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# Determination of major ions in snow and ice cores by ion chromatography

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## ABSTRACT

The determination of major anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) in snow and ice cores by ion chromatography at trace level concentrations (ng/g) is presented. Total acidity ( $\text{H}^+$ ) was determined using an acid titration method in order to complete the ionic balance. Unique sampling techniques and sample preparation methods were developed to avoid contamination of the snow and ice samples.

## INTRODUCTION

Recently, there has been a great amount of work and interest dedicated to the understanding of climatic changes in the paleoenvironment. Among the powerful tools which are available to scientists to examine global climatic records are the physical and chemical analyses of snow and ice cores collected at such locations as Antarctica and Greenland [1,2].

The deposition and subsequent burial of gases, aerosols, and particles onto the glacier surfaces provides a unique archive of paleoenvironmental data. The snow and ice may then be recovered and analyzed for a wide variety of physical properties (*i.e.*, density, texture, stratigraphy) and chemical species (*i.e.*, stable isotopes, radionuclides, major ions).

Since the introduction of ion chromatographic methods in 1975 by Small *et al.* [3], ion chromatography has found widespread applications. Early work by Legrand *et al.* [4] determined major ions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) at ng/g concentrations in Antarctic snow and ice cores by ion

chromatography. Mayewski *et al.* [5] analyzed a South Greenland ice core for trace level anion ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) concentrations by ion chromatographic methods. This paper describes an ion chromatographic method for determining major anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) at trace level concentrations (ng/g) without the use of concentrator columns. The mono- and divalent cations were separated in a single isocratic run via column switching. Total acidity ( $\text{H}^+$ ) was determined by using an acid titration method developed by Legrand *et al.* [6] in order to complete the ionic balance. Unique sampling techniques and sample preparation methods were developed to avoid contamination of the snow and ice samples.

## EXPERIMENTAL

### *Sampling techniques and sample preparation*

Depending on the sample density (snow, firn, ice), different sampling techniques and sample preparation methods were required to avoid contamination of the samples. Field sampling and processing personnel handling the snow and ice samples wore

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non-particulating suits, face masks, and polyethylene gloves to minimize sample contamination. All sample containers, sampling tools, and processing equipment and clothing that came into contact with the samples were cleaned using Milli-Q ultrapure water (Millipore, Bedford, MA, USA). The cleaning procedure consisted of rinsing three times, followed by an extensive soaking period of 1–6 months, and rinsed for a final three times prior to use. All materials were tested for possible contamination using the ion chromatographic method. The samples were processed in a cold room ( $-20^{\circ}\text{C}$ ) and kept frozen prior to the laboratory sample preparation step.

Snow pit samples were collected using specially designed sampling tools and transferred to 125-ml polypropylene containers with polyethylene screw caps (Becton-Dickinson, Rutherford, NJ, USA). The snow samples were transferred directly to 250-ml polypropylene containers (Nalge, Rochester, NY, USA) in the laboratory. The samples were melted using a circulating hot water bath.

Firn and ice core samples were processed using commercially available Sears Craftsman bandsaws (Sears Roebuck, Chicago, IL, USA) after careful and thorough cleaning to remove all grease and dust. Tabletops, saw guides, and tools were modified or covered with either Teflon or Plexiglas. Lexan or flame-hardened steel blades (Sears Roebuck) were used. Firn and ice core samples were processed at measured intervals by removing the outside sections of the core to obtain a contamination-free center. Samples were then placed into polyethylene bags (Nasco-West, Modesto, CA, USA) and removed to a clean freezer for further processing, if necessary. At the time of laboratory analysis, samples were transferred to 250 or 500 ml polypropylene containers (Nalge) for melting. Ice samples were rinsed with Milli-Q ultrapure water (25–35%, w/w, sample weight loss) using a pair of surgical stainless steel tweezers prior to the melting of the sample to remove any possible contamination.

All melted laboratory samples were swirled at room temperature to obtain a homogenous solution, then 5.0-ml aliquots were placed into polypropylene sample tubes (Helena Plastics, San Rafael, CA, USA) for immediate analysis or refrozen. The laboratory sample preparation step was performed in rapid fashion on open laboratory benches without a clean hood.

#### *Acidity measurements*

Total acidity ( $\text{H}^+$ ) was determined by using an acid titration method developed by Legrand *et al.* [6] with slight modifications to the original method.

#### *Ion chromatography*

A Dionex Series 4000i ion chromatograph (Dionex, Sunnyvale, CA, USA) was used for the determination of the major ions. The Dionex Series 4000i ion chromatograph was divided into two dedicated systems (anion and cation) and consisted of: two gradient pump modules, two conductivity detector modules (output range =  $3\ \mu\text{s}$ ), and LCM-2 chromatography module. The samples for each system were introduced into 0.5-ml sample loops via two fixed-speed peristaltic pumps which initially draws approximately 1.0 ml of Milli-Q ultrapure water followed by approximately 2.0 ml of sample guaranteeing no cross contamination from the previous sample. The sampling system was automated using two AutoAnalyzer autosamplers. All time events and data collection were processed through the Dionex Autoion 450 Data software package and Advanced Computer Interface unit via personal computer. The analog output was recorded on two strip-chart recorders.

For the anion chromatographic system, the columns used for all experiments were a Dionex IonPac AS4A separator column with an Dionex IonPac AG4 guard column. A Dionex anion micro-membrane suppressor was placed in line prior to the conductivity cell resulting in a background conductivity of approximately 11.0–15.0  $\mu\text{S}$ . The mobile phase was 0.0018  $M$   $\text{Na}_2\text{CO}_3$ –0.0017  $M$   $\text{NaHCO}_3$ ; 0.0125  $M$   $\text{H}_2\text{SO}_4$  was used as the regenerant. The flow-rates for the mobile phase and regenerant were 2.0 and 4–5 ml/min, respectively.

For the cation chromatographic system, the columns used for all experiments were Dionex IonPac Fast Cation I and Cation II columns in conjunction with a high-pressure switching valve in order to separate the mono- and divalent cations in one isocratic run. A Dionex cation micromembrane suppressor was placed in line prior to the conductivity cell resulting in a background conductivity of approximately 450 nS–1.5  $\mu\text{S}$ . The mobile phase was 19 mM  $\text{HCl}$ –0.3 mM DL-2,3-diaminopropionic acid monohydrochloride (DAP); 100 mM tetrabutylammonium hydroxide (TBAOH) was used as the regenerant. The flow-rates for the mobile phase and

TABLE I  
LIMITS OF DETECTION ESTIMATED FOR THE ION CHROMATOGRAPHIC METHOD

Ion	Concentration (ng/g)	Ion	Concentration (ng/g)
Cl <sup>-</sup>	0.5	NH <sub>4</sub> <sup>+</sup>	0.2
NO <sub>3</sub> <sup>-</sup>	0.5	K <sup>+</sup>	0.1
SO <sub>4</sub> <sup>2-</sup>	0.5	Mg <sup>2+</sup>	0.1
Na <sup>+</sup>	0.1	Ca <sup>2+</sup>	0.1

regenerant were 3.0 and 10–15 ml/min, respectively. The cation regenerant waste (TBACl) was collected and recycled off-line using a series of Dionex Auto-Regen cation cartridges.

RESULTS AND DISCUSSION

Due to the large sample volumes available (10–25 ml), an injection volume of 0.5 ml was selected to avoid the use of concentrator columns. Larger injection volumes were not used because of the broad water peak resulting in poor resolution of the early eluting peaks. Excellent sensitivity was achieved for trace level concentrations (ng/g) for the ions. Limits of detection for the ion chromatographic method are shown in Table I. The limit of detection for the

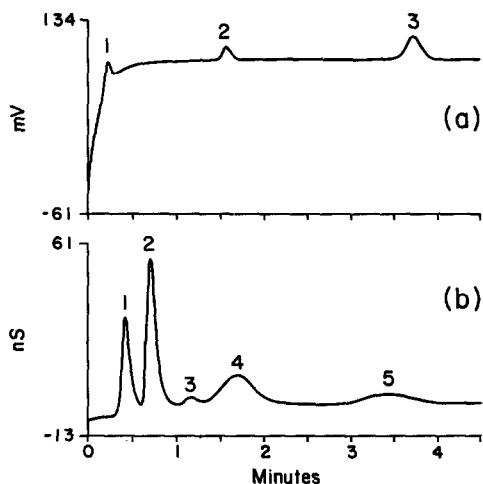


Fig. 1. (a) Anion standard solution: 1 = Cl<sup>-</sup> (3 ng/g), 2 = NO<sub>3</sub><sup>-</sup> (5 ng/g), 3 = SO<sub>4</sub><sup>2-</sup> (10 ng/g). (b) Cation standard solution: 1 = Na<sup>+</sup> (2 ng/g), 2 = NH<sub>4</sub><sup>+</sup> (2 ng/g), 3 = K<sup>+</sup> (0.5 ng/g), 4 = Mg<sup>2+</sup> (1 ng/g), 5 = Ca<sup>2+</sup> (1 ng/g).

chromatographic method was defined as the amount of solute producing a signal-to-noise ratio of 2–3.

Isocratic separations for anion and cation standard solutions are shown in Fig. 1. The anion system was significantly more stable than the cation system in terms of the daily background conductiv-

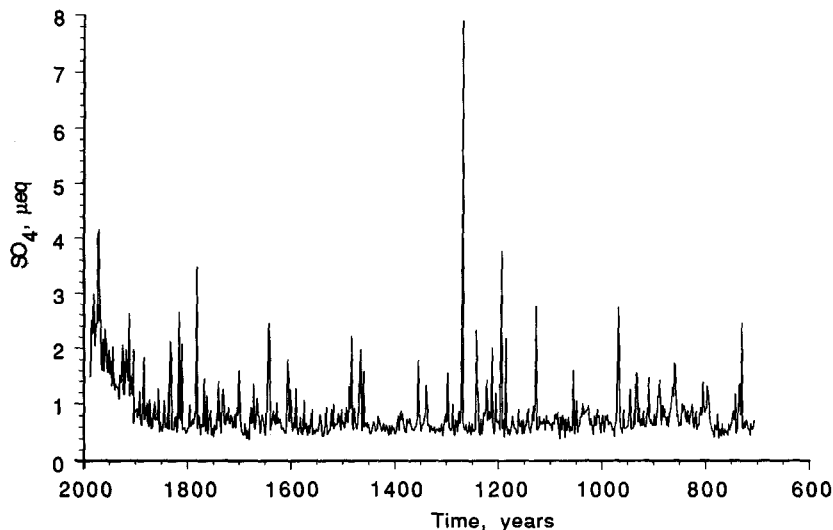


Fig. 2. Time-series of non-sea-salt sulfate concentration (in μequiv.) collected in Central Greenland.

ity. This problem was a result of the quality of recycled cation regenerant (TBAOH). The cation regenerant waste (TBACl) was collected and recycled off-line via a series of Dionex AutoRegen cation cartridges. The active sites in the cartridges are exhausted over time causing the cation regenerant waste (TBACl) not to be fully regenerated back to its original form (TBAOH). As a result, the daily background conductivity increased over time. The AutoRegen cation cartridges were regenerated with 1.0 M NaOH on a weekly basis to extend the life of the cartridges. It was found that the background conductivity of the cation system was influenced greatly by the flow-rate of the regenerant through the micromembrane suppressor.

The melting of all laboratory samples were conducted rapidly on open laboratory benches and not under a clean hood. A contamination control study conducted in our laboratories showed that the ammonium concentration in sample container blanks was approximately five times greater when sampled under a clean hood. This anomaly is due to the increased gas exchange caused by the continuous airflow of the clean hood. To further reduce the ammonium blank value to less than 0.5 ng/g, all sample tubes were kept tightly capped until approximately 1.0 min prior to the sample injection on the ion chromatograph. No chromatographic interferences were observed and filtering the samples was not necessary.

The ion chromatographic method described has been used for the investigation of various glaciochemical studies. An example is provided in Fig. 2 with the non-sea-salt sulfate time-series for the upper section of an ice core retrieved in Central Greenland as part of the Greenland Ice Sheet Pro-

ject Two (GISP II). Detailed discussions concerning the glaciochemical data sets are presented in several of the references 7–12.

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