4^{2-}	Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}
Analytical column	Ion Pac-AS4A	Ion Pac-CS12 (4 mm)
Guard column	Ion Pac-AG4A	Ion Pac-CG12 (4 mm)
Suppression	AMMS II (using a pressurized delivery system)	CSRS-I (4 mm)
Eluent	4 mM Na_2CO_3 1.5 mM NaHCO_3	21 mM Methanesulfonic acid
Regenerant	12.5 mM H_2SO_4	
Eluent flow-rate	2 ml/min	1 ml/min
Run time	3.0 min	8.5 min
Background conductivity	20 $\mu\text{S}/\text{cm}$	1 $\mu\text{S}/\text{cm}$

A three-level quadratic calibration is used, standards are external.

2.3. Contamination problems

Contamination of the sample

In the laboratory sample contamination occurs from the moment the sample bottle is opened until the sample is injected into the chromatographic system. To estimate the amount of sample contamination by the laboratory air we analysed ultrapure water of 18.1 M Ω cm resistivity.

No anions and no ammonium and potassium were detected in the ultrapure water. For magnesium we measured a mean concentration of 0.8 $\mu\text{g}/\text{kg}$, for calcium of 1.1 $\mu\text{g}/\text{kg}$. Standard deviation amounted to 0.3 $\mu\text{g}/\text{kg}$ for magnesium, respectively 0.6 $\mu\text{g}/\text{kg}$ for calcium. Sodium concentrations showed the highest variations. We found samples without sodium as well as samples with sodium concentrations up to 3 $\mu\text{g}/\text{kg}$.

This ion content represents a mean, but generally varying contamination of any sample, that cannot be avoided in our laboratory. The concentrations of magnesium, calcium and sodium are considered as “blank” values. They increase the real ionic concentrations and should thus be subtracted from measured values of any sample.

Contamination of the instrument

From every vial used with the Dionex auto-sampler up to three injections can be made.

We found that there are differences in ionic concentrations between the first and the second injection at the 3 $\mu\text{S}/\text{cm}$ and lower detection ranges. Concentration values of most ionic species analysed diminish from the first to the second injection. No further decrease, however, was observed between the second and the third injection.

This effect was most pronounced for chloride and sodium, while no changes could be seen for nitrate, ammonium and potassium. The difference between the first and the second injection appeared to be independent of the measured concentration. It varied from 17 $\mu\text{g}/\text{kg}$ for

sodium and 13 $\mu\text{g}/\text{kg}$ for chloride to 4 $\mu\text{g}/\text{kg}$ for sulphate down to 2–3 $\mu\text{g}/\text{kg}$ for calcium and about 1 $\mu\text{g}/\text{kg}$ for magnesium.

In view of this reproducible value of the difference we concluded that the effect was introduced in the process of extracting the sample from the vial into the analytical system. The first injection has higher concentrations since it contains not only the ions of the sample but also rinses away ions that have been deposited before on surfaces coming into contact with the sample during the injection process, e.g. the filter or the end of the tubing connecting the sampler to the injection valve.

This contamination effect can put a limit to analysis at the lower detection ranges, as it was observed especially with sodium. No reproducible results could be achieved in ranges of less than 0.1 $\mu\text{S}/\text{cm}$. For both calibration and analysis of samples that require detection ranges of 0.3 to 3 $\mu\text{S}/\text{cm}$, only values of the second injection were used. Detection ranges of 10 $\mu\text{S}/\text{cm}$ are not sensitive enough to resolve this contamination effect.

2.4. Detection limits

Measurements to determine detection limits were performed with artificial samples of low ionic content. From a series of 8 injections for both anions and cations method detection limits (MDL) were established according the US Environmental Protection Agency (EPA) definition [6]:

$$\text{MDL} = t(n - 1, 1 - \alpha)R = 0.99)\sigma \quad (1)$$

σ is the standard deviation for the particular ion, t is the Student factor amounting to 3.499 for $n - 1$ degrees of freedom and a significance at the 1% level ($1 - \alpha = 0.99$).

Results for anions and cations are summarised in Table 2. Apart from sodium and chloride method detection limits of about 1 $\mu\text{g}/\text{kg}$ were found for all ions. The comparatively high MDL of almost 4 $\mu\text{g}/\text{kg}$ for sodium was attributed to contamination effects, which were most pro-

Table 2

Method detection limits for anions and cations (MDL), mean concentrations (\bar{x}) and standard deviations (σ) in $\mu\text{g}/\text{kg}$

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
MDL	1.7	0.9	1.2	3.7	1.1	1.4	1.0	1.2
\bar{x}	12.2	17.3	18.2	12.8	2.9	1.9	3.4	5.4
σ	0.49	0.26	0.33	1.06	0.32	0.40	0.30	0.33

nounced and showed the highest variation for this ion.

MDL for chloride amounted to almost $2 \mu\text{g}/\text{kg}$. The wider scattering compared to nitrate or sulphate was due to the overlapping of the chloride peak with the negative water peak in the detection ranges of $3 \mu\text{S}/\text{cm}$ and less. Using a lower concentrated eluent this effect may be diminished.

The detection limits we determined for our application lie in the range reported in literature (e.g. refs. 3, 7 and 8). The variety in experimental conditions of ion chromatographic analysis and the different definitions used to establish detection limits, however, restrict a direct comparison.

2.5. Ionic balance

A common method for evaluating analytical results of water samples is to calculate the ionic balance:

$$C = [\text{H}^+] + [\text{Na}^+] + [\text{NH}_4^+] + [\text{K}^+] + [\text{Mg}^{2+}] + [\text{Ca}^{2+}] - [\text{Cl}^-] - [\text{NO}_3^-] - [\text{SO}_4^{2-}] \quad (2)$$

We found a general anion deficit in agreement with other studies of snow (e.g. refs. 1, 9 and

10). The mean ratio Σ anions/ Σ cations amounted to 0.43, ranging from 0.3 to 0.6.

The anion deficit may be due to any not measured anion (we did not measure hydrogencarbonate and organic compounds like formic and acetic acid), or to analytical errors, whose relative importance increases with decreasing ionic loads, especially near the detection limit.

3. Results

The ionic concentrations we measured in the high Alpine snowpack cover a range of three orders of magnitude, from about $3 \text{ mg}/\text{kg}$ for nitrate in spring down to some $\mu\text{g}/\text{kg}$ for alkali and alkaline earth metals (Table 3). During our investigations ion chromatography has proved to be a very practicable and sensitive method for the detection of major ions in Alpine snow.

Even in snow of low ion content concentrations of anions and ammonium lie a ten to hundred times higher than the corresponding detection limits (Fig. 1a). For metals, however, concentration values in the range of the corresponding detection limit are frequent. In a few cases concentrations below the detection limit are found, especially for magnesium (Fig. 1b).

Table 3

Ionic concentrations ($\mu\text{g}/\text{kg}$) found in distinct snow layers at about 3000 m above sea level; April 17, 1993 and June 25, 1993

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
April	50	2600	980	35	693	10	11	70
June	21	79	43	9	18	1	1	9

The concentration difference between June and April is caused by the release of pollutants from the snowpack during melting.

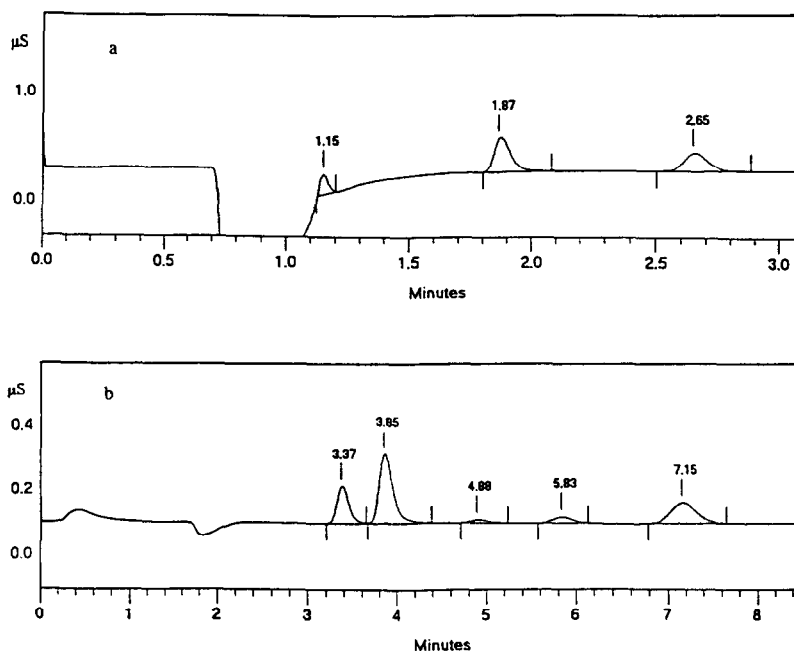


Fig. 1. Typical chromatogram of Alpine snow of low ionic concentrations. (a) Anions (chloride $16.5 \mu\text{g}/\text{kg}$, nitrate $65.1 \mu\text{g}/\text{kg}$, sulphate $36.7 \mu\text{g}/\text{kg}$). (b) Cations (sodium $4.9 \mu\text{g}/\text{kg}$, ammonium $16.5 \mu\text{g}/\text{kg}$, potassium $2.3 \mu\text{g}/\text{kg}$, magnesium $0.1 \mu\text{g}/\text{kg}$, calcium $4.2 \mu\text{g}/\text{kg}$).

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