Comparison of analytical methods used for measuring major ions in the EPICA Dome C (Antarctica) ice core

GENEVIEVE C. LITTOT, ROBERT MULVANEY, REGINE RÖTHLISBERGER, ROBERTO UDISTI, ERIC W. WOLFF, EMILIANO CASTELLANO, MARTINE DE ANGELIS, MAGARETA E. HANSSON, STEFAN SOMMER, JÖRGEN P. STEFFENSEN

1British Antarctic Survey, Natural Environment Research Council, Madingley Road, Cambridge CB3 0ET, England
E-mail: gcl@bas.ac.uk
2Climate and Environmental Physics, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland
3Department of Chemistry, University of Calabria, I-87030 Arcavacata di Rende (Cosenza), Italy
4Department of Chemistry, University of Florence, I-50121 Florence, Italy
5Laboratoire de Glaciologie et Géophysique de l’Environnement du CNRS, 54 rue Molière, BP 96, 38402 Saint-Martin-d’Hères Cedex, France
6Department of Physical Geography and Quaternary Geology, Stockholm University, S-106 91 Stockholm, Sweden
7Department of Geophysics, The Niels Bohr Institute, University of Copenhagen, Juliane Maries Væg 30, DK-2100 Copenhagen, Denmark

ABSTRACT. In the past, ionic analyses of deep ice cores tended to consist of a few widely spaced measurements that indicated general trends in concentration. The ion-chromatographic methods widely used provide well-validated individual data, but are time-consuming. The development of continuous flow analysis (CFA) methods has allowed very rapid, high-resolution data to be collected in the field for a wide range of ions. In the European Project for Ice Coring in Antarctica (EPICA) deep ice-core drilling at Dome C, many ions have been measured at high resolution, and several have been analyzed by more than one method. The full range of ions has been measured in five different laboratories by ion chromatography (IC), at resolutions of 2.5–10 cm. In the field, CFA was used to measure the ions Na$^+$, Ca$^{2+}$, nitrate and ammonium. Additionally, a new semi-continuous in situ IC method, fast ion chromatography (FIC), was used to analyze sulphate, nitrate and chloride. Some data are now available to 788 m depth. In this paper we compare the data obtained by the three methods, and show that the rapid methods (CFA and FIC) give an excellent indication of trends in ionic data. Differences between the data from the different methods do occur, and in some cases these are genuine, being due to differences in speciation in the methods. We conclude that the best system for most deep ice-core analysis is a rapid system of CFA and FIC, along with in situ meltwater collection for analysis of other ions by IC, but that material should be kept aside for a regular check on analytical quality and for more detailed analysis of some sections.

INTRODUCTION

Ice cores are an excellent medium for understanding past changes in the climate and atmospheric environment, because so many parameters are recorded in the same core. As well as the basic climate variables such as temperature (from water isotope ratios) and accumulation rate, ice cores contain information about a host of climatic forcing factors and related environmental changes. Much of this information is tied up in the water-soluble chemical components (LeGrand and Mayewski, 1997). From among these components, one can hope to derive information about, for example, the volcanic history of the Earth (Zielinski and others, 1996), marine biogenic activity in the oceans (LeGrand and others, 1991), atmospheric circulation (Mayewski and others, 1994) and sea-ice extent (Grumet and others, 2001). There have been hundreds of such studies, although the interpretation of the chemical data in terms of environmental variables is rather difficult (Wolff, 1996). However, the need to obtain large amounts of accurate high-resolution chemical data remains.

For both deep and shallow ice cores, it has now become routine to measure the ionic chemistry of the ice core, and until now this has most commonly been done by ion chromatography (IC). Several ice cores have already been analyzed continuously at high resolution in order to capture detailed signals (e.g. Greenland Ice Sheet Project 2 (GISP2) (Mayewski and others, 1997) and Taylor Dome, Antarctica (Mayewski and others, 1996)). However, because it is time-consuming to cut and analyze samples by IC, chemical datasets from many deep ice cores have been discontinuous (e.g. LeGrand and others, 1988). Partly for this reason, and partly to analyze new species not available from IC, continuous flow analysis (CFA) methods have been introduced in the last few years (Fuhrer and others, 1993), and expanded to a range of ions and neutral chemicals. Such methods allow a rapid analysis to be made in the field, and at high resolutions (one to a few cm) in order to capture the annual variability of the signal. While at present not all the ions measured by IC can be measured with sufficient sensitivity by CFA, the range that can be determined is increasing (Rothlisberger and others, 2000). A third method, known as fast ion chromatography (FIC), has recently been devel-
oped (Udisti and others, 2000). This uses the IC analytical method, but adapted to work at high resolution in the field. The EPICA (EPICA) has as its first target a drilling to bedrock at the central Antarctic site, Dome C (75°30’S, 123°24’E). All three methods (IC, CFA and FIC) are being used along the entire length of the core. Data are available at present to compare the data retrieved by the three methods, and to discuss the advantages and disadvantages of each.

**ANALYTICAL METHODS**

**Ion chromatography**

IC was used to determine a large number of anions (F−, methanesulphonate (MSA), Cl−, NO3−, SO42−, acetate, oxalate, formate) and cations (Na+, NH4+, K+, Mg2+ and Ca2+).

For the top 580 m, the samples for analysis were obtained from 55 cm long subsections of the core, shipped back to Switzerland. For the next 200 m, a faster alternative was used to produce the samples: meltwater was collected directly into sample bottles from the CFA meltwater stream, sampling at 10 cm resolution. Each laboratory received samples from one in every five 1.1m subsections of the core.

The IC analysis varied for one laboratory in the range 4–10 % depending on the species and concentrations.

**Fast ion chromatography**

The anions, Cl−, NO3− and SO42− were also determined by a semi-continuous method, in which a part of the output

**Table 1. Experimental conditions for the IC analysis**

<table>
<thead>
<tr>
<th>Lab</th>
<th>Instrument</th>
<th>Columns/Sample loop</th>
<th>Eluent</th>
<th>Suppressor</th>
<th>Sample loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flo</td>
<td>A - DX300</td>
<td>CG2 4 mm</td>
<td>Isocratic</td>
<td>ASRS-ultra 4 mm</td>
<td>Peristaltic pump</td>
</tr>
<tr>
<td></td>
<td>C - DX120</td>
<td>CS2 4 mm</td>
<td>Na2CO3, 18 mM</td>
<td>external water mode</td>
<td>Gibson minipump3</td>
</tr>
<tr>
<td>Sto</td>
<td>A - DX300</td>
<td>CG2 2 mm</td>
<td>Isocratic</td>
<td>ASRS-1 2 mm</td>
<td>Dionex AS40 autosampler</td>
</tr>
<tr>
<td></td>
<td>C - DX300</td>
<td>CS2 2 mm</td>
<td>NaOH 2.5 mM</td>
<td>external water mode</td>
<td>continuously flushed with clean air</td>
</tr>
<tr>
<td>BAS</td>
<td>A - DX300</td>
<td>CG2 4 mm</td>
<td>Isocratic</td>
<td>ASRS-ultra 4 mm</td>
<td>Dionex AS-300 autosampler</td>
</tr>
<tr>
<td></td>
<td>C - DX300</td>
<td>CS2 4 mm</td>
<td>NaOH 100 mM</td>
<td>recycle mode</td>
<td></td>
</tr>
<tr>
<td>A - 200i</td>
<td>ATC 1</td>
<td>CG2 4 mm</td>
<td>Isocratic</td>
<td>ASRS-ultra 4 mm</td>
<td>Dionex AS40 autosampler</td>
</tr>
<tr>
<td>BAS</td>
<td>C - DX300</td>
<td>CS2 4 mm</td>
<td>NaOH 100 mM</td>
<td>recycle mode</td>
<td></td>
</tr>
<tr>
<td>Cph</td>
<td>A - DX300</td>
<td>CG2 2 mm</td>
<td>Isocratic</td>
<td>ASRS-ultra 2 mm</td>
<td>Hand injection</td>
</tr>
<tr>
<td></td>
<td>C - DX300</td>
<td>CS2 2 mm</td>
<td>MSA 20 mM</td>
<td>recycle mode</td>
<td></td>
</tr>
<tr>
<td>Notes: All laboratories used Dionex systems with the corresponding standard pumps and conductivity detectors. Lab, laboratory; Flo, Florence; Sto, Stockholm; BAS, British Antarctic Survey; LGGE, Laboratoire de Glaciologie et Géophysique de l’Environnement; Cph, Copenhagen.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
from the CFA melter (again the stream from the inner part of the core) was directed to an ion chromatograph (Udisti and others, 2000). A sample was injected into the IC every 1 min, giving approximately one measurement for every 4 cm of ice. A volume of 0.75 mL of meltwater was loaded onto a pre-concentrator column, and then eluted through the IC using 1–2 mM Na$_2$CO$_3$ and 0.1–0.5 mM NaHCO$_3$. The method was initially designed for sulphate only, so determinations of the other anions carried out in the 1997/98 field season (depths 990–5386 m) at Dome C are only approximate, especially since the non-sulphate peaks were close to the water dip. In the 1998/99 field season, conditions were optimized, and then further improved for the final section of processing (core below 580 m) that occurred in 2000. Injecting a lower sample volume into a pre-concentration column and increasing the eluent concentration allowed separation of the peaks from the water dip. It is estimated that detection limits of 0.5 μg kg$^{-1}$ were achieved, with reproducibility at typical concentrations at Dome C of 2% for NO$_3^-$ and SO$_4^{2-}$ and 4% for Cl$^-$ (Udisti and others, 2000).

### Inter-laboratory comparison between the five IC groups

An inter-laboratory comparison exercise was undertaken in 1999 using Dome C ice samples. Identical samples were supplied to each laboratory, taken from a pooled sample of melted ice. The laboratories were asked to analyze each sample on two separate occasions, using their normal methods. A second intercomparison is currently underway.

### RESULTS AND DISCUSSION

#### Inter-laboratory comparison between the five IC groups

In this exercise, two samples of Holocene ice (with low concentrations of many ions) were analyzed. There was good agreement between the laboratories for some ions. However, only for sulphate (around 100 μg kg$^{-1}$) was the agreement between the laboratories better than 5%, the uncertainty often quoted by IC laboratories. This variation corresponds to a ±2.5% spread of the results from each laboratory around the mean, with the spread expressed as the standard deviation of the results from the five laboratories. For Cl$^{-}$ (5–20 μg kg$^{-1}$ range) and Na$^+$ (around 20 μg kg$^{-1}$), the spread around the mean was about ±10%, and it was around ±15% for MSA (2–4 μg kg$^{-1}$ range) and Mg$^{2+}$ (2–3 μg kg$^{-1}$ range). Considering the very low levels of these last ions, the ability to discriminate confidently between samples that are <1 μg kg$^{-1}$ different is encouraging. The concentrations of these Holocene samples are among the lowest that are encountered in polar snow for many elements, and some laboratories are having to learn to operate nearer to their detection limits than is customary for them.

The agreement for some other ions was not so good. For nitrate (around 10 μg kg$^{-1}$), the spread was >±50%, but comparison of the data generated by the laboratories subsequently suggests that better performance is achieved in routine analysis. We could not rule out the possibility that nitrate had been affected by problems in sample preparation and storage. Finally, for the cations, K$^+$ (around 2 μg kg$^{-1}$) and Ca$^{2+}$ (around 10 μg kg$^{-1}$), the agreement was poor with a spread of order ±30%. In the combined record from all the laboratories, and for low-concentration Holocene ice, it would be difficult confidently to differentiate short-term changes in background concentration from inter-laboratory differences, although there should be no difficulty in identifying and quantifying sporadic peaks or long-term trends, or in analyzing the dustier ice of the pre-Holocene period.

#### Comparison of sample-analysis statistics from the five IC groups

Because the inter-laboratory comparison was quite limited, we also tested whether similar populations of samples from the five laboratories were reported as having similar mean concentrations. This acts as a further check on the calibration between the laboratories.

This comparison concerns the 200 m section of glacial ice at 385–788 m depth, and the 330 samples received by each laboratory were evenly distributed across the full section. The overall mean concentrations from each laboratory for each species measured are generally similar, as shown in Figure 1. For most species, at least four of the mean results reported lie within the range of the confidence interval. The main differences between the mean values can probably be ascribed to the analytical source, and may only partly be influenced by unusual concentrations in certain sections. Sulphate is a clear exception to this rule, though we are confident that this is a result of an uneven distribution of sample values. Superimposed on the general background sulphate value of around 130–20 μg kg$^{-1}$ lie many large volcanic spikes, some >3000 μg kg$^{-1}$, but these large peaks are not distributed evenly among the laboratories. From the result of the inter-laboratory comparison exercise, we know that the five laboratories are very consistent in the reporting of sulphate (this result is compared in Figure 1 with the actual ice analyses).
Sodium: CFA vs IC

To handle the wide difference in resolution between the two methods, we compile the data into 55 cm (“bag”) averages and plot in Figure 2 the comparison in results from identical bags. Overall, the two methods are in good agreement: linear regression slope of 1.04 ($r^2 = 0.946$), and even distribution on both sides of the theoretical line $y = x$ up to 90 µg kg$^{-1}$. At higher concentrations (90–140 µg kg$^{-1}$), the CFA tends to overestimate Na$^+$, probably due to a calibration uncertainty. These results were determined using a linear calibration, and then applying a general correction above 50 µg kg$^{-1}$ to compensate the non-linearity of the response at high concentrations. The method has now been improved by using a non-linear calibration. One can occasionally note a deviation higher than the average: a clear example is point “a” in Figure 2. A detailed examination of this section showed that an erroneous calibration of the CFA has caused a systematic offset. The CFA produces a large number of data, and only a careful repesenting could allow us to discard such a point. The detailed sections (Figs 3 and 4a) confirm the quantitative agreement of the two methods, respectively at both low (10–20 µg kg$^{-1}$) and higher concentrations (60–90 µg kg$^{-1}$). Some variations can occasionally occur due to the different resolutions and some slight depth shifts between the two methods (e.g. in Figure 3, peaks at 349.9 and 351.1 m). With a 5 cm sample resolution (Fig 3), the IC detects most of the peaks, whereas only the main features remain with a 10 cm resolution (Fig 4a). The high resolution of the CFA captures the detailed structure of the signal, providing further information for an analysis of the high-frequency variability.

Fig. 2. CFA vs IC for the sodium 55 cm mean values up to 670 m.

Fig. 3. Comparison of CFA (- - -) and IC 5 cm resolution (●●●) sodium data at low concentrations. The vertical lines delimit the 55 cm sections of the core. For each section the IC laboratory that carried out the analysis is indicated. The horizontal lines represent the corresponding 55 cm CFA (- - -) and IC (—) mean values.

Fig. 4. Some detailed results for the depth interval 663–670 m: (a) CFA (- - -) and IC 10 cm resolution (●●●) sodium data. The vertical lines delimit the 1.10 m sections of the core. The horizontal lines represent the corresponding 1.10 m CFA (- - -) and IC (—) mean values. For each section the IC laboratory that carried out the analysis is indicated (also applicable to (b–d)). (b) CFA (- - -) and IC 10 cm resolution (●●●) calcium data. (c) CFA (- - -), FIC (○○○) and IC 10 cm resolution (●●●) nitrate data. (d) FIC (○○○) and IC 10 cm resolution (●●●) chloride data.
Calcium: CFA vs IC

Data from the high-resolution CFA analyses and the lower-resolution IC analyses are available through the Holocene, transition and late glacial periods, allowing us to compare data across a wide range of concentrations. According to the 55 cm (bag) averages analysis (Fig. 5), we can claim that in general the two methods produce similar values: the actual gradient of CFA vs IC is 1.04 ($r^2 = 0.934$), close to unity. Over a 6 m section (Fig. 4b) the IC data have the appearance of a smoothed version of the high-resolution CFA data, and the values measured appear consistent. However, when we compare some sections in detail (Fig. 6) we can see problems arising. At low concentrations (Fig. 6a) the IC records values rather higher than the CFA; this is common throughout the Holocene samples. This discrepancy could arise from a difference in the ability of the two methods to measure all the Ca$^{2+}$ present; the eluent used in IC (see Table 1) means that IC measures at approximately pH2, where more particulate Ca$^{2+}$ will be soluble. However, the poor comparison between the five IC laboratories at the lowest concentrations for Ca$^{2+}$ in the inter-laboratory comparison also raises doubts about the IC analysis near to the detection limit. Further work is needed to decide which, if either, method, is quantitatively accurate at low concentration. At higher concentrations, such as found in the transition (Fig. 6b), the concentration recorded by the two techniques is broadly similar, but it is clear that the CFA captures details that the low-resolution IC sampling does not.

Ammonium: CFA vs IC

Ammonium (NH$_4^+$) was analyzed by CFA in the field and by IC in three laboratories. The available data up to 580 m show two distinct parts depending on the depth. For the top 100 m, the concentrations determined by IC are 5–50 times higher than the CFA ones (Fig. 7). This section of the core corresponds to the porous firm easily contaminated by trace gases from the ambient air. The level of contamination decreases progressively from the surface as the density of the firm increases. The schedule of the sampling may explain the difference between the CFA and IC results: the CFA analysis was carried out in the field 1–2 years earlier than the processing of the firm core for IC analysis in Europe. It seems difficult during a long storage and transport to prevent the NH$_4^+$ contamination of the firm sections. Below 100 m, the majority of the IC concentrations are lower, but the two methods still show a significant difference. When plotting the CFA results against the IC (Fig. 8), we notice a considerable deviation from the theoretical line $y = x$, but one laboratory did produce more consistent results than the others. Despite all the usual precautions taken for the IC analysis (minimize the...
contact with the ambient air, analysis as soon as the samples are melted, etc.), it seems difficult to avoid some contamination. It is well known that the ammonia present in the ambient air easily contaminates liquid samples (Legrand and others, 1984), hence the CFA method seems more appropriate than the IC as the meltwater does not come into contact with the ambient air before analysis.

Nitrate: CFA vs IC and FIC vs IC

“Bag” average concentrations of nitrate measured by IC and CFA are available from the whole of the Holocene, through the transition and into the early part of the glacial period: 0–584 m (except 123–320 m for the CFA when the data are considered unreliable) plus one deeper section. For the FIC technique, while the full range of ice between 0 and 788 m was measured, the section 99–358 m was also considered unreliable due to the immaturity of the technique. Figure 9 plots the data from the two rapid techniques against the IC results. The linear regression of FIC on IC gives a slope of 1.05 ($r^2 = 0.88$), while CFA on IC has a slope of 1.15 ($r^2 = 0.88$), implying that the rapid techniques generally give higher values than the IC. CFA and FIC appear to agree better, with a linear regression slope CFA on FIC of 1.02 ($r^2 = 0.92$). Examination of a 6 m section of the core in detail (Fig. 4c) shows the origin of this general result. The IC data track the pattern of the high-resolution CFA profile but at a lower concentration, and without capturing the sharp, high-value peaks, while the FIC technique appears slightly better at these sharp peaks. One bag section of IC data appears anomalously low, with CFA and FIC agreeing closely across this bag. Other bag sections show a better correspondence between FIC and IC. Generally, once the three techniques were mature, they all gave good, reliable data, with the occasional short section where each of the techniques gave poor results.

Sulphate: FIC vs IC

The FIC method was originally developed for $\text{SO}_4^{2-}$, so it is pleasing to note that the agreement between the techniques for this ion is good, both quantitatively and qualitatively. Detailed features are seen similarly in both methods (Fig. 10), and although there is in some cases an offset (indicating a calibration difference) between the two methods, the average of the absolute difference between the methods for a single 55 cm interval is <10%, only slightly larger than the precision of IC by itself. The linear regression of FIC on IC for 55 cm averages has a slope of 1.03 and a correlation coefficient of 0.92. FIC therefore seems to be suitable for analysis of $\text{SO}_4^{2-}$ in the Dome C ice core.

Chloride: FIC vs IC

With the very short analysis time of FIC, the Cl peak is hard to capture, and may be found in the water dip present at the start of the chromatogram. In the 1997/98 season, Cl by FIC was not considered a mature method, while improvements for the 1998/99 season allowed reporting of results. Further improvements for the processing carried out in 2000 seem to have solved remaining problems, and the two methods now show very similar results, both in detail (Fig. 4d) and on average (Fig. 1). Quantitative accuracy is of particular importance when data are used to derive ratios between ions (such as Cl/Na$^+$), and is achieved in data from 585 m downwards.
CONCLUSIONS

The IC, widely used until now for ice-core ionic analysis, is a well-established method to determine a wide range of ions. It benefits from the ability to calibrate carefully and, frequently, and re-analyze samples when problems are identified, but is very time-consuming. The slow sample preparation and analysis make the method unsuitable for high-resolution analysis in the field.

The development of the CFA has allowed fast analysis to be carried out in the field for a smaller range of ions. The method provides very high-resolution results, but requires careful attention to calibration and to processing of the large number of data. The comparison clearly showed that the CFA gives better results than the IC for NH$_4^+$, as it reduces the risk of contamination. For other ions (Na$^+$, Ca$^{2+}$, NO$_3^-$), the CFA generally gives good results.

The other fast technique (FIC) developed to provide high-resolution data in the field covers a few ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$) and offers a complement to the CFA by rapidly analyzing ions not previously available by CFA (Cl$^-$, SO$_4^{2-}$). It has proved to give excellent results for SO$_4^{2-}$. Initially, it was able to capture peaks and trends for the other ions, but could not be used in situations where accurate quantification was important. However, after improvements to the method in the later analyses, it now also gives good results for Cl$^-$ and NO$_3^-$.

We conclude that the determination of the full range of species still requires a combination of analytical methods. The CFA and FIC can be used to measure the main species (Na$^+$, NH$_4^+$, Ca$^{2+}$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$), and the IC allows analysis of the other ions, as well as checking the analytical quality of the results obtained by the two fast techniques. Some of the speed advantages of the in situ methods can be kept for the IC by collecting meltwater in the field for the IC samples.

ACKNOWLEDGEMENTS

This work is a contribution to the “European Project for Ice Coring in Antarctica” (EPICA), a joint European Science Foundation (ESF)/European Commission (EC) scientific programme, funded by the EC and by national contributions from Belgium, Denmark, France, Germany, Italy, the Netherlands, Norway, Sweden, Switzerland and the United Kingdom. This is EPICA publication No. 39. We would like to thank the many people involved in the collection, cutting and analysis of the Dome C core.

REFERENCES


Mayewski, P.A. and 15 others. 1996. Climate change during the last deglaciation in Antarctica. Science, 272(5268), 1536–1538.


