Simple procedure for ion chromatographic determination of anions and cations at trace levels in ice core samples

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Abstract

Several suppressed and non-suppressed ion chromatography (IC) elution systems were compared for the determination of ng ml\textsuperscript{−1} levels of major cations and anions, including formate and methyl sulphonate, in ice core samples using a small (0.2–0.8 ml) sample volume. The use of a suppression unit considerably enhanced the sensitivity of the anion determinations, but had no remarkable effect on the sensitivity of the cation determinations. Optimized analytical conditions were further validated in terms of accuracy, precision and total uncertainty and the results showed the reliability of the IC methods. In addition, contamination problems associated with handling the ice core were investigated, and a simple and almost contamination free ice handling procedure is presented. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ice core; Ion chromatography; Anions; Cations

1. Introduction

Low detection limits and high measurement sensitivity to anions and cations with a small sample volume are needed in several applications of ion chromatography (IC), e.g. ice core research for paleoclimatic purposes. Much attention has been paid to optimizing these factors and various analytical methods have been developed [1–9]. Many of the methods are based on the use of a preconcentration column [2,4,6,8,10] or a large sample loop [1,3,5,7–9] to lower the detection limits. In addition, suppressor units have been widely used with conductivity detectors as this lowers background conductance and enhances the overall conductance of the analyte [11] leading to lower detection limits. Suppressors also facilitate the use of gradient elution, which has been essential for the determination of early eluted carboxylic acids and methyl sulphonate (MSA\textsuperscript{−}) in the same run with common anions [4]. Thus with the suppressor there is no need for isoconductivity gradient elution which is used with non-suppressed IC [12]. Recently, MSA\textsuperscript{−} has attracted growing interest as it contributes to the sulphur budget and is indicative of biological activity [13–16].

Since the ion concentrations in ice core samples are generally low, great efforts have been made to prevent contamination of the samples. The problem of contamination can be derived from two major sources.
First, as the outer part of the core is significantly contaminated during drilling, there has to be an effective procedure for removing the surface of the ice, e.g. by saw/knife/scalpel [1,4,5,9], wash melting [6,7,17] or sub-drilling [8–10]. Secondly, care should be taken to prevent further contamination from instruments, containers, vials, laboratory air, etc. Measurements have even been performed in the field to reduce the risk of contamination [4].

The aim of this study was to improve our IC methods for determining several anions (formate, MSA\(^{-}\), chloride, nitrate, sulphate) and cations (sodium, ammonium, potassium, magnesium, calcium) at trace levels in ice core samples using small sample volumes. Several suppressed and non-suppressed elution systems were critically tested, and the reliability of the optimized analytical methods was further validated in terms of accuracy, precision and total uncertainty. In addition, the contamination problem associated with handling the ice has been addressed and an almost contamination free method of handling the ice is fully described.

2. Experimental

2.1. Instrumentation

The chromatograph used in this study consisted of a Waters 600e gradient pump, a Waters 431 conductivity detector and a Waters 715 ultra wisp sample processor (injector, autosampler). The recently developed Alltech ERIS 1000HP autosuppressor was used in the suppressed analyses. The suppressor uses packed-bed suppressor cartridges (14×7.5 mm, Alltech) which are regenerated via an electrothermal process that allows continuous operation of the chromatograph. The suppressor requires two cartridges because while one cartridge is being used, the other is being regenerated. The principles of the ERIS have been described in detail elsewhere [11,18].

The separation columns used for the anions were a Waters IC Pak A/HR and Dionex Ionpac AG9-HC, and for the cations a Waters IC Pak Cation M/D, Dionex Ionpac CS12A and Alltech Universal Cation Column were used. The same columns were used for the suppressed and non-suppressed systems. The columns were heated to 35±1°C during operation.

The chromatograms were recorded and handled with Millenium 2.15 software, which was also used for controlling the pumps and injector. The ERIS was controlled via the injector.

2.2. Reagents and standard solutions

Pure water (resistivity>17 MΩ cm\(^{-1}\)), obtained from a Millipore Milli-Q (MQ) water purification system, was used to prepare standards and for cleaning the containers and bottles. Working standard solutions were prepared daily by further dilution of 2 mg l\(^{-1}\) stock solutions, apart from formate and MSA\(^{-}\) which were made daily from their 2000 mg l\(^{-1}\) stock solutions. The stock solutions were prepared weekly by dilution of Merck 1000 mg l\(^{-1}\) solutions, except in the case of formate which was prepared from its sodium salt (Merck, p.a.), and MSA\(^{-}\) which was diluted from its 99% solution (Fluka, puriss.).

All reagents used in the preparation of eluents were at least p.a. purity grade. Ascariite (Fluka, 10–35 mesh) was used to prevent the dissolution of CO\(_{2}\) in alkaline eluents.

2.3. Cleaning of plasticware and glassware

All bottles and containers were soaked in Milli-Q water overnight at least, and then placed for 10–15 min in an ultrasonic bath and rinsed three times with Milli-Q water prior to use. The equipment was dried under a laminar air flow hood. Masks and PE gloves were used during the cleaning procedures.

2.4. Samples

Ice samples were taken from a 120 m deep ice core which was drilled on Lomonosovfonna (1230 m a.s.l.), one of the highest ice fields in Svalbard, in spring 1997. Samples were handled with strict contamination control as described in the next section, and stored in a cold room (−22°C) in Stockholm University.

2.5. Sample preparation

It has been reported that 50% of the ice volume (approximately 30% of initial radius) has to be removed to obtain a contamination-free center of
the ice core [4,6,8,9,17]. In our procedure, the ice core (diameter of 10 cm) was cut into 5 cm sections using a band saw. Then the outer 2–2.5 cm parts of the ice (ca. 40% of volume) were removed by band saw (rough cleaning) and stainless steel knife (fine cleaning) inside a clean air bench. The saw and knife blades were cleaned by repeatedly cutting MQ ice. The cleaned ice samples were divided into several pieces for separate cation, anion and pH measurements, and the pieces were placed in clean PE bags (Seward). In addition, some special samples were taken for the determination of metals and carbon. The bags were heat sealed and then placed in another plastic bag for transporting in cold boxes to Rovaniemi Research Station for analysis. The samples were stored in a –22°C cold room until chemical analysis.

On the day of analysis the bags were opened inside a laminar air flow hood in the cold room and the samples were transferred into cleaned melting containers (PE/PP, Kartell or Nalgene). The containers were tightly sealed and the ice melted in a hot water bath. Melted samples were not filtered in order to minimize contamination and sample consumption. Disposable PS vials (Sarstedt) were used for introducing the sample solution into the chromatograph. Face masks and PE gloves were used continuously during the sample preparation step.

To monitor the contamination level of the sample handling procedure, Milli-Q water was frozen in a PE measuring cylinder (2000 ml) to make a pure MQ-ice core which was then handled in the same way as the sample cores.

3. Results and discussion

3.1. Determination of anions

Three elution systems – one non-suppressed and two suppressed – were tested for the determination of common anions (Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup> and SO<sub>4</sub><sup>2−</sup>). Both suppression methods provided high sensitivity determinations with low sample consumption (Table 1). An optimized suppressed system gave detection limits that were about 10 times lower than the non-suppressed system.

Weaker eluents with high column efficiency are needed for adequate separation of fluoride, acetate, formate and MSA<sup>−</sup>. High resolution is especially important for separating two ions which have a high concentration ratio in ice as pointed out by Udisti et al. [3]. This is true particularly in the case of formate and MSA<sup>−</sup> ions. Only the Ionpac AG9-HC column with 2.5 mM Na<sub>2</sub>CO<sub>3</sub> or 12 mM NaHCO<sub>3</sub> eluents achieved sufficient resolution of formate and MSA<sup>−</sup> (resolution 1.3). However, the isocratic elution of all anions in one run using a weak eluent is not possible because it leads to excessively long retention times for NO<sub>3</sub><sup>−</sup> and SO<sub>4</sub><sup>2−</sup> and very broad peaks. Gradient elution was found to be inadequate as the suppressor was not able to lower the baseline conductivity efficiently during strong eluent conditions, e.g. the baseline was raised from 16 to 30 µS with a gradient from 2.5 to 9 mM Na<sub>2</sub>CO<sub>3</sub> preventing accurate determination of NO<sub>3</sub><sup>−</sup> which was eluted during the baseline rise. Thus the anions were determined in two steps:

Table 1

<table>
<thead>
<tr>
<th>Column</th>
<th>Eluent</th>
<th>Detection limit of ion (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cl&lt;sup&gt;−&lt;/sup&gt;</td>
</tr>
<tr>
<td>IC Pak A/HR Borate–gluconate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.4</td>
<td>16</td>
</tr>
<tr>
<td>IC Pak A/HR NaHCO&lt;sub&gt;3&lt;/sub&gt;+Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt; (S)</td>
<td>0.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Ionpac AG9-HC Na&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (S)</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Ionpac AG9-HC NaHCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (S)</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Results based on chromatograms of 10–100 ng ml<sup>−1</sup> standard solutions. (S)=suppressed IC.

<sup>a</sup> 0.5 mg/l Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, 0.32 mg/l C<sub>6</sub>H<sub>11</sub>NaO<sub>7</sub> and 0.36 mg/l boric acid in 0.5 vol% glycerin, 2 vol% butanol and 12 vol% acetonitrile. 0.4 ml injection volume.

<sup>b</sup> 1.1 mM NaHCO<sub>3</sub>+1.1 mM Na<sub>2</sub>CO<sub>3</sub>, 0.2 ml injection volume.

<sup>c</sup> 12.5 mM Na<sub>2</sub>CO<sub>3</sub>, 0.3 ml injection volume.

<sup>d</sup> 12 mM NaHCO<sub>3</sub>, 0.8 ml injection volume.
first, the MSA$^-$ and formate with 12 mM NaHCO$_3$ eluent and later, after 1–2 days, the common anions with Na$_2$CO$_3$ eluent. An Ionpac AG9-HC column was used in both steps. Regression analysis (not shown) confirmed that the concentrations of Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ were unchanged prior to determination as the same sample solutions were used in both steps. Examples of the chromatograms are shown in Fig. 1. It should be noted that during the determination of MSA$^-$ and formate, the column was flushed with strong eluent after 2–3 samples in order to remove all the trapped ions which can have an influence on the efficiency of the column.

The accuracy and precision over a wide concentration range, and total uncertainty (including random and systematic errors reported at the 95% confidence level) of anion determinations were further estimated and the values were found to be sufficient for analysis of the ice (Tables 2 and 3). Direct accuracy of the formate determination could not be tested and that of MSA$^-$ was derived from an interlaboratory test between three laboratories. The variance test indicated the absence of systematic error between laboratories at the 95% confidence level ($P$-value=0.227, $n=11$). The lower precision of the MSA$^-$ and formate determinations may be related to the gradient nature of their determination (two eluents are used – one for determining and the other for flushing) compared with isocratic determination [3]. In addition, contamination from laboratory air has an effect on the accuracy and precision of the formate determination as discussed later. System peaks can occur with Cl$^-$, SO$_4^{2-}$ and formate, leading to less analytical reliability at low concentrations.

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**Fig. 1.** Typical chromatograms of (A) common anions at 100 ng ml$^{-1}$ and (B) acetate, formate and MSA$^-$ at 30 ng ml$^{-1}$. Analytical conditions: (A) Ionpac AG9-HC column, 12.5 mM Na$_2$CO$_3$ eluent, 0.3 ml injection volume, 0.8 ml min$^{-1}$ flow rate, (B) Ionpac AG9-HC column, 12 mM NaHCO$_3$ eluent, 0.8 ml injection volume, 0.8 ml min$^{-1}$ flow rate.
Sub ng ml\(^{-1}\) levels of potassium, magnesium and calcium are often present in polar ice samples, and this requires measurement under well-optimized analytical conditions. In addition, high resolution is needed, especially between Na\(^+\) and NH\(_4^+\). Table 4 summarizes the detection limits of all the relevant cations and the Na\(^+\)--NH\(_4^+\) resolution obtained with various elution systems. With suppressed IC, low concentrations of divalent cations could not be determined as the peaks suffered from a strong band-broadening effect, which also occurred at higher concentrations. Even at the 100 ng ml\(^{-1}\) level, Mg\(^{2+}\) and Ca\(^{2+}\) peaks were not observed with the methane sulphonic acid eluent. The same problem also occurred with the H\(_2\)SO\(_4\) eluent (a strong eluent for doubly charged cations) when the Universal cation or Ionpac CS12A columns were used, indicating a malfunction of the suppressor cartridges or process in our experiments. In addition, the suppression cartridges had insufficient capacity for the Ionpac CS12A column which requires a high eluent concentration.

Based on Table 4, the non-suppressed Universal cation column with MSA eluent, which allows ng ml\(^{-1}\) detection of cations, with reasonable Na\(^+\)--NH\(_4^+\) resolution, was used for determination of the cations. The resolution of Na\(^+\)--NH\(_4^+\) was usually sufficient as the Na\(^+\)/NH\(_4^+\) ratio in the ice samples

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### Table 2

<table>
<thead>
<tr>
<th>Ion</th>
<th>Measurement concentration (ng ml(^{-1}))</th>
<th>RSD (%)</th>
<th>Day-to-day reproducibility (%)</th>
<th>Total uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>100</td>
<td>0.5</td>
<td>5.0</td>
<td>14</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>50</td>
<td>1.7</td>
<td>2.1</td>
<td>6</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>100</td>
<td>2.7</td>
<td>4.4</td>
<td>12</td>
</tr>
<tr>
<td>Formate</td>
<td>5</td>
<td>7.9</td>
<td>4.8(^a)</td>
<td>25</td>
</tr>
<tr>
<td>MSA(^-)</td>
<td>5</td>
<td>6.7</td>
<td>4.6(^a)</td>
<td>21</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>100</td>
<td>2.3</td>
<td>3.9</td>
<td>11</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>10–20</td>
<td>5.1</td>
<td>7.6</td>
<td>21</td>
</tr>
<tr>
<td>K(^+)</td>
<td>5</td>
<td>15.8</td>
<td>6.0(^b)</td>
<td>62</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>10–15</td>
<td>2.6</td>
<td>3.3</td>
<td>9</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>10–15</td>
<td>2.3</td>
<td>5.1</td>
<td>14</td>
</tr>
</tbody>
</table>

The precision is based on the relative standard deviation (RSD) for 4–7 successive determinations, day-to-day reproducibility is based on results from control solutions analyzed once a day (\(n=5\)) and the total uncertainty is based only on day-to-day reproducibility (as systematic errors were not found) reported at the 95% confidence level. Analytical conditions: see captions to Figs. 1 and 3.

\(^{a}\) Measured at 45 ng ml\(^{-1}\). Estimation of total uncertainty based on RSD which was measured at 5 ng ml\(^{-1}\).

\(^{b}\) Measured at 15 ng ml\(^{-1}\). Estimation of total uncertainty based on RSD which was measured at 5 ng ml\(^{-1}\).

### Table 3

<table>
<thead>
<tr>
<th>Ion</th>
<th>Certified value ((\mu g) ml(^{-1}))</th>
<th>Measured value ((\mu g) ml(^{-1}))(^a)</th>
<th>Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>30.5±0.7</td>
<td>32.1±1.5</td>
<td>1:1000</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>101±2</td>
<td>98±2</td>
<td>1:1000</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>151±3</td>
<td>153±5</td>
<td>1:1000</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>201±5</td>
<td>181±4</td>
<td>1:20000</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>400±8</td>
<td>369±19</td>
<td>1:20000</td>
</tr>
<tr>
<td>K(^+)</td>
<td>202±4</td>
<td>197±13</td>
<td>1:20000</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>202±4</td>
<td>192±4</td>
<td>1:20000</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1006±18</td>
<td>989±14</td>
<td>1:20000</td>
</tr>
</tbody>
</table>

\(^{a}\) Mean and 95% confidence interval (\(n=6\)).
was generally about 6–10. The chromatogram in Fig. 2 shows a large, early eluted injection peak, which interfered with the Na⁺, NH₄⁺, and K⁺ determinations. However, further tests indicated that the cation system had high precision and reproducibility (Table 2). The accuracy test showed slightly lowered Na⁺ and NH₄⁺ values (Table 3) probably due to the presence of high concentrations of Li⁺ in the reference

Table 4
Detection limits for Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ with Na⁺–NH₄⁺ resolution obtained by several cation elution systems

<table>
<thead>
<tr>
<th>Column</th>
<th>Eluent</th>
<th>Detection limit of ion (ng ml⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Na⁺</td>
</tr>
<tr>
<td>IC Pak Cation</td>
<td>HNO₃–EDTA⁴⁻</td>
<td>1.6</td>
</tr>
<tr>
<td>M/D</td>
<td>Universal cation</td>
<td>0.5</td>
</tr>
<tr>
<td>Universal Cation</td>
<td>MSAᵇ</td>
<td>(S)</td>
</tr>
<tr>
<td>Universal Cation</td>
<td>MSAᶜ</td>
<td>(S)</td>
</tr>
<tr>
<td>Ionpac CS12A</td>
<td>MSAᵈ</td>
<td>(S)</td>
</tr>
<tr>
<td>Universal cation</td>
<td>HClᵉ</td>
<td>(S)</td>
</tr>
</tbody>
</table>

Values based on chromatograms of 100 ng ml⁻¹ standard solutions. (S)=suppressed IC.

ᵃ 1 mM EDTA and 3 mM HNO₃, injection volume 0.4 ml.
ᵇ 2.5 mM MSA, injection volume 0.8 ml.
ᶜ 3.0 mM MSA, injection volume 0.2 ml.
ᵈ 15 mM MSA, injection volume 0.030 ml. Values based on results for 2 µg ml⁻¹ solution.
ᵉ 3.0 mM HCl, injection volume 0.8 ml.
ᶠ No peaks were obtained with 100 ng ml⁻¹ standard solution.

Fig. 2. Example of a chromatogram of cation determination at 100 ng ml⁻¹. Conditions: Universal cation column, 2.5 mM MSA eluent, 0.8 ml sample volume, 0.9 ml min⁻¹ flow rate.
sample, thus making determination of the baseline more difficult. However, sodium concentrations in the ice core samples analyzed by this method agreed well with those reported by another laboratory according to regression analysis (not shown). The total uncertainties of the results at typical concentration levels of the ions were between 10% and 20%. The uncertainties for NH$_4^+$ and K$^+$ were higher because of the well-known contamination problem associated with NH$_3$ (see next paragraph) and extremely low concentrations of K$^+$ in the ice samples.

3.3. Contamination

Contamination caused by the dissolution of ammonium, nitrate, fluoride, formate and acetate from laboratory air has been studied by several authors [3–10,17]. Typically, samples have been melted just before analysis to prevent the contamination, and in some cases an air purification system has been used during melting [6,7,17]. We found that the dissolution of ammonium and formate ions had a linear relationship with time, as demonstrated in Fig. 3. The average contamination rates were between 0.3 and 0.6 ng ml$^{-1}$ h$^{-1}$ which are generally lower than those reported by others [3,4,6,9,17]. For estimating the amount of dissolved ions (i.e. contamination), the time interval between the melting and determination steps was calculated for every sample and then, using regression lines as in Fig. 3 (a new line was produced each day), the concentrations of dissolved NH$_4^+$ and formate were obtained. These values were later subtracted from the analysis result. This allows stand alone operation of the chromatograph, but the uncertainty of the results is increased and thus leads to semi-quantitative determinations at low concentration levels.

To investigate the contamination sources in our sample preparation procedure a MQ-ice core was made and cleaned with a stainless steel knife as described earlier. The ion concentrations were measured from (i) pure MQ water (contamination mainly from vials), (ii) MQ water used for rinsing the melting containers (contamination from vials and containers), (iii) cleaned MQ ice which was melted in containers (contamination from vials, containers and the ice handling procedure) and (iv) cleaned MQ ice which had been stored in a plastic bag (contamination from vials, containers, ice handling and storing). In addition, (v) washing the MQ ice with MQ water before analyzing was tested for the removal of particles that may have become adsorbed on the surface of the samples during sample handling and storing. The results of the tests show (Fig. 4) that contamination was generally low; sub-detection limit contamination was obtained for K$^+$, Mg$^{2+}$, NO$_3^-$ and MSA$^-$. Even contamination from the plastic bags (storage) was shown to be negligible, indicating the purity of the bags. However, this value could be higher than that observed here because the storage time in the test was short compared with the possible several months or years of storage. Washing the ice was shown to have a significant reduction effect on the contamination levels for cations, unlike the anions. The procedure cannot be used for porous snow and firn samples because of dilution. The results of the test are in good agreement with the long term results of the MQ core analyses (Table 5). Even contamination by ammonium, which is generally considered to be a sensitive indicator of contamination level [7], was minimal.

The formate concentration was generally high in the blank core (Fig. 4). This may be due to the use of a plastic measuring cylinder in the preparation of the MQ core and/or plastic vials because plastic is known to be a source of contamination by formate and acetate [6,17]. However, after comparison of the PS vials with disposable glass vials (Brown), the formate concen-
trations in the MQ water were found to be considerably higher in the glass vials than in the PS vials, viz. $27\pm9\text{ ng ml}^{-1}$ and <detection limit (DL), respectively ($n=4$). The reason for this was not further studied, but it could be related to the overall uncleanliness of the glass vials. PS vials were not found to release formate because the subsequent contamination (Fig. 3) is mainly of laboratory air origin. Thus we conclude that the source of the high formate contamination was primarily the measuring cylinder, and therefore, the concentration of the blank was not subtracted from the results of formate determinations.

4. Conclusions and application

The detection limits for anions can be lowered by about a factor of 10 using suppression IC mode compared with non-suppressed IC. In the case of cations, there is less difference between suppressed and non-suppressed systems. In general, it can be concluded that the detection limits for ions can easily be lowered by using larger injection volumes, thus avoiding the need for preconcentration columns. However, very large injection volumes should be avoided as they lead to broad peaks and thus to low resolution. In addition, it was found that the contamination associated with the sample-handling procedure can be reduced below the detection limits for most ions. External contamination can easily be taken into account by using an MQ ice core, except in the case of carboxylic acids.
The methods developed here have been used for measuring the ions in the Svalbard ice core down to a depth of 20 m. Several control solutions (high and low concentrations) were used daily to ensure day-to-day accuracy of the results. In addition, intercepts of the calibration lines were monitored for evaluating the contamination of standard solutions. Some statistics of the application are analyzed in Table 6 and they confirm the usefulness of the IC methods developed here for ice core research. However, the considerable sensitivity problems in the detection of potassium and MSA$^-$ and also the low Na$^+$–NH$_4^+$ resolution need further development work.

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