

Cation trace analysis of snow and firn samples from high-alpine sites by ion chromatography

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Abstract

Ion chromatography with self-regenerating suppression and conductivity detection was used for the simultaneous determination of Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} in melted snow samples from high-alpine sites. Concentrations in the samples showed a high variability and were in the range of 0.3 to 800 $\mu\text{g}/\text{kg}$. Samples with concentrations higher than 2 $\mu\text{g}/\text{kg}$ representing summer snow were analyzed using a 100- μl sample loop. In order to determine the low concentrations in winter snow samples (<2 $\mu\text{g}/\text{kg}$), preconcentration of 2-ml samples was applied resulting in improved detection limits of 0.1–0.4 $\mu\text{g}/\text{kg}$ depending on the cation.

1. Introduction

Cold glaciers from high-alpine sites represent important archives to study the regional climate history. Firn and ice cores from such glaciers can be used to reconstruct the anthropogenic emissions in Europe [1]. Furthermore, they are the only archives allowing the reconstruction of the free tropospheric conditions. Free tropospheric conditions prevail during winter at high-alpine sites [2].

In the framework of the Swiss National Research Program NFP 31 "Climate Changes and Natural Disasters" an ice core drilling project was started at the Monte Rosa massif, Switzerland, in 1993. Test drillings of 5 to 7 m depth were performed to find a suitable site for a later deep core drilling. Snow samples from the test drilling of shallow cores were analyzed for Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . These cations can be

considered as tracers for different sources: Ca^{2+} and Mg^{2+} are components from the earth crust and indicate the amount of mineral dust; NH_4^+ is a tracer for anthropogenic activities while Na^+ is usually a mixture from two sources, seaspray and mineral dust [3].

As analytical method ion chromatography (IC) was applied, since only small sample volumes are available and the limits of detection are generally low. After the introduction of IC in the 1970s [4] a fast development of different techniques followed. However, the improvements were less pronounced for cation than for anion chromatography. For many years the analysis of samples with monovalent (Na^+ , NH_4^+ and K^+) and divalent cations (Mg^{2+} and Ca^{2+}) was not possible by a single chromatographic run under fixed conditions [5]. Since then three different approaches for the determination of all cations in a single run were described: (a) using a gradient eluent [6], (b) eluent step change [6,7] and (c) column switching [6,8]. Quite recently the suc-

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cessful separation of mono- and divalent cations by isocratic, single chromatography was introduced [9,10]. In order to decrease the detection limits to ultra-low ranges, preconcentration techniques using 5-ml samples were applied [9] or a larger sample loop of 500 μl was used requiring 5 ml of sample volume [8]. Both techniques consume relatively large sample volumes.

The concentrations of mono- and divalent cations in winter snow layers of high-alpine sites are very low and detection limits of about 0.1 $\mu\text{g}/\text{kg}$ are needed. In order to achieve a good depth and corresponding time resolution, and to enable the determination of other parameters from the same core with comparable resolution, only small sample volumes are available for IC analysis. Therefore a preconcentration technique using a sample volume of 2 ml was developed, followed by separation in a single isocratic run. The concentrations of Na^+ , K^+ , Mg^{2+} and Ca^{2+} determined by ion chromatography were compared to analyses by inductively coupled plasma optical emission spectrometry (ICP-OES).

2. Experimental

2.1. Sampling

Firn core drilling was performed in June 1993 on Grenzgletscher (Monte Rosa massif) at an altitude of about 4200 m above sea level. The core was drilled with a 6 cm diameter electrical drill with an aluminum core barrel. Core sections with a length of 40 to 70 cm were recovered and packed in polyethylene tubes. During sample handling polyethylene gloves were worn to minimize contamination of the core surface. The packed core sections were transported in insulation boxes using dry ice to keep them frozen. Samples were stored in a deep-freeze and further sample preparation was performed in a cold room, maintained at -15°C . Core sections were cut into 5-cm pieces using a stainless steel knife on a PTFE plate. For each 5-cm sample a recoring technique was applied, by cutting out the inner part with a sampling vial (Sarstedt polypropylene, 2.8 cm I.D.). These decontami-

nated samples were melted prior to analysis using a microwave oven. The samples were not filtered before analyses to minimize contamination and sample consumption. The use of unfiltered samples did not influence the analytical performance of the column. More than thousand samples could be analyzed with the same column since only in very few samples a particle sedimentation was visible. All instruments and sample vials were firstly rinsed, secondly soaked for at least one week, and thirdly rinsed again with ultrapure water (18 M Ω cm quality).

2.2. Ion chromatography

Analyses were performed by a Sykam IC system consisting of a pump (S 8110), and a conductivity detector (S 3110, with a cell constant of 0.4), complemented by a Dionex pre-column (CG 12), a Dionex column (CS 12) and a cation self-regenerating suppressor [CSRS-I(4 mm)]. As eluent 6.5 mM methanesulfonic acid was used with a flow-rate of 1 ml/min. The obtained background conductivity was in the range of 0.62–0.88 μS . To inject samples without preconcentration an autosampler (Talbot ASI-5), equipped with a 100- μl sample loop, was used. In order to preconcentrate, the sample loop was replaced by a concentrator column (CG 12). The concentrator column was loaded by pumping 2 ml of the sample through it, using an infusion pump (Predicor 5003-1) equipped with a polyethylene syringe. After switching the injection valve the concentrator column was left in the eluent flow. Data were recorded with a Hewlett-Packard multichannel interface (HP 35900C) connected to a personal computer. Data evaluation was performed by ChemStation software (HP3365).

Standard solutions were prepared with the concentrations of NH_4^+ and Ca^{2+} being about five times higher than those of Na^+ , K^+ , Mg^{2+} , according to the usual composition of the snow samples. Stock standard solutions were prepared by diluting commercial standard solutions (Merck; 1000 mg/kg) every week, which were stored at 5°C in a refrigerator. Standard solu-

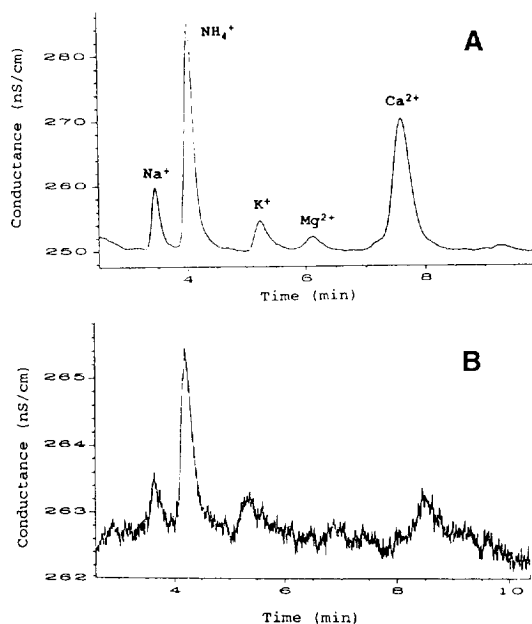


Fig. 1. Chromatograms of the same snow sample with (A) and without (B) pre-concentration, with the following measured concentrations: $1.3 \mu\text{g/kg Na}^+$, $4.5 \mu\text{g/kg NH}_4^+$, $1.8 \mu\text{g/kg K}^+$, $0.3 \mu\text{g/kg Mg}^{2+}$ and $5.7 \mu\text{g/kg Ca}^{2+}$.

tions with concentrations $< 1 \text{ mg/kg}$ were prepared just before calibration. All dilutions of standard solutions and all blank measurements were performed with ultrapure water ($18 \text{ M}\Omega \text{ cm}$ quality).

2.3. ICP-OES

The decontaminated samples were also analyzed by ICP-OES (ARL3410). For this analyses every sample (5 ml) was acidified with HNO_3 to about 0.1 M .

3. Results

Only with the pre-concentration technique the very low cation concentrations in the winter snow samples could be determined, as shown in Fig. 1. The achieved limits of detection and the measuring ranges are listed in Table 1. To compare the achieved limits of detection with already published values, they were defined as the amount of solute producing a signal-to-noise ratio of 3. Previously reported values for Na^+ and Mg^{2+} [8,9] could be improved by a factor of about 2.5. The limit of detection for Ca^{2+} was lower by about a factor of 4 than that from Legrand et al. [9] and was similar to that from Buck et al. [8]. For K^+ similar values were obtained by our method and by Legrand et al. [9] and Buck et al. [8]. When the autosampler was used blank concentrations of about $8 \mu\text{g/kg Ca}^{2+}$ and about $4 \mu\text{g/kg NH}_4^+$ were measured, resulting in relatively high limits of detection. With the pre-concentration technique no Ca^{2+} peak above the background was observed, in-

Table 1
Measuring ranges and limits of detections with and without pre-concentration

Cation	Without pre-concentration		With pre-concentration	
	Measuring range ($\mu\text{g/kg}$)	Detection limit ($\mu\text{g/kg}$)	Measuring range ($\mu\text{g/kg}$)	Detection limit ($\mu\text{g/kg}$)
Na^+	2–200	1.6	0.2–8.0	0.1
NH_4^+	15–200	7.5^a	2.0–15.0	0.4^a
K^+	4–200	3.2	0.2–8.0	0.2
Mg^{2+}	2–200	1.5	0.2–8.0	0.1
Ca^{2+}	20–300	10^a	1.0–30.0	0.2

The limits of detection were defined as the amount of solute producing a signal-to-noise ratio of 3.

^aThe limits of detection were defined as the blank value plus $3 \times$ the standard deviation of the blank value.

dicating that the autosampler caused some contamination. The blank concentration of NH_4^+ could also be reduced but not entirely eliminated. The blank value determined after pre-concentration was in the range of $0.3 \mu\text{g}/\text{kg}$, presumably caused by laboratory air. A dissolution of ammonia from laboratory air causing contamination was also observed by Legrand et al. [11] and Saigne et al. [12]. Our blank value could be kept stable by handling samples, standards, and blanks under identical conditions. The measuring ranges shown in Table 1 were suitable for most samples except for a few summer snow samples which were analyzed after diluting the sample. The relation between NH_4^+ concentration and conductivity was linear up to $200 \mu\text{g}/\text{kg}$.

Ca^{2+} concentrations of the firn core samples analyzed by IC as well as by ICP-OES agreed well (Fig. 2). The same was true for Na^+ , K^+ and Mg^{2+} (not shown). It is assumed that with IC only the dissolved part of the components is detected. However, the very good agreement with ICP-OES indicates that for this concentration range the undissolved mineral dust does

not lead to an underestimation by the IC analyses. Limits of detection achieved by IC for K^+ and Na^+ were one order of magnitude lower than by ICP-OES and they were comparable for Ca^{2+} and Mg^{2+} .

With the developed method concentrations of Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} in 2-ml samples of a firn core have been determined.

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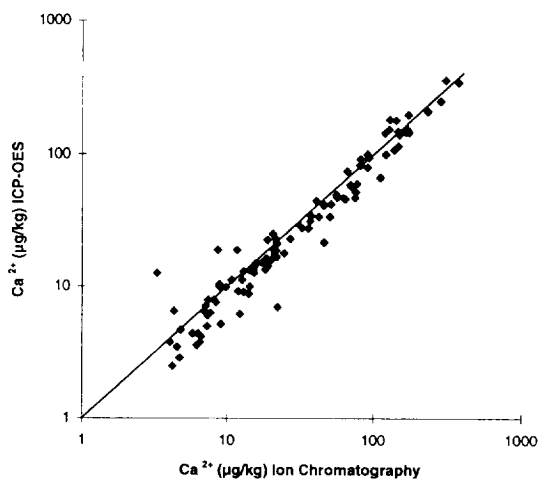


Fig. 2. Concentration of Ca^{2+} measured by ICP-OES as a function of the Ca^{2+} concentration measured by IC. The solid line represents the 1:1 relationship.