Essential Role of Ion Chromatography in Constructing Ice Core Paleoclimatic Records

by Estrella Sanz Rodriguez[a,], Paul R. Haddad[a] and Brett Paull[a]*

[a]Australian Centre for Research on Separation Science, School of Physical Sciences, University of Tasmania, GPO Box 252-75, Hobart, Tasmania 7001, Australia.

**Corresponding author: Ph: +61 3 6226 1073; Fax: +61 3 6226 2858.*

E-mail address: Estrella.SanzRodriguez@utas.edu.au

This short review highlights the application of modern ion chromatography to the quantification of the most significant inorganic anions found in such ice core samples, including fluoride, chloride, sulphate and nitrate, and small organic acids, such as methanesulfonic acid. The most significant challenges associated with this important application of modern ion chromatography are discussed, together with the various solutions developed by the leading research groups involved. The inclusion of capillary ion chromatography for the determination of inorganic and organic anions in ice core samples is also included, specifically with regard to its potential when hyphenated with mass spectrometry for future ice core paleoclimate studies.

Glacial–interglacial cycles can be visible in a variety of marine and terrestrial paleoclimatic records, including for example, deep sea sediments, continental deposits of flora, fauna and loess, and ice cores [1]. Of these examples, ice cores specifically provide an important natural long-term and stable repository for chemical and biochemical proxies for the study of climate change. To provide useful information, such proxies must yield a proportional response to a particular event or cycle, and remain in a stable state with minimal diffusion within the glacial ice following their deposition [2]. Among the various ice core proxies, inorganic anions such as chloride, sulphate, nitrate and fluoride, form an important group, which together support investigations into ancient climatic conditions, and provide an insight into seasonal weather cycles - in addition to provision of accurate tie-points for volcanic events, among other globally significant events.

A significant element within the polar climate system, and subsequently a vital contributor to wider paleoclimate studies, is the Antarctic sea ice, and records of its annual cycle and extension are of particular importance. However, a lack of satellite observations of the sea ice before the 1970s means that there is a lack of reliable data when assessing the sensitivity and rate at which sea ice dynamics are involved in amplifying or revealing climate changes. Over the last ten years, considerable research efforts have been focused on the search for a useful proxy to reliably estimate the annual extent of sea ice, leading to the consensus that concentration of the organic anion, methanesulfonic acid (MSA), is indeed a dependable proxy for such information [3].

Ion chromatography (IC) with suppressed conductivity detection is the gold standard analytical technique

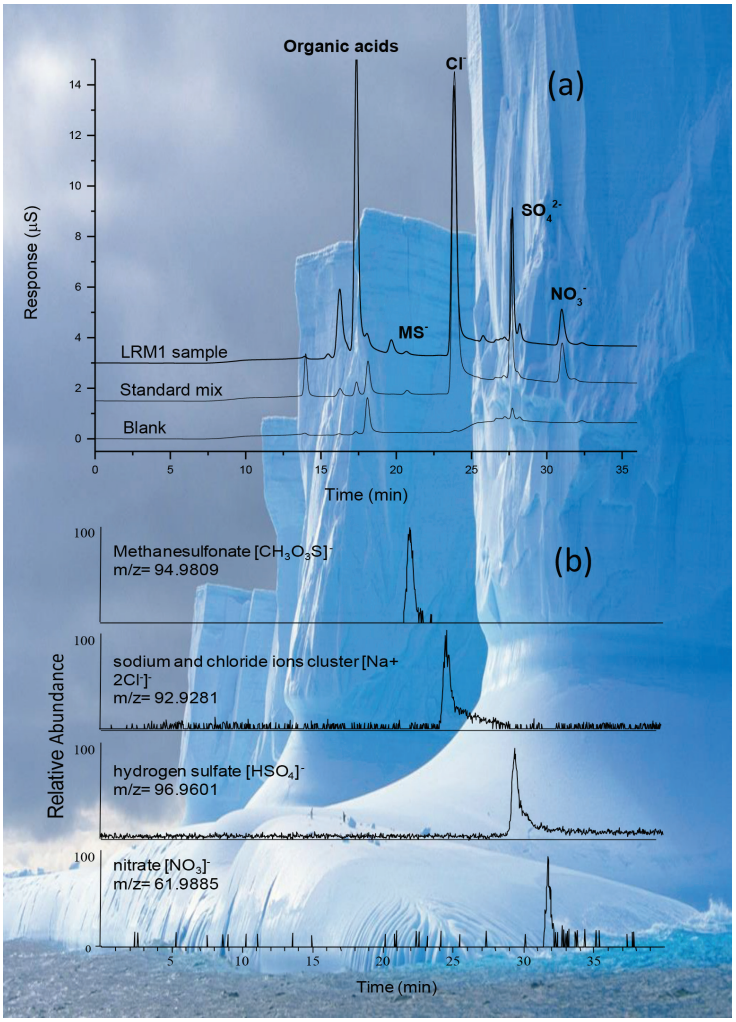

Figure 1. (a) Cap-IC chromatogram obtained for LRM1 standard, blank and standard solution containing fluoride (F^-) and methanesulfonate (MS^-), 10 µg L^{-1}; chloride (Cl^-), 200 µg L^{-1}; sulphate (SO_4^{2-}) and nitrate (NO_3^-), 50 µg L^{-1}. (b) Extracted ion chromatograms for selected m/z obtained for the analysis of LRM1 sample by Cap-IC-HRMS.

to provide quantification of inorganic and organic anions in these highly valuable ice core samples. Ice core samples are first melted to their liquid phase, either on- or off-line, and analysed either immediately or typically within 24 h [2]. IC provides the quantitative performance required for this type of analysis, with many of the proxies present at trace levels, based upon its continued development over the past 35 years as the only truly reliable method for the simultaneous determination of inorganic anions and small organic anions [4].

Inorganic anions present within ice cores originate from various sources, both marine and atmospheric, including particulate contributions. While chloride, sulphate and nitrate are found at microgram- milligram per litre concentrations, others such as fluoride are normally only present at ultra-trace levels, typically less than 500 nanograms per litre. MSA is also found in ice core samples at low microgram per litre concentrations, but in this case the origin is specifically from biological activity, being the only known source for MSA [2,6,8,13]. MSA is a product of the oxidation of dimethylsulphide (DMS), which is produced by phytoplankton, particularly phytoplankton species associated with sea ice. As such it is found in relatively high levels in the sea ice zone around Antarctica [5,6]. This represents the source of MSA found within ice core samples, having been transported there via the atmosphere and deposited during precipitation events. This is then retained within the deposited subsequently compacted ice. Currently, assembling ice core records based upon these various anions typically involves a minimum of one IC measurement for every 5 cm of ice core, corresponding to time periods ranging from about 1 year (for the shallow part of the ice core) to more than 40 years (at the deeper compacted zones of the ice core). This means that the sub-sample volume available for IC is usually around 4–5 mL, or less if higher resolution is desired [7].

However, constructing such records from an ice core using IC presents a number of analytical and practical challenges, essentially centred on contamination, selectivity, sensitivity and analysis costs. There are many sources of contamination that can interfere with reliable and consistent anion determination when working at such trace levels. The sources are widespread and include the operator, laboratory material, consumables, equipment and atmosphere. Thus, strict adherence to well-established sample handling protocols throughout the analytical process is essential. Obviously, separation selectivity leading to the baseline separation o fall anions of interest is required if reliable quantification is sought. However, this is also a challenge as target anions are present across a very wide range of concentrations, from nanogram per litre for fluoride and MSA to milligram per litre for some matrix ions, such chloride or sulphate. This diversity has necessitated the use of columns with high selectivity (and ion-exchange capacity), ideally compatible with hydroxide-based gradient elution, or alternatively the use of more than one chromatographic system (multidimensional approaches). Specifically, the separation and quantification of fluoride and MSA can prove difficult due to weak retention on most IC stationary phases, and the co-elution of MSA and other organic acids, such as acetate and formate, which can often be present within samples from contamination, also poses a challenge. The detection sensitivity of suppressed IC is known to be excellent for relatively simple sample matrices, however the low microgram per litre concentrations of certain target ions often requires on- or off-line sample preconcentration and/or the injection of large sample volumes. As a consequence, most former IC methods developed for this type of study have required in the order of 1–5 mL of sample volume for each measurement. This volume requirement is nowadays impractical given the very valuable nature of each ice core 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 carry-over issues. Finally, in the generation of such proxy profiles, to obtain improved temporal resolution, a large number of samples analyses are necessary (typically 4000 samples for a 300 year record). This demand for increased sample numbers, combined with the inherent value of each sample (arising from the huge costs associated with core sample collection and preparation), provides a significant challenge in terms of costs and time.

Over the past decade or so, there have been many studies carried out generating these important records, whilst simultaneously attempting to solve the accompanying analytical challenges. For example, an IC method developed in 2001 by Curran *et al.* [8] provided for the simultaneous determination of MSA, chloride, sulphate and nitrate anions in ice core samples, based upon the use of a single analytical column and a combination of in-line sample preconcentration and gradient elution using a sodium tetraborate eluent. The limits of detection (LODs) were the lowest reported at that time, although the sample volume required was 5 mL. Similarly, in 2006 Morganti *et al.* [7] developed a method which claimed significantly lower LODs than those reported previously in the literature, but which also required a preconcentration column. In this case, anions, including fluoride and MSA, were determined using a relatively small sample volume (although still requiring 1.5 mL per single analysis). The methods of Curran *et al.* [8] and Morganti *et al.* [7] 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. These methods were also applied within later studies carried out at Mount Brown, Wilhelm II Land (East Antarctica) by Foster *et al.* [9], Talos Dome (East Antarctica) by Becagli *et al.* [10] and, most recently, by Criscitiello *et al.* [11,12] at coastal West Antarctica.

Cole-Dai *et al.* [13] obtained detection limits similar to those obtained by Morganti *et al.* [7], using an approach which saw continuous flow analysis (CFA) coupled with IC (CFA-IC), although the method was not applied to the determination of MSA. The use of CFA for on-line sample handling/preparation was first proposed by Sigg *et al.* in 1994 [14], after which Huber *et al.* developed this approach for the determination of organic and inorganic ions in ice cores [15]. The method combined the advantages of CFA (less-time consuming sample preparation and a lower risk of contamination) with the advantages of IC, including simultaneous multi-analyte quantification for both organic and inorganic species. However, in this example almost 2 mL of sample were required for each analysis, and the process resulted in the highly valuable ice core being completely (continuously) melted, removing the possibility of replicates or to continue analysing the inner fraction for other purposes.

Other reported IC methods have required two separate chromatography systems, one for the determination of inorganic anions and a second system for the specific determination of MSA. Obviously this increases the complexity and cost of the analysis, but most significantly also increases the total sample amount required [16-22]. In these examples, LODs were in the low $\mu g\ L^{-1}$ range, but large injection loops were employed for ion preconcentration, with the total amount of sample required to carry out the two sets of analyses being between 1

and 2 mL. In many such studies, certain ions of potential significance (e.g. fluoride—a potential time-point marker from volcanic activity) were not always discussed [19-21].

Various other records of MSA and inorganic anions in ice cores have been reported over the past decade, obtained using IC [22–27], although in many instances reporting of actual analytical method details has been rather limited. For example, MSA and inorganic anions in ice cores from the high plateau of Dronning Maud Land (DML), Antarctica, were investigated by Fundel *et al.* [25] in 2006, based on the methods previously developed by Traufetter *et al.* [26] and Göktas *et al.* [27]. However, in each case, little information is given by the authors in terms of required sample amount and whether or not they employed a preconcentrator column.

Recently, capillary ion chromatography has become a commercial reality (Cap-IC). Despite having a relatively long history within the research lab [28], and offering many advantages, such as a low consumption of reagents, high mass sensitivity and efficiency, Cap-IC has not gained popular acceptance until relatively recently [29]. One of the major reasons for this was the limited variety of available columns. Today Cap-IC columns are readily available packed with the same material as the equivalent standard bore version, and providing the same separation selectivity and performance, yet requiring 100 fold less eluent flow and sample volumes typically below 0.4 µL. Commercial high-pressure Cap-IC systems include the use of robust capillary suppressors and capillary conductivity detectors, with flow and cell volume being optimised for capillary applications.

The emergence of Cap-IC technology has coincided with the call from those involved in ice core studies for new analytical methods which are capable of providing selectivity and sensitivity equal to, or greater than, previous approaches, but which require 10-100 fold less sample volume. Recently, work within the Australian Centre for Research on Separation Science (ACROSS), based upon a collaborative project with the Australian Antarctic Division, has resulted in the development of a Cap-IC method (Reagent-Free™ hydroxide eluent generation Cap-IC (RFIC™) and suppressed conductivity detection) for the simultaneous determination of organic and inorganic anions (including MSA) in ice core samples [30]. Using direct on-column sample injection and focusing, the elimination of the requirement for off-column sample preconcentration was shown, and the required sample volume was reduced to 300 µL per analysis, thus providing the possibility for triplicate analyses from less than 1 mL of sample. This represented a major step forward in ice core analysis by significantly reducing the volume of ice required for IC analysis, thereby freeing up potential samples for other uses. Moreover, for the first time Cap-IC was coupled to high resolution mass spectrometry (HRMS) to confirm the presence and identity of MSA, with chloride, sulphate and nitrate in an Antarctic ice core laboratory reference material 1 (LRM1). Figure 1(a) shows a Cap-IC chromatogram obtained for the LRM1 standard, blank and standard solution containing fluoride, MSA, chloride, sulphate and nitrate. As can be observed, several anions are eluted between fluoride and methanesulfonate. Two of these were tentatively identified by standard retention times as acetate and formate. While the other contaminants were also likely to be organic acids, their identities were not seen as crucial to the outcomes of that study. However, in order to confirm the specificity of the method for methanesulfonate, which elutes close to the same region as those known and unknown organic acids, the LRM1 sample was again analysed using the Cap-IC method coupled with mass spectrometry detection. The identity of methanesulfonate, sulphate (as hydrogen sulphate) and nitrate was confirmed based upon their accurate mass and retention time (with a retention time delay from coupling of ~2 min), as can be seen in Figure 1(b).

The application of the Cap-IC system with eluent generation and capillary suppression technology converts the hydroxide eluent to water prior to entering the mass spectrometer. This, together with the low flow-rates employed in Cap-IC, makes the hyphenation of Cap-IC and mass spectrometry an interesting and promising technique for various applications in the near future, providing species identification, structural interpretation and lower LODs. Specifically in the field of ice core studies, coupling of these technologies could assist in the search for new or alternative climate proxies which may support new climate models.

Acknowledgments

Financial support from Ian Potter Foundation Grant 20160229 is gratefully acknowledged.

References

[1] J.R. Petit, J. Jouzel, D. Raynaud, N.I. Barkov, J.M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V.M. Kotiyakov, M. Legrand, V.Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E. Saltzman,M. Stievenard, Nature 399 (1999) 429.

[2] N.J. Abram, E.W. Wolff, M.A.J. Curran, Sci. Rev. 79 (2013) 168.

[3] M.A.J. Curran, T.D. van Ommen, V.I. Morgan, K.L. Phillips, A.S. Palmer, Science 302 (2003)1203.

[4] P.R. Haddad, P.N. Nesterenko, W. Buchberger, J. Chromatogr. A 1184 (2008) 456.

[5] M.A.J. Curran, G.B. Jones, J. Geophys. Res. 105, 20451 (2000).

[6] S.M. Turner, P.D. Nightingale, W. Broadgate, P.S. Liss, Deep-Sea Research Part II-Topical Studies in Oceanography 42 (4-5) (1995) 1059.

[7] A. Morganti, S. Becagli, E. Castellano, M. Severi, R. Traversi, R. Udisti, Anal. Chim. Acta 603 (2) (2007) 190.

[8] M.A. Curran, A.S. Palmer, J. Chromatogr. A 919 (2001) 107.

[9] A.F.M. Foster, M.A.J. Curran, B.T. Smith, T.D. van Ommen, V.I. Morgan, Ann. Glaciol. 44 (2006) 429.

[10] S. Becagli, E. Castellano, O. Cerri, M. Curran, M. Frezzotti, F. Marino, A. Morganti, M. Proposito, M. Severi, R. Traversi, R. Udisti, Atmos. Environ.43 (5) (2009) 1051.

[11] A.S. Criscitiello, S.B. Das, M.J. Evans, K.E. Frey, H. Conway, I. Joughin, B. Medley, E.J. Steig, J. Geophys. Res. 118 (2013) 118.

[12] A.S. Criscitiello, S.B. Das, K.B. Karnauskas, M.J. Evans, K.E. Frey, I. Joughin, E.J. Steig, J.R. McConnell, B. Medley, J. Clim. 27 (2014) 1343.

[13] J. Cole-Dai, D.M. Budner, D.G. Ferris, Environ. Sci. Technol. 40 (2006) 6764.

[14] A. Sigg, K. Fuhrer, M. Ankiln, T.Staffelbach, D. Zurmuhlet, Environ. Sci. Technol. 28 (1994) 204.

[15] T.M. Huber, M. Schwikowski, H.W. Gäggeler, J. Chromatogr. A 920 (2001) 193.

[16] R. Udisti, S. Bellandi, G. Piccardi, Fresenius J. Anal. Chem. 349 (1994) 289.

[17] G.C. Littot, R. Mulvaney, R. Röthisberger, R. Udisti, E.W. Wolff, E. Castellano, M. de Angelis, M.E. Hansson, S. Sommer, J.P. Steffensen, Ann. Glaciol. 35 (2002) 299.

[18] S. Becagli, S. Benassai, E. Castellano, O. Largiuni, A. Migliori, R. Traversi, O. Flora, R. Udisti, Intern. J. Environ. Anal. Chem. 84 (2004) 523.

[19] N.A.N. Bertler, P.A. Mayewski, P.J. Arrett, S.B. Sneed, M.J. Handley, K.J. Kreutz, Ann. Glaciol. 39 (2004) 139.

[20] R. Udisti, S. Becagli, S. Benassai,

E. Castellano, I. Fattori, M. Innocenti, A. Migliori, R. Traversi, Ann. Glaciol.39 (2004) 53.

[21] R.H. Rhodes, N.A.N. Bertler, J.A. Baker, S.B. Sneed, H. Oerter, K.R. Arrigo, Geophys. Res. Lett. 36 (2009) L10704.

[22] R. Traversi, S. Becagli, E. Castellano, O. Cerri, A. Morganti, M. Severi, R. Udisti, Microchem. J. 92 (2009) 7.

[23] N.J. Abram, E.R. Thomas, J.R. McConnell, R. Mulvaney, T.J. Bracegirdle, L.C. Sime, A.J. Aristarain, J. Geophys. Res.: Atmos. 115 (2010) D23101.

[24] N.J. Abram, R. Mulvaney, C. Arrowsmith, J. Geophys.Res.: Atmos.116 (2011) D20116,

[25] F. Fundel, H. Fischer, R. Weller, F. Traufetter, H. Oerter, H. Miller, J. Geophys. Res. 111 (2006) D04103

[26] F. Traufetter, H. Oerter, H. Fischer, R. Weller, H. Miller, J. Glaciology 50 (2004) 137.

[27] F. Göktas, H. Fischer, H. Oerter, R. Weller, S. Sommer, H. Miller, Ann. Glaciol. 35 (2002)347.

[28] S. Rokushika, Z.Y. Qiu, Z.L. Sun, H. Hatano, J. Chromatogr. 280 (1983)69.

[29] P.R. Haddad, P.N. Nesterenko, W. Buchberger, J. Chromatogr. A 1184 (2008) 456.

[30] E. Sanz Rodriguez, S. Poynter, M.Curran, P.R. Haddad, R. A. Shellie, P.N. Nesterenko, B. Paull, J. Chromatogr. A 1409 (2015) 182.