High Speed, High Resolution, and Continuous Chemical Analysis of Ice Cores Using a Melter and Ion Chromatography

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Measurement of trace chemical impurities in ice cores contributes to the reconstruction of records of the atmospheric environment and of the climate system. Ion chromatography (IC) is an effective analytical technique for ionic species in ice cores but has been used on discretely prepared ice samples, resulting in extensive and slow sample preparation and potential for contamination. A new technique has been developed that utilizes IC as the online detection technique in a melter-based continuous flow system for quantitative determination of major ionic chemical impurities. The system, called CFA-IC for continuous flow analysis with ion chromatography detection, consists of an ice core melter, several ion chromatographs, and an interface that distributes meltwater to the IC instruments. The CFA-IC technique combines the accuracy, precision, and ease of use of IC measurement with the enhanced speed and depth resolution of continuous melting systems and is capable of virtually continuous, high-speed and high-resolution chemical analysis of long ice cores. The new technique and operating procedures have been tested and validated with the analysis of over 100 m of ice cores from Antarctica. The current CFA-IC system provides an all-major-ion analysis speed of up to 8 m a day at a depth resolution of approximately 2 cm.

Introduction
Polar ice cores provide records of the atmosphere over time periods as long as thousands of years (1, 2). Ice core chemical analysis reveals temporal variations of the amount or concentration of chemical impurities in ice. Those variations directly or indirectly reflect the history of atmospheric chemical composition and its relationship with important atmospheric qualities, such as climatic conditions and the impact of human activities (3, 4). In addition, appropriate chemical analysis can assist in the reconstruction of high quality paleoclimatic records. For example, accurate and precise chronology of long (over 1000 m) ice cores can be established with high-resolution chemical analysis of very large numbers of samples (3). With accurate dating and high resolution measurements, additional useful information, such as temporal relationships between components of the climate/atmosphere system, could be obtained from ice cores (3).

Quantitative measurement of soluble chemical impurities is a basic and integral part of many ice core research projects (2–5). Major chemical impurities found in polar snow and ice are inorganic acids and salts that exist as ionic species in meltwater samples, typically at nanogram per gram of ice (ng g⁻¹ or ppb) concentration levels. Measurement of these requires analytical methodology and instrumentation appropriate for trace analysis. The technique of ion chromatography (IC) was first used for this purpose in the early 1980s (6). IC has become the common and preferred technique for ice core chemical analysis (7, 8), owing to its superior technical qualities (low detection limits, small sample volume requirement, and automated operation). All of the major ionic species (except H⁺ and carbonate ions) commonly found in polar ice can be routinely measured using IC (7–9).

High-resolution chemical analysis requires substantially increased analytical effort and consequently much longer times than has been practical for long ice cores, if the analysis speed is not increased. Ice core drilling and handling prior to laboratory analysis expose core surfaces to contamination over the extremely low concentrations of ionic impurities in most polar ice cores (Table 1). Sample decontamination, traditionally done with the mechanical removal (e.g., bandsaw cutting) of contaminated surfaces resulting in discretely prepared samples (9, 10), is time-consuming and therefore significantly limits the number of samples analyzed and the analysis speed. To solve this problem, Sigg et al. (11) used an electrically heated melting device to generate uncontaminated flowing meltwater streams to be analyzed with instrumental techniques. The ice core melter, with subsequent improvements (e.g., ref 12), has significantly improved the speed and reliability of ice core sample preparation for chemical analysis. Furthermore, the melter can be coupled with online detection techniques to effect continuous and automated measurement at high speed. For example, the use of absorption and fluorescent spectrometry as the analytical detection technique resulted in continuous flow analysis (CFA) systems (11, 13) that measure several ionic as well as nonionic species. McConnell et al. (14) and KnuÈsel et al. (15) further expanded the CFA systems by adding or using inductively coupled plasma-mass spectrometers (ICP-MS) as online detectors. ICP-MS measurements (12, 14, 15) demonstrate that the melter approach of ice core sample preparation is also appropriate for trace metal analysis at parts per trillion levels. The increase in speed by using a melter with online detection has in turn allowed chemical analysis to be performed with faster speed and higher temporal resolution than previously possible (4, 8).

By using absorption and fluorescent spectrometry as instrumental techniques for the detection and quantification of chemical species in the meltwater streams, the current.

| TABLE 1. Typical Concentrations of Major Ionic Impurities in Polar (Antarctic) Snow and Ice and Detection Limits (DL) by IC on Discrete Samples and by CFA-IC |
|---|---|---|---|---|---|
| species | concn ppb (ng g⁻¹) | DL by IC | RSD (7%) | CFA-IC blank ppb | CFA-IC DL (19) ppb |
| Anions | | | | | |
| Cl⁻ | 1–50 | ~0.5 | ~0.5 | 0.4 |
| NO₃⁻ | 10–300 | ~0.5 | ~2 | 0.02 |
| SO₄²⁻ | 1–200 | ~0.5 | ~3 | ~1.5 | 0.07 |
| Cations | | | | | |
| Na⁺ | 1–50 | ~0.3 | ~2 | 0.04 |
| NH₄⁺ | 1–5 | ~0.3 | ~5 | 0.06 |
| K⁺ | 0–10 | ~0.5 | ~16 | 0.7 |
| Mg²⁺ | 0–20 | ~0.5 | ~3 | 0.004 |
| Ca²⁺ | 1–50 | ~0.5 | ~2 | 0.004 |

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CFA systems measure only several of the major ions listed in Table 1. This is because, since none of the ions absorbs or fluoresces, an ion must be converted, usually by complexation, to an absorbing or fluorescent species through reactions with added reagents for online detection and measurement. Ions for which suitable absorbing or fluorescent complexes or derivatives have been found include Ca$^{2+}$, NH$_4^+$, Na$^+$, and NO$_3^−$. Others (K$^+$, Mg$^{2+}$, Cl$^−$, and SO$_4^{2−}$) cannot be determined with the CFA systems because appropriate or sensitive complexes or derivatives have not been found (8, 13). ICP-MS allows metal cations (Na$^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$) to be measured as elements but cannot directly measure the anions (14, 15). There appears to be an obvious advantage, in comparison with spectrometry and ICP-MS, in using IC as the detection technique because of its ability to measure all ionic species in polar ice, as with discrete samples. To utilize this advantage of IC, particularly its ability to determine SO$_4^{2−}$ of low ppb concentrations, Udisti and colleagues (16, 17) developed a fast ion chromatography (FIC) detection technique for a melter system. Huber et al. (18) used two ion chromatographs as continuous, online detectors to measure 8 anions and 5 cations in ice cores. However, the slow development of an ion chromatogram (a minimum of several minutes) makes IC detection somewhat incompatible with the high sample preparation speed offered by the melter. The 8-min chromatograms used by Huber et al. (18) to allow online IC detection to proceed continuously resulted in slow ice melting rate and poor ice core depth resolution. The FIC technique used extremely short (1 min) and under-resolved chromatograms to keep up with a fast melting speed (4 cm per min) and could only measure major anions at a moderate depth resolution (16, 17). Consequently, for routine and complete chemical analysis of ice cores at high resolution (<4 cm per measurement), IC measurement is still needed, often on discrete samples prepared separately from or by the melter (4, 12). The overall speed of complete ion analysis in ice core research is limited by either the slow discrete sample preparation or the lack of a fast, all-ion, online detection technique in CFA systems (4, 8, 12).

We describe here a new ice core chemical measurement system, called CFA-IC, in which several IC instruments are interfaced with an ice core melter to serve as the detection device for major ionic species. Our objective is to develop a fast and continuous measurement technique for routine ice core chemical analysis that utilizes the technical strengths and advantages of the ion chromatography technique.

**Methods**

**Melter.** Our melter is similar to the Desert Research Institute (DRI) melter described by McConnell et al. (14). The DRI melthead design divides the melt area into three zones, in order to generate two separate meltwater streams for ICP-MS and spectrometric measurements and one waste stream. Two zones are used in our melthead: a 2.5 cm square inner zone inside a 4.0 cm square melt area. During melting and analysis, an ice core “stick” with a cross section slightly larger (e.g., 3.5 cm square) than the inner zone is placed on the heated melthead and melted continuously. The meltwater from the inner zone is drained through holes at the bottom of the melt area into the sample stream, while the potentially contaminated melt from the outer zone is channeled to the waste stream. A peristaltic pump maintains flow in the sample stream. The much faster waste streamflow, maintained by a slight vacuum (~1 × 10$^5$ Pa), ensures that the direction of horizontal flow at the melt area, if any, is outward, to prevent contamination of the sample stream by melt from the outer zone. The melthead, of aluminum metal, is maintained at a selected temperature by an electronic temperature controller through a thermocouple and four heat rods inside an aluminum base in contact with the melthead (14). Selection of melter temperature, melt rate, and sample streamflow rate is discussed later.

**Ion Chromatography Instruments.** Dionex (Sunnyvale, CA) Models DX-600 and ICS-1500 ion chromatographs with Dionex IC columns are used as the online analytical measurement device or detector. Control of and data acquisition from the IC instruments are accomplished through Dionex chromatography software on portable computers. A group of three IC instruments is used for anion measurement and another group of three ICs for cation measurement. No spectrometric instruments are used.

**Melter-IC Interface.** The sample meltwater stream from the melter passes through first a debubbler (to remove air bubbles in ice) and then the cell of an optional conductivity measurement device or detector. Control of and data acquisition from the IC instruments are accomplished through Dionex chromatography software on portable computers. A group of three IC instruments is used for anion measurement and another group of three ICs for cation measurement. No spectrometric instruments are used.

**CFA-IC Operation.** The melter and ice core support stand are inside a −20 °C cold room. Plastic tubings through a small wall opening connect the melter, and channel the meltwater, to the interface and IC instruments located in an adjacent room at normal room temperature (Figure 1).

In a routine operation, all IC instruments are first individually calibrated using an external blank (ultrapure
deionized water) and standard solutions. The feed to IC instruments is then switched to the analytical sample stream. The three IC instruments for anion measurement inject meltwater in their injection loops onto their separation columns in sequence, such that a constant time interval is maintained between two successive injections. Similar operation is performed simultaneously on the three cation instruments. Chromatographic data are continuously acquired, stored, and processed by the chromatography software.

The melter temperature (33–40 °C) is empirically selected to provide the desired ice melt rate (1–2 cm min$^{-1}$) and meltwater streamflow rate (∼3.5 mL min$^{-1}$) compatible with the feed speed (3.0 mL min$^{-1}$) to the IC instruments. Ultimately, the ice melt rate and the injection interval of the IC instrument determine the temporal resolution of this technique in ice core analysis (see later discussion).

Three 3.5 × 3.5 cm are cut from cylindrical ice cores and mounted inside the vertical support stand, with the square cross section centered on the inner zone. About 0.5 cm of core is removed from each end of a core stick prior to mounting onto the support stand. The open-ended support stand holds up to 1.4 m and allows the mounting of an ice stick of about 1 m in length, while the previous stick is still being melted. After melting is finished, the feed to the IC instruments is switched back to the external blank and standard solutions for calibration validation. Subsequently, IC data are processed (19) offline in which ion concentrations of each pair (anion and cation) of injections are assigned to a specific depth interval of the ice core.

Results and Discussion

Ion Chromatography and Optimization. In a routine analysis of discretely prepared ice core samples, a typical ion chromatogram, in which peaks of all anions or cations are resolved and accurately measured, takes 8–12 min (7, 9). This time is too long for an IC instrument to keep up with the practical melting speeds in CFA, typically at 1–5 cm of ice or firn per minute (11, 13, 14). When one IC instrument is used as the online detector, the melt rate must be slowed down to allow continuous detection (18). In the CFA-IC system, this problem of compatibility between slow IC and fast melter is solved with two experimental approaches. First, the chromatogram length (i.e., runtime) was reduced from the 8–12 min range in routine IC analysis of discrete samples. However, unlike the approach by Udisti and colleagues (16, 17), it was necessary in our system to achieve complete baseline separation or resolution of all chromatographic peaks in a chromatogram for anions or cations. This required a minimum runtime (∼1 min), which is determined mainly by the separation efficiency of available IC columns. In addition, the runtime depends on a number of chromatographic variables with a given column type: column size, mobile phase (i.e., eluent) strength, and flow rate through the column. For discrete samples, we have used Dionex IonPac AS11 and CS12A analytical columns (4 mm (i.d.) × 250 mm (L)) for anions and cations, respectively, with satisfactory results. In CFA-IC, we chose the AS11 and CS12A microbore columns (2 mm (i.d.) × 250 mm (L)) which offer similar separation performance at reduced column size and runtime. Various combinations of eluent (dilute NaOH) strength and eluent flow rate were tested, and an 8 mM NaOH eluent at 0.75 mL min$^{-1}$ was found to yield chromatograms with completely resolved anion peaks in 4.0 min on an AS11 2 × 250 mm column. Similarly, an eluent of 11 mM H$_2$SO$_4$ at 0.60 mL min$^{-1}$ on a CS12A 2 × 250 mm column was found optimal for the five cations (Figure 2). A relatively large injection loop (0.25 mL) was used to ensure appropriate detection limits for all ions.

![FIGURE 2. Optimized chromatograms of anions (A) and cations (B) in typical South Pole ice core samples. Blank (deionized water) chromatograms are indicated by thin lines. Anions (23 ppb Cl$^-$, 54 ppb NO$_3^-$, and 61 ppb SO$_4^{2-}$) were separated on a Dionex IonPac AS11 microbore column (2 mm (i.d.) × 250 mm) with an 8 mM NaOH eluent at a flow rate of 0.75 mL min$^{-1}$. The carbonate peak is the result of dissolved CO$_2$ in solution. Cations (24 ppb Na$^+$, trace NH$_4^+$, 2 ppb K$^+$, 3 ppb Mg$^{2+}$, and 6 ppb Ca$^{2+}$) were separated on a Dionex IonPac CS12A microbore column and an 11 mM H$_2$SO$_4$ eluent at 0.60 mL min$^{-1}$.

The reduced runtime allowed a measurement of anion or cation concentrations of the meltwater stream to be made every 4 min by one IC instrument. This measurement frequency is still insufficient to keep up with practical melting speeds and, if used in actual ice core analysis, would result in poor depth resolution (e.g., ref 18). In the CFA-IC system, the 4 min gap between successive samplings of the meltwater stream by the first IC pair is sampled by two additional pairs of IC instruments, with a total of six IC instruments in the system, reducing the interval between samplings and therefore increasing the depth resolution. Measurement by three pairs of IC instruments with 4 min chromatograms is equivalent to one pair performing measurement of 1.33 min chromatograms (3 injections in 4 min).

Blanks, Detection Limits, and Reproducibility. CFA-IC procedural blanks were routinely analyzed. Blank chromatograms are presented in Figure 2. Typical blank values and detection limits for all major ions are listed in Table 1. System reproducibility was verified with replicate analysis of short ice core sections.

Temporal Resolution. In ice core analysis, depth resolution is defined as the core depth interval covered or represented by a single analytical measurement. For example, depth resolution in discrete sampling is equal to the length or size of an ice sample cut vertically from a core (Figure 3A). That sample, when melted and analyzed, yields a single measurement (e.g., the ion concentration). Since core depth represents the progression of time, high depth resolution, or small sample size, is equivalent to high temporal resolution.

In CFA systems in which the analytical measurement on the meltwater sample stream is either theoretically (spectrometry) or practically (ICP-MS) instantaneous and continuous with the meltwater flow, the depth or temporal resolution does not depend on analytical sampling rate of the meltwater streams as illustrated in the discrete sampling example. Rather, the depth resolution is determined by the dispersion of analyte concentrations in the meltwater before they reach the detection device (11, 20).

In CFA-IC, the determination of depth resolution is similar to discrete sampling, since chromatographic measurement is achieved with a finite number of samplings (i.e., injections) of the meltwater stream. When the ice melt rate is $M$ (cm
min$^{-1}$) and the IC sampling frequency is $I$ (minute per measurement), the depth interval nominally represented by a single injection is $R_N = I \times M$. For example, with a typical melt rate of 1.5 cm min$^{-1}$ and frequency of 1.33 min per measurement, the nominal depth resolution is 2.0 cm per measurement (Figure 3B).

**Discontinuous or Continuous Analysis?** In the discrete sampling method, the analytically measured concentration is an average of analyte concentrations in the depth range of the individual sample (Figure 3A). Therefore, the result is a continuous histogram of the analyte concentration as a function of depth, for no gaps are usually left between discrete samples. The IC sampling of the meltwater stream in the CFA-IC system is not continuous, for only a portion of the meltwater stream continuously fed into the IC injection loop is injected onto the column and actually measured by the instrument. The nominal depth resolution only represents the measurement frequency along the core.

The portion of the 2.0 cm ice actually injected into the IC is estimated with the following calculations. In 1.33 min, the volume sampled by the IC instruments is 6 × 0.25 mL (6 injection loops) or 1.5 mL (only one-third of this volume in a pair of loops (0.50 mL) is actually injected, but the injected volume is drawn from a well-mixed 1.5 mL). Therefore, the sampled volume is 37% (1.5 mL of 4.0 mL). (4.0 mL of 3.0 mL min$^{-1}$ = 1.33 min, in which 3.0 mL min$^{-1}$ is the postdebubbler flow rate of the sample stream) of the meltwater in the sample stream. Assuming the meltwater in the sample stream is representative of all melted ice (4.0 mL is approximately 45% of the total melt volume (8.8 mL = 2.0 cm × 2.5 cm × 2.5 cm × 0.7 mL cm$^{-3}$; 2.0 cm is the length of melted ice with a 2.5 × 2.5 cm area and a typical density of 0.7 mL water per cm$^3$)), this indicates that 0.75 cm of the 2.0 cm ice is represented by the IC-analyzed meltwater. Figure 3B illustrates that, in our configuration of the melter, the interface, and IC operating parameters, an approximately 37% (0.75 cm) portion of the 2.0 cm ice core depth interval is sampled and measured chromatographically. It appears that the analysis is discontinuous.

However, the meltwater volume actually injected comes not only from the center 0.75 cm of the 2.0 cm ice. Because of dispersion or volume mixing in the melter-IC interface, with an estimated system void volume of 15 mL, the injected volume contains meltwater from ice adjacent to the 0.75 cm portion. As a consequence of the mixing, the analyte concentration in the injected volume represents a weighted average, or convolution ($11$), of concentrations in the dispersion-affected volume (Figure 3C). The size of this dispersion-affected volume is estimated with the following experiments and calculations.

Dispersion occurs when the meltwater is flowing from the melthead to the detection device and, in this case, may be viewed as the mixing of the meltwater volume from the 0.75 cm ice with that from adjacent ice. If the analyte concentration is $x$ in the 0.75 cm ice and zero in the adjacent ice, the extent of mixing can be estimated by measuring the time or volume in which $x$ is attenuated. A simple experiment was performed to estimate this time in our system: A conductivity meter placed at the location of IC injection loops in the flow line measured continuously the conductivity of flow from the melter; the flow was switched from the solution (X) of certain concentration or conductivity ($x$) to another (Y, deionized water of near zero conductivity). The decrease in conductivity, or the drop in a step function, is proportional to the extent of mixing between the two solutions (11). At 1.6 min ($t_e$, Figure 4A), the conductivity (or analyte concentration) decreases to 1/e (0.37) of its original value ($e$-folding time). At this point, a small volume interval contains 37% Solution X and 63% of Solution Y. In other words, 63% of the volume in the interval is contributed by volume originally adjacent to the interval. We assume that this extent of mixing is sufficient ($11, 21$) so that analytic concentrations in the ice melted during this time are all represented by weighted averaging. At the 1.5 cm min$^{-1}$ melt rate ($M$), this mixing time corresponds to $t_e \times M = 1.5 \times 1.6 = 2.4$ cm of ice that contributes to the analyte concentrations measured by an IC injection.

It has been observed that, when firn or bubbly ice cores are melted, frequent air bubbles are present in the stream before the meltwater reaches the debubbler. Because air bubbles minimize dispersion in the tubing between the melthead and the debubbler, the experiment described above probably overestimates the extent of dispersion, owing to the absence of air bubbles in the test solutions. We repeated the experiment but fed the test solution and deionized water into the flow system at the debubbler, bypassing the tubing between the melthead and the debubbler. The results (Figure 4B) show that the $e$-folding time is 1.1 min, corresponding to $t_e \times M = 1.5 \times 1.1 = 1.6$ cm of ice that contributes to the IC-measured analyte concentration.
The validation tests are shown in Figure 5. The results of these tests indicate that the CFA-IC technique, as configured in our system, performs virtually continuous measurement.

The depth interval ($R_0 = t_m \times M$) of ice corresponding to the dispersion-affected volume can be viewed as the practical or actual resolution (Figure 3C) of the CFA-IC technique. Therefore, the actual depth resolution is between 1.6 and 2.4 cm, consistent with the nominal resolution ($R_n$) of 2.0 cm, under the typical operating conditions of the system. Resolution can be enhanced (reducing $R_n$ or $R_0$) by decreasing the melt rate, $M$. In addition to the melt rate, other factors such as variations in the flow rate of the meltwater stream, flow turbulence, and total system void volume can, through $t_m$, affect dispersion and therefore the actual resolution ($11$).

Technique Testing and Validation. We varied the size of the inner melt zone (2.0 × 2.0 to 2.5 × 2.5 cm), ice melt rate (1–2 cm min$^{-1}$), and sample streamflow rate (3–4 mL min$^{-1}$) for optimal system performance. The optimized CFA-IC system (2.5 × 2.5 cm, 1.5 cm ice min$^{-1}$, and 3.5 mL min$^{-1}$, respectively) was tested with the analysis of over 100 m of ice cores from Antarctica. In addition, a specific test was performed to validate the CFA-IC technique. A 3-m section of a recent South Pole ice core was first analyzed using the CFA-IC technique, and after optimizing the melter-IC interface, we were able to achieve a practical resolution of about 2 cm. Similar dispersion-limited resolution has been reported for other CFA systems ($13$, $14$, $21$). In comparison, the practical resolution in routine discrete sampling by bandsaw cutting is usually limited to 2–3 cm per sample ($8$–$10$).

High Analysis Speed. The speed of chemical analysis is critical to the amount of analytical data to be obtained from long ice cores. The major factor in determining CFA speed is the ice melt rate, $M$, which can be increased by elevating the melter temperature. However, this will reduce the dispersion-affected depth resolution ($R_n = t_M \times M$) and the nominal depth resolution ($R_0 = I \times M$). We found that melt rates from 1.0 to 2.0 cm min$^{-1}$ in our system provide the desired 2 cm resolution for ice density ranging from that of shallow firn (0.5–0.9 g cm$^{-3}$) near the top of the South Pole ice core to ice well below the firm-ice transition (0.9 g cm$^{-3}$) while maintaining a reasonably fast analysis speed. At 1.5 cm per min, for example, the analysis speed would be 0.90 m per hour or 7–8 m a day. Other factors, such as the time needed for IC operation preparation and eluent-column equilibration, could further limit the daily analysis speed. In our test analysis of over 100 m of ice core using the CFA-IC system, daily analysis speed varied between 5 and 8 m. In comparison, discrete sampling with IC determination typically allows one analyst to analyze 1–2 cm of ice core a day. This substantial increase in analysis speed or data productivity is achieved primarily with a melter and multiple IC instruments.

Reduced Ice Requirement. In our routine analysis using the discrete sampling method, a minimum of 15 mL meltwater is needed for the determination by IC of all major anions and cations. In CFA-IC, the ice stick of 2.5 cm square provides more than sufficient meltwater for the same analytical measurement at 2 cm resolution, whereas a minimum of 3.2 × 3.2 cm cross section at 2 cm resolution (assuming 0.7 mL water per cm$^2$ of ice) is needed to generate sufficient meltwater in a discrete sample. The overall cross section of the ice stick (3.5 × 3.5 = 12 cm$^2$) in our tests, which can be reduced through waste reduction, is also much less than the cross section area of at least 20 cm$^2$ needed to obtain a clean sample for discrete analysis ($22$).

Reduced Contamination. In the discrete sampling method, extensive handling of the ice is necessary, and numerous sample containers must be used in melting and IC sample loading. Therefore, contamination of individual samples is frequently a serious concern, even for experienced analytical chemists. In CFA-IC, as in other CFA systems, the handling of ice and contact with sample containers are substantially reduced. Consequently, the potential for contamination is significantly less in CFA-IC than in discrete sampling. For example, a spuriously high $\text{SO}_4^{2-}$ concentration in one of the discrete samples (at approximately 79.0 m depth in Figure 5C) was likely caused by contamination during discrete sample preparation, whereas the CFA-IC results show no such high $\text{SO}_4^{2-}$ concentrations in that depth interval.

Comparison with Other CFA Systems. The CFA-IC system significantly improves major ion analysis of ice cores over traditional IC analysis with the discrete sampling method. Furthermore, the combination of melter-based sample preparation and IC determination allows major ion concentrations to be measured at speed and resolution similar to those of IC analysis using the discrete sampling method (Table 1).

High Resolution. While the temporal trends of ion concentrations are the same in the results by the discrete sampling method and by CFA-IC (Figure 5), more details or temporal variations are seen in the CFA-IC data, owing to the enhanced depth resolution. Given the chromatography parameters (4-min chromatograms and 6 IC instruments), and after optimizing the melter-IC interface, we were able to achieve a practical resolution of about 2 cm. Similar dispersion-limited resolution has been reported for other CFA systems ($13$, $14$, $21$). In comparison, the practical resolution in routine discrete sampling by bandsaw cutting is usually limited to 2–3 cm per sample ($8$–$10$).
to those achieved by existing CFA systems. The CFA-IC all-ion capability eliminates the need for offline IC measurements (4, 12) and therefore can significantly increase the overall speed of major ion analysis of long ice cores.

The CFA-IC technique appears less cumbersome than spectrometric CFA for a number of other reasons. Only two (anion and cation) meltwater streams are needed in CFA-IC, whereas spectrometric CFA requires one stream for each ion measured (11, 13). In addition, a reagent solution must be added to each stream to generate absorbing or fluorescent complexes, requiring long liquid lines for sufficient reaction time and resulting in large void volume. In CFA-IC, no chemical alteration of the analyte ions in the meltwater stream is required. In fact, no chemical reagents are used in CFA-IC operation, except for dilute NaOH and H₂SO₄ solutions as IC eluent.

Future Improvements. The current CFA-IC system can be improved in several aspects. Here we outline two potential improvements in the near future.

One of the goals of CFA-IC development is to increase the data volume of long ice cores through high resolution analysis at practical speeds. The ice melt rate of 1–2 cm min⁻¹ in the current CFA-IC system is slow, compared with those (3–5 cm per min) of the CFA systems with spectrometry and ICP-MS detection (13, 14). In future work, we will investigate ways to increase the melt rate, thereby increasing the overall analysis speed. One approach is using more IC instruments. For example, the addition of one pair of IC instruments would allow the melt rate to increase by 33%, from 1.5 to 2.0 cm min⁻¹, without reduction in the 2 cm resolution. This would likely increase the daily analysis speed by 20–30%.

Another area of potential improvement is resolution, as depth resolution of 1 cm or less is desirable in the analysis of very old ice (4, 5). It is clear from our discussion that the dispersion-affected resolution (Rd) determines the actual resolution of ion analysis with this technique. At a constant melt rate, more IC instruments can improve nominal resolution (Rn) but cannot improve Rd, which is determined by the extent of dispersion, τo. To improve resolution, our main efforts will be to decrease τo by reducing system void volume.

Acknowledgments

Funding for this work was provided by NSF Awards 0216152 and 0337933. We wish to thank G. Lamorey and J. McConnell for assistance in fabricating the ice core meter. S. Klein, C. Duval (undergraduate students), and C. Reecy of the Department of Chemistry and Biochemistry, South Dakota State University contributed to the laboratory testing of the CFA-IC system. We are grateful for anonymous reviews that helped improve the manuscript.

Supporting Information Available

Detailed procedures for obtaining blanks and detection limits, comparison of results by discrete sampling and CFA-IC for all cations (Figure S1) and anions (Figure S2), and results of replicate measurements of a short ice core section (Figure S3) demonstrate the reproducibility of the CFA-IC system. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review May 17, 2006. Revised manuscript received August 23, 2006. Accepted August 30, 2006.

ES061188A