



Capillary ion chromatography with on-column focusing for ultra-trace analysis of methanesulfonate and inorganic anions in limited volume Antarctic ice core samples



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ABSTRACT

Preservation of ionic species within Antarctic ice yields a unique proxy record of the Earth's climate history. Studies have been focused until now on two proxies: the ionic components of sea salt aerosol and methanesulfonic acid. Measurement of the all of the major ionic species in ice core samples is typically carried out by ion chromatography. Former methods, whilst providing suitable detection limits, have been based upon off-column preconcentration techniques, requiring larger sample volumes, with potential for sample contamination and/or carryover. Here, a new capillary ion chromatography based analytical method has been developed for quantitative analysis of limited volume Antarctic ice core samples. The developed analytical protocol applies capillary ion chromatography (with suppressed conductivity detection) and direct on-column sample injection and focusing, thus eliminating the requirement for off-column sample preconcentration. This limits the total sample volume needed to 300 μ L per analysis, allowing for triplicate sample analysis with <1 mL of sample. This new approach provides a reliable and robust analytical method for the simultaneous determination of organic and inorganic anions, including fluoride, methanesulfonate, chloride, sulfate and nitrate anions. Application to composite ice-core samples is demonstrated, with coupling of the capillary ion chromatograph to high resolution mass spectrometry used to confirm the presence and purity of the observed methanesulfonate peak.

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1. Introduction

Antarctic ice cores provide an important natural repository for chemical and biochemical proxies which allow interpretation of ancient climatic conditions. Inorganic ions form an important group of chemical proxies, giving an insight into seasonal weather cycles and providing accurate tie-points for volcanic events, among other observations. To provide a valid proxy response, these ions must yield a proportional response to a particular event or cycle, and remain in a stable state with minimal diffusion within glacial ice following their deposition. Estimation of the extent of winter sea ice is a valuable climate record, for which the concentration of methanesulfonic acid (MSA) has proved reliable. It has a single source from marine algae and the highest producers in the southern ocean are

associated with sea ice. MSA reaches a peak concentration in winter, when sea ice is at its maximum extent [1]. In the generation of such proxy profiles, to obtain suitable temporal resolution, a large number of samples analyses are necessary (typically 4000 samples for a 300 year record). This presents a significant challenge, as the costs associated with the collection and preparation of such ice core samples are extraordinarily high (often running into millions of dollars for sample collection), with huge demand from laboratories worldwide and collaborating research groups for aliquots generated from the cores.

In a recent review on sea ice proxies, Abram et al. [2] summarised the reported MSA sea ice data for Antarctic ice cores and snow pits from the 1990s to date. In most reported cases, to provide a quantitative measurement of methanesulfonate, as well as other ions of interest, samples are melted to their liquid phase and are typically analysed using ion chromatography (IC) with suppressed conductivity detection. However, most IC approaches for trace analysis need in the order of 1–5 mL of sample volume for each

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measurement, based upon the need for pre-column sample preconcentration for ions present at ultra-trace concentrations [3]. Such is the case of the IC method developed in 2001 by Curran et al. [4] in which the simultaneous determination of methanesulfonate, chloride, sulfate and nitrate anions in ice core samples was achieved through a combination of sample preconcentration and gradient elution using a sodium tetraborate eluent. The LODs were the lowest reported at that time but the sample volume required was 5 mL. Similarly, in 2006 Morganti et al. [5] developed a method which claimed significantly lower LODs than those reported previously in the literature, but which also required a preconcentration column. Anions, including fluoride and methanesulfonate, were determined using a relatively small sample volume (although still requiring 1.5 mL per single analysis). The methods of Curran et al. [4] and Morganti et al. [5] were applied to the analysis of a large number of samples from Law Dome, East Antarctica, and to the analysis of samples from Dome C ice core, respectively. Both methods were also applied in later studies carried out at Mount Brown, Wilhelm II Land (East Antarctica) by Foster et al. [6], Talos Dome (East Antarctica) by Becagli et al. [7] and, most recently, by Criscitiello et al. [8,9] at coastal West Antarctica.

Other reported IC methods have required two separate IC systems, one for the determination of inorganic anions and a second system for the determination of methanesulfonate, resulting in an increase of the total sample amount required [10–16]. The limits of detection (LODs) were of a suitably low concentration ($\mu\text{g L}^{-1}$) but large injection loops were employed for ion concentration, with the total amount of sample required to carry out the two sets of analyses being between 1 and 2 mL. Moreover, in many such studies, certain ions of potential significance (e.g. fluoride—a potential time-point marker from volcanic activity) were not always discussed [13–15].

Various other records of methanesulfonate and inorganic anions in ice cores have been reported over the past decade obtained using IC [16–21], although in many instances reporting of actual analytical method details is limited. For example, methanesulfonate and inorganic anions in ice cores from the high plateau of Dronning Maud Land (DML), Antarctica, were investigated by Fundel et al. [19] in 2006, based on the methods previously developed by Traufetter et al. [20] and Göktas et al. [21]. Little information is given by the authors in terms of required sample amount and whether or not they employed a preconcentrator column.

Whilst the mentioned methods above have provided the desired selectivity and sensitivity for certain target ions, collectively they exhibit a number of common, yet significant, shortcomings. The volume requirements are impractical given the high value of each sample and the need for improved analytical precision (demanding duplicate and even triplicate sample analysis). Moreover, handling of large sample volumes and off-column preconcentration procedures commonly incur a high risk of sample contamination and/or carryover issues. Thus currently there is a need for new analytical methods which are capable of providing selectivity and sensitivity equal to, or greater than, existing technologies, but which require 10–100 fold less sample volume.

Capillary ion chromatography (Cap-IC) is an important new separation technology wherein the column size, injection volumes and flow-rates are reduced by a factor of 10–100. Cap-IC offers a potential solution to limited sample volume issues which have emerged for ice cores, together with other general benefits such as eluent economy (~ 5 L/year), improved performance from systems capable of continuous long term operation, and increased mass sensitivity [3,22]. For the analysis of inorganic ions, Cap-IC has also been described as a more suitable approach than other capillary separation techniques, such as capillary electrophoresis (CE), due to its favourable reliability, sensitivity and stability [23]. However, Cap-IC is still a relatively new technique, and so to-date, has not

been applied to the analysis of ice core samples, and its potential to address some of the aforementioned limitations of standard-bore IC methods has not been explored. Therefore, herein a new Cap-IC based analytical method has been developed for quantitative analysis of organic and inorganic anions from limited volume Antarctic ice core samples. The study was focused on three main goals, namely to provide the required chromatographic selectivity for organic and inorganic anions (specifically for methanesulfonate in the presence of much greater concentrations of common matrix anions such as chloride, sulfate and nitrate), to eliminate the pre-column concentration step, and to use the minimum amount of sample required to achieve the necessary LODs.

2. Experimental

2.1. General procedures for trace and ultra-trace anion analysis

There are many sources of contamination that can interfere with reliable and consistent anion determination at trace levels. The sources are widespread and include the operator, laboratory material, consumables, equipment and atmosphere. Strict adherence to established work routines throughout the analytical process was found to be essential in this work to obtain reproducible blanks. These routines included the exclusive use of freshly generated 18.2 M Ω cm deionised water (DIW) supplied by a Milli-Q Element system (Millipore, USA), the use of Rainin Bioclean pipette tips (Mettler Toledo, Australia), and the use of polypropylene/polyethylene/Nalgene containers and polyethylene gloves. Solution preparation within an Air Science laminar flow cabinet (Bio-Cabinets, Australia) was proven to help avoid contamination from the laboratory atmosphere. Additionally, a rigorous cleaning protocol for all laboratory materials, consisting of soaking all plastic-ware, including vials, caps, septa, containers and tips, for 3 days in DIW, with rinsing every 24 h, was also applied.

2.2. Standards

High-purity DIW was used for preparation of standard solutions. 1000 mg L $^{-1}$ stock solutions fluoride, methanesulfonate, chloride, sulfate and nitrate, were prepared by dissolving appropriate amounts of sodium fluoride (R. P. Normapur, purity 99%), sodium methanesulfonate (Aldrich, purity 98%), sodium chloride (Sigma-Aldrich, purity >99%), sodium sulfate (AnalaR-BDH, purity >99%) and sodium nitrate (Griffin, purity >98%). All these solutions were kept at 4°C and stored in polypropylene containers until used. Working solutions, containing a mixture of all anions at concentrations similar to those expected in ice cores samples, were prepared daily.

2.3. Samples and procedural blanks

Ice core samples and procedural blanks were produced by manual scraping 2 mm of ice from the outside of a 3 × 3 cm ice stick, and sectioning into samples (typical 5 cm long), using the method described in Curran et al. [4]. Procedural blank ice was produced by freezing Milli-Q water, and cutting 3 × 3 cm ice sticks from this frozen Milli-Q water [4]. Two laboratory reference materials (LRMs) were analysed for the purposes of method validation for the study reported here. LRMs were prepared by combining the small amount of remaining samples previously analysed by the method developed by Curran et al. [4]. The remaining samples (typically >1 mL) were combined in clean plastic Nalgene bottles to provide standard samples from two particular ice core sites. LRM1 corresponds to the firn core drilled at the W10k site at Law Dome, East Antarctica in the austral summer of 2008/2009. This site is 100 km from the coast and 1300 m elevation. LRM2 was prepared from a firn core drilled at

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