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## Continuous melting and ion chromatographic analyses of ice cores

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### Abstract

A new method for determining concentrations of organic and inorganic ions in ice cores by continuous melting and contemporaneous ion chromatographic analyses was developed. A subcore is melted on a melting device and the meltwater produced is collected in two parallel sample loops and then analyzed simultaneously by two ion chromatographs, one for anions and one for cations. For most of the analyzed species, lower or equal blank values were achieved with the continuous melting and analysis technique compared to the conventional analysis. Comparison of the continuous melting and ion chromatographic analysis with the conventional analysis of a real ice core segment showed good agreement in concentration profiles and total amounts of ionic species. Thus, the newly developed method is well suited for ice core analysis and has the advantages of lower ice consumption, less time-consuming sample preparation and lower risk of contamination. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ice cores; Water analysis; Inorganic anions; Inorganic cations; Organic acids

### 1. Introduction

Cold glaciers and polar ice sheets are important archives of the chemical composition of the atmosphere, since atmospheric constituents are deposited with precipitating snow and accumulated in the ice. By analyzing ice cores, historical records of atmospheric trace species, e.g. ammonium, chloride, nitrate, and sulfate, can be reconstructed. This allows a deeper understanding of atmospheric transport mechanisms, climatic changes and the impact of human activities on the chemistry of the atmosphere [1,2]. The extraction of the full glacio-chemical information preserved in ice cores is particularly demanding on the analytical techniques. Sensitive and fast

multi-component methods are required, which are capable to produce continuous, high-resolution chemical profiles. A high spatial resolution is extremely useful in studying glacier archives with low annual accumulation of snow, e.g. in Central Antarctica (see e.g. [3,4]) and at high-elevated mountain glaciers (e.g. [5–7]). It is essential for the detection of particular events such as volcanic eruptions (see e.g. [8–11]) or biomass burning events [12–16], which is needed in order to correlate climatic and atmospheric changes on a global scale and to compare different ice cores by using well-defined temporal horizons [17–23]. In addition, studies of temporal trends require continuous concentration records of chemical species, for instance to identify the anthropogenic impact on the composition of the atmosphere (e.g. [24–31]).

The common way of analyzing ice cores is to remove the possibly contaminated outer parts, for instance with a band-saw, to cut the inner core in

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pieces, melt them and analyze each piece separately, for example with ion chromatography for ionic species. Limits of detection for ionic species depend on the chromatographic conditions, the sample volume, and the respective species, but are generally in the order of few tenths to a few  $\mu\text{g l}^{-1}$  [4,32–36]. As this sample preparation procedure is time consuming and prone to contamination, a new technique was developed by Sigg et al. [37]. With the so-called continuous flow analysis (CFA) of ice cores, a subcore is melted continuously lengthwise and the meltwater divided into an inner and an outer fraction. Whereas the outer fraction might be contaminated by the ice core drill and the polyethylene tubes used for packing the ice cores, the inner fraction is assumed to be uncontaminated. This inner part of the melted sample is then analyzed using a separate detector for each species, based on fluorometric and absorption techniques.

The CFA technique has been used successfully in ice core drilling projects in Antarctica and Greenland, see for example [38,39]. The major advantage of this method compared to the conventional way of analyzing ice cores (see e.g. [33,35,40]) is a less time-consuming and much simpler sample preparation step, resulting in a reduced risk of contamination. In addition, a higher spatial and subsequently temporal resolution can be achieved compared to the conventional decontamination method, which is limited due to mechanical cutting. Detection limits of CFA are better or comparable with those of ion chromatography for ammonium, calcium, sodium, and nitrate ( $0.1\text{--}1.0 \mu\text{g l}^{-1}$ ) [39]. Disadvantages of the CFA technique are that a separate detector is used for every species, which makes the system complex to operate and maintain. Furthermore, for certain species of interest a sensitive detection reaction does not exist. Organic acids like acetate, formate and methanesulfonate cannot be determined with CFA technique until now. As these species normally occur at low level concentrations, they are prone to contamination. Due to their importance in atmospheric chemistry [26,41,42], it would be desirable to have a continuous analysis technique. CFA techniques for the determination of fluoride, chloride, potassium and magnesium do not exist either. For sulfate, the detection limit for the existing CFA technique is still too high ( $20 \mu\text{g l}^{-1}$ ) to determine

low level sulfate concentrations [39]. Therefore, Udisti et al. used a continuous melting device coupled with an ion chromatograph [43,44], in order to determine concentrations of chloride, nitrate and sulfate. Detection limits for all three species are below  $0.5 \mu\text{g l}^{-1}$ . However, only semi-continuous data sets could be achieved.

Our approach is to take advantage of the full potential of ion chromatography as a multicomponent analytical method and couple it to a melting device, in order to determine continuously not only selected components, but the whole range of inorganic as well as organic anions and cations present in ice cores and detectable by ion chromatography.

## 2. Experimental

### 2.1. Sample preparation, melting device and ion chromatographic systems

With the melting device, ice subcores are melted continuously and the meltwater is separated into an inner and an outer fraction. The inner, uncontaminated fraction is pumped over valve connections into two parallel sample loops, one for anions and one for cations. By switching the valves after a definite time, the samples are eluted from the sample loops onto the two corresponding ion chromatographs, where the ions are separated and detected. During these ion chromatographic analyses, the newly melted sample is collected in two different sample loops and analyzed afterwards. This approach allows continuous high-resolution concentration records of the species of interest in the ice core to be obtained.

An aluminum melting head coated with PTFE was built according to Sigg et al. [37] (Fig. 1). The head is heated by three heat sources of 100 W each, which are controlled by a thermocouple. The melting speed can be adjusted by varying the temperature. At a temperature of  $35^\circ\text{C}$ , a melting speed of  $0.45 \text{ cm min}^{-1}$  is achieved. During the analytical runtime of 8.6 min, 4 cm of the ice core are melted. A subcore sample with a cross-section of  $2.5 \times 2.5 \text{ cm}^2$  and a length of approximately 70 cm is placed on top of the melting head, stabilized by a sample holder and loaded with a mass of about 150 g. As shown in Fig.

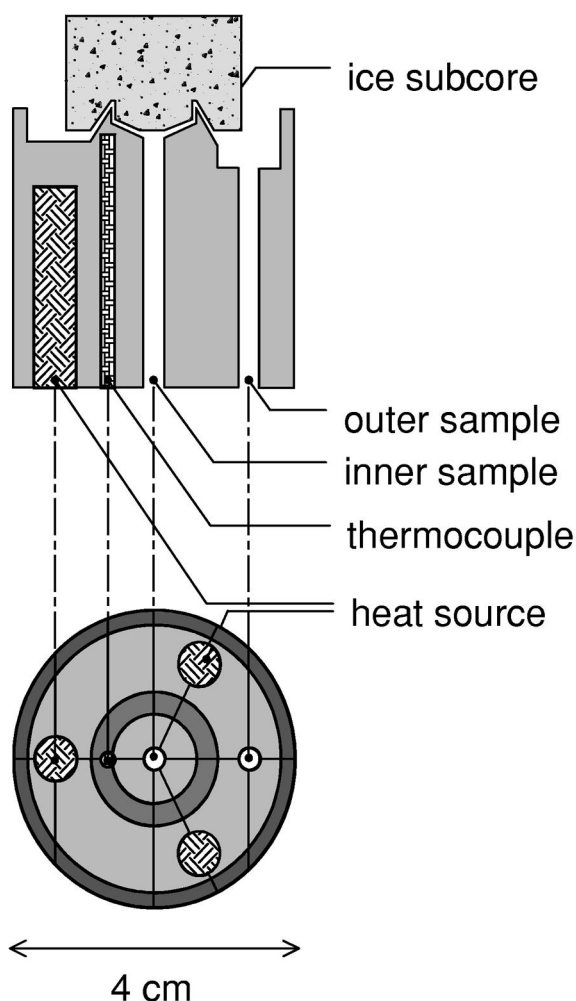


Fig. 1. Cross-section (upper panel) and top view of the melting head (lower panel).

2, this part of the device is installed in a deep-freeze at  $-23^{\circ}\text{C}$ .

The meltwater is divided into an inner and an outer fraction by the geometry of the melting head (Fig. 1). Both fractions are pumped away separately with a peristaltic pump. In order to guarantee that the inner fraction is not mixed with the outer fraction, the pump speed for the inner fraction is lower than necessary to remove all the meltwater produced. Conversely, the pump speed for the outer fraction is higher than necessary to remove the remaining meltwater. Thus, meltwater can only flow from the inner to the outer fraction. The inner fraction is used

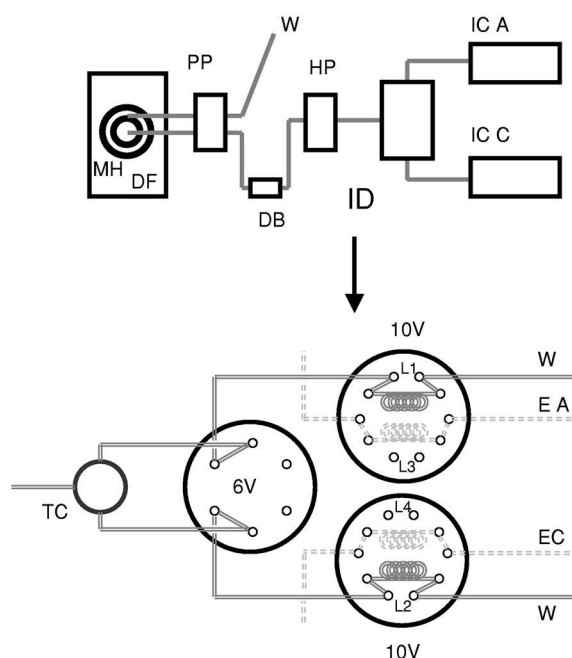


Fig. 2. Schematic of the apparatus (upper panel) and of the sample collection and injection device (lower panel). MH, melting head, DF, deep-freeze, PP, peristaltic pump, DB, debubbler, W, waste, HP, HPLC-pump, ID, sample collection and injection device, IC A and IC C, ion chromatographs for anions and cations analysis, TC, tee-connector, 6V, six-port valve, 10V, ten-port valves, L1–L4, sample loops, EA, eluent anions (KOH), EC, eluent cations ( $\text{H}_2\text{SO}_4$ ).

for the ion chromatographic analyses while the outer fraction is discarded, or collected and stored for the analysis of species not sensitive to contamination.

A debubbler, which is installed behind the melting head and the peristaltic pump, removes air from the inner meltwater fraction. A P 580A Bio HPLC pump (Gynkotech, Switzerland) transports the meltwater from the debubbler to the sample collection and injection system (Fig. 2). The sample stream is divided by a tee connector and distributed by a six-port valve into two sample loops, each of 1.4 ml volume. The samples from the two loops L1 and L2 are injected into the corresponding ion chromatographs and during the subsequent analyses, the next meltwater fraction is simultaneously collected in sample loops L3 and L4. After the analysis, all three valves are switched and the sample is now collected in loops L1 and L2, while the sample in loops L3 and L4 is analyzed.

Sample loops were used instead of concentrator columns, because of possible column overload and loss of low affinity ions (e.g. sodium, fluoride) by high concentrations of high affinity ions (e.g. calcium, sulfate) acting as an eluent.

Chemical analysis of anions was performed using an IC 320 system (Dionex, Switzerland) equipped with an EG 40 eluent generator, an AS 17 anion separator column, an ASRS Ultra conductivity suppressor and an IC 20 conductivity detector. A gradient elution was applied using potassium hydroxide (KOH), produced by the EG 40, as eluent with a flow rate of  $2 \text{ ml min}^{-1}$ . The gradient was  $1 \text{ mmol l}^{-1}$  KOH from 0 to 1.8 min,  $1$  to  $34 \text{ mmol l}^{-1}$  KOH from 1.8 to 5.8 min and  $1 \text{ mmol l}^{-1}$  KOH from 5.9 to 8.6 min.

Chemical analysis of cations was performed using a S 1100 pump (Sykam, Germany), a CS 12 cation separator column (Dionex), a CSRS Ultra conductivity suppressor (Dionex) and a S 3110 conductivity detector (Sykam). As eluent,  $15.5 \text{ mmol l}^{-1}$  of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was applied at a flow rate of  $1 \text{ ml min}^{-1}$ .

PeakNet 5.1 Software (Dionex) was used for data acquisition and peak integration.

Under these conditions, it was possible to determine the concentrations of the inorganic anions fluoride ( $\text{F}^-$ ), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ), and the organic components acetate ( $\text{CH}_3\text{CO}_2^-$ ), formate ( $\text{CHO}_2^-$ ), methanesulfonate ( $\text{CH}_3\text{SO}_3^-$ ) and oxalate ( $\text{C}_2\text{O}_4^{2-}$ ), as well as of the cations sodium ( $\text{Na}^+$ ), ammonium ( $\text{NH}_4^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ) and calcium ( $\text{Ca}^{2+}$ ), within a runtime of 8.6 min. This short runtime is important to minimize analysis time, and thus allows to achieve high resolution analyses in a reasonable time. In Fig. 3, chromatograms of an ice sample from Grenzletscher (Swiss Alps, Monte Rosa Massif, 4200 m above sea level) and of a blank are shown.

## 2.2. Determination of blank values

Blank values were derived from an artificial ice core, which was analyzed by the continuous melting and analyzing technique as well as by the conventional technique. An artificial ice core was prepared

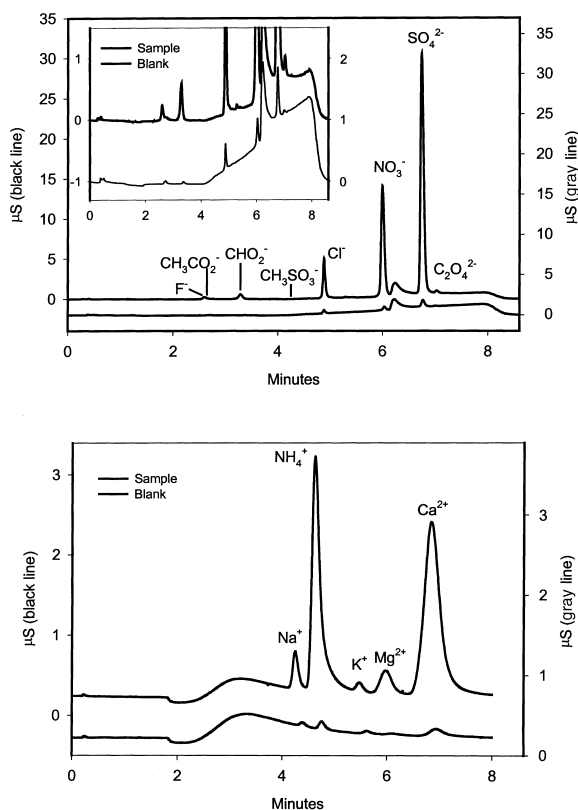


Fig. 3. Chromatograms of an ice sample from Grenzletscher (black line) and of a blank (gray line), for anions (upper panel) and cations (lower panel). Concentrations in  $\mu\text{g l}^{-1}$  for the ice sample: 2.8 ( $\text{F}^-$ ), 1.6 ( $\text{CH}_3\text{CO}_2^-$ ), 17.9 ( $\text{CHO}_2^-$ ),  $\leq\text{D. L.}$  ( $\text{CH}_3\text{SO}_3^-$ ), 50.7 ( $\text{Cl}^-$ ), 81.6 ( $\text{NO}_3^-$ ), 268.3 ( $\text{SO}_4^{2-}$ ), 4.1 ( $\text{C}_2\text{O}_4^{2-}$ ), 15.5 ( $\text{Na}^+$ ), 191.2 ( $\text{NH}_4^+$ ), 7.4 ( $\text{K}^+$ ), 11.6 ( $\text{Mg}^{2+}$ ), 194.1 ( $\text{Ca}^{2+}$ ). Concentrations in  $\mu\text{g l}^{-1}$  for the blank: 0.5 ( $\text{F}^-$ ),  $\leq\text{D. L.}$  ( $\text{CH}_3\text{CO}_2^-$ ),  $\leq\text{D. L.}$  ( $\text{CHO}_2^-$ ),  $\leq\text{D. L.}$  ( $\text{CH}_3\text{SO}_3^-$ ), 3.2 ( $\text{Cl}^-$ ), 5.2 ( $\text{NO}_3^-$ ), 5.6 ( $\text{SO}_4^{2-}$ ), 0.7 ( $\text{C}_2\text{O}_4^{2-}$ ), 1 ( $\text{Na}^+$ ), 2.4 ( $\text{NH}_4^+$ ),  $\leq\text{D. L.}$  ( $\text{K}^+$ ),  $\leq\text{D. L.}$  ( $\text{Mg}^{2+}$ ), 4.8 ( $\text{Ca}^{2+}$ ).

by freezing of ultra-pure water (resistance  $>18 \text{ M}\Omega \text{ cm}$ ) in a pre-cleaned polyethylene tube. This artificial ice core was processed like an actual ice core, i.e. it was cut with a band-saw into two subcores, each of length 40 cm, one with a cross-section of  $1 \times 2.5 \text{ cm}^2$  and the other with a cross-section of  $2.5 \times 2.5 \text{ cm}^2$ . The smaller subcore was further cut into sections of 4 cm in length, which were analyzed conventionally after melting in pre-cleaned containers, whereas the larger subcore was analyzed by the continuous melting technique. In addition, the blank value originating from ultra-pure water, melting head, and

sample collection and injection device (Fig. 2) was determined by analyzing liquid ultra-pure water supplied through the melting head.

### 2.3. Comparison of continuous melting and analysis with conventional sample preparation and analysis

In order to compare conventional sample preparation and analysis with continuous melting and analysis, a 95.5 cm long core section of an ice core from Grenzgletscher (density  $0.87 \text{ g cm}^{-3}$ ) was analyzed by both methods. The core was prepared as described in Section 3.2.

## 3. Results and discussion

### 3.1. Determination of blank values

By analyzing the artificial core with the continuous melting and analysis and the conventional sample preparation and analysis, both with a resolution of 4 cm, 10 blank values were obtained for each method. In addition, 10 blank values of ultra-pure water supplied through the melting device were determined. Detection limits and average blank values (see above) with standard deviations for all the analyzed species are listed in Table 1. The

detection limits are defined as the amount of solute producing a signal-to-noise ratio of 3. Median, 10<sup>th</sup> and 90<sup>th</sup> percentiles determined by conventional analysis of the entire ice core from Grenzgletscher are depicted as well [45], to give an idea about the range of concentrations of ionic species in Alpine glaciers.

The blank values determined for the artificial core are not only derived from the sample preparation and analysis, but also from the blank value of the ultra-pure water and the production of the artificial core. When analyzing real ice cores, these latter two do not exist. Therefore, the blank values and detection limits determined with the artificial ice core have to be considered as upper limits.

The obtained blank values allow to divide the different species into groups. For  $\text{F}^-$ ,  $\text{CH}_3\text{SO}_3^-$ , and  $\text{NH}_4^+$ , all blank values are below or equal to the detection limits. The lower concentrations found in the real ice core section from Grenzgletscher are well above the detection limits. These components are not very sensitive for contamination and there are no significant differences for the two analyzing methods. This is valid for  $\text{C}_2\text{O}_4^{2-}$ , too, except that the lowest concentrations found in the ice core from Grenzgletscher are in the region of the detection limit.

For  $\text{CH}_3\text{CO}_2^-$ ,  $\text{CHO}_2^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$  blank values for continuous melting and analysis are also

Table 1

Detection limits (D. L.) and average blank values (B. V.) with standard deviations (number of values=10) of all species determined in ultra-pure water and in an artificial core by continuous melting and analyzing and by conventional analysis<sup>a</sup>

	$\text{F}^-$	$\text{CH}_3\text{CO}_2^-$	$\text{CHO}_2^-$	$\text{CH}_3\text{SO}_3^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{C}_2\text{O}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
D. L.	0.1	0.4	0.3	1.2	0.1	0.5	1.0	1.5	0.8	1.4	1.8	1.1	2.6
B. V., ultra-pure water	0.4 ±0.1	≤D. L. ±0.4	0.6 ±0.4	≤D. L.	0.6 ±0.2	≤D. L.	7.7 ±0.3	1.5 ±0.3	≤D. L.	≤D. L.	2.9 ±1.4	≤D. L.	5.5 ±1.2
B. V., continuous melting and analyzing	≤D. L.	≤D. L.	≤D. L.	≤D. L.	0.3 ±0.1	≤D. L.	6.4 ±3.3	≤D. L.	≤D. L.	≤D. L.	≤D. L.	≤D. L.	3.8 ±1.2
B. V., conventional analysis	0.3 ±0.2	3.2 ±1.1	3.1 ±1.3	1.2 ±1.2	4.2 ±0.6	5.8 ±0.2	12.4 ±2.9	1.9 ±0.3	4.7 ±2.6	1.1 ±0.8	3.9 ±1.3	2.8 ±0.4	3.6 ±0.8
G. G. median	1.6	12.0	35.5	2.6	23.6	132.7	281.7	3.4	11.3	72.9	8.8	8.6	77.2
10 <sup>th</sup> percentile	0.4	3.1	6.9	1.4	6.6	40.3	72.5	≤D. L.	3.3	10.9	2.5	1.9	15.3
90 <sup>th</sup> percentile	4.5	33.2	156.4	6.1	91.7	451.2	1252.2	18.4	50.6	229.9	27.6	34.7	437.0

<sup>a</sup> The detection limits are defined as the amount of solute producing a signal-to-noise ratio of 3. In addition, median, 10<sup>th</sup> and 90<sup>th</sup> percentiles of all species determined by conventional analysis in a 125 m core from Grenzgletscher (G. G.) are depicted. Concentrations are given in  $\mu\text{g l}^{-1}$ .

below or equal to the detection limits, while for the conventional sample preparation and analysis blank values are about 2–4  $\mu\text{g l}^{-1}$  higher than detection limits. This indicates a contamination during conventional sample preparation and analysis. Especially for the organic acids, contamination by laboratory air is assumed. The lowest concentrations found in the core section from Grenzgletscher are in the regions of the detection limits. For the determination of low level concentrations continuous melting and analysis is therefore better suited than the conventional analysis.

For  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$ , blank values for the conventional technique are enhanced (5.8  $\mu\text{g l}^{-1}$  for  $\text{NO}_3^-$ , 3.6  $\mu\text{g l}^{-1}$  for  $\text{Ca}^{2+}$ ) compared to blank values of ultra-pure water and of the continuous melting and analysis. This again indicates a contamination by conventional sample preparation and analysis.

$\text{Cl}^-$  shows contamination of less than 1  $\mu\text{g l}^{-1}$  due to ultra-pure water, melting head and sample collection and injection device. A major contribution to the blank value, about 4  $\mu\text{g l}^{-1}$ , resulted from the conventional sample preparation and analysis. For  $\text{SO}_4^{2-}$  all determined blank values are significantly higher than the detection limits, indicating not only a contamination originating from the conventional handling (about 7  $\mu\text{g l}^{-1}$ ), but also from ultra-pure water, melting head and sample collection and injection device (about 5  $\mu\text{g l}^{-1}$ ).

Since the concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  in the real ice core section from Grenzgletscher are several times higher than the blank values, contamination in this order of magnitude is not critical.

Thus, the newly developed continuous melting and analyzing technique is for all species better or equally suited for determination of low level concentrations than the conventional analysis method.

### 3.2. Comparison of continuous melting and analysis with conventional sample preparation and analysis

Concentration profiles of  $\text{Cl}^-$ ,  $\text{CHO}_2^-$ , and  $\text{NH}_4^+$  obtained with the two different methods are shown in Fig. 4 as examples. Profiles of  $\text{Cl}^-$  and  $\text{NH}_4^+$  agree well, i.e. both the absolute values and the spatial patterns are reproduced by the two methods. The

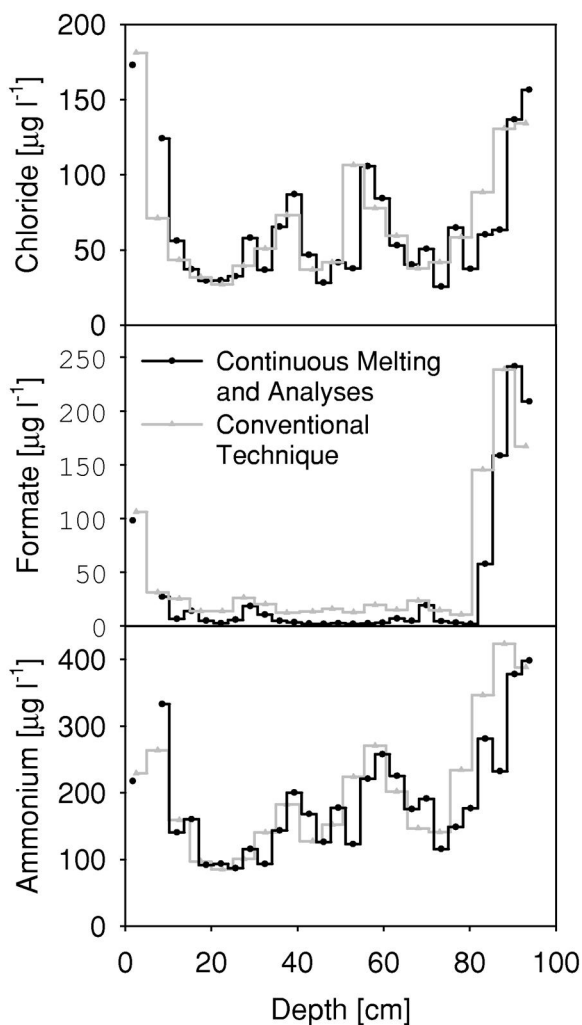


Fig. 4. Concentration profiles of ammonium, chloride and formate obtained by conventional sampling and analysis and by the continuous melting and analyzing technique. The concentrations are not blank corrected.

concentrations of  $\text{CHO}_2^-$  determined with the continuous melting and analysis technique tend to be lower than those obtained with conventional analysis, particularly when  $\text{CHO}_2^-$ -concentrations in the ice are below 20  $\mu\text{g l}^{-1}$ . This compares well with the results of the artificial ice core, where the higher values determined with conventional analysis could be explained by contamination during sample preparation and contact with laboratory air.

In order to compare the performance of the two

Table 2

Total amounts of ions of a hypothetical subcore of the real ice core segment from Grenzgletscher (cross-section: 1 cm<sup>2</sup>, length: 95.5 cm) obtained by the continuous melting and analyzing method and by conventional analysis<sup>a</sup>

	F <sup>-</sup>	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	CHO <sub>2</sub> <sup>-</sup>	CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
Continuous melting and analyzing	0.32 ±0.05	0.48 ±0.07	3.2 ±0.5	0.08 ±0.01	6.5 ±0.7	41.7 ±3.6	81.6 ±8.8	1.05 ±0.14	2.7 ±0.3	18.1 ±1.5	1.6 ±0.2	1.8 ±0.2	32.3 ±3.8
Conventional analysis	0.24 ±0.04	4.3 ±1.2	4.6 ±0.9	0.06 ±0.01	6.7 ±0.9	48.3 ±6.8	80.5 ±13.3	0.79 ±0.15	2.6 ±0.4	19.6 ±2.5	1.7 ±0.2	1.8 ±0.3	29.4 ±4.9

<sup>a</sup> Seventeen of nineteen CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> concentrations analyzed by conventional method were below the detection limit, which was then taken to calculate the total amount. Concentrations are given in μg l<sup>-1</sup>.

methods for all species analyzed, the total amounts of ions were calculated for a hypothetical subcore of 1 cm<sup>2</sup> cross-section and 95.5 cm length (Table 2). Errors were estimated by the law of error propagation on the basis of a 10% error for a single measurement of a component.

The amounts calculated for both analytical methods agree well (linear regression: correlation coefficient: 0.991, slope: 0.991, intercept: -0.575), except for CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> and CHO<sub>2</sub><sup>-</sup>. For CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, the discrepancy is due to high concentration of CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> (up to 330 μg l<sup>-1</sup>) in the lowest 5 cm of the ice core analyzed by the conventional technique. These high values were not reproduced by continuous melting and analysis, which might indicate heterogeneity in the ice core.

The higher total amount of CHO<sub>2</sub><sup>-</sup> found with conventional analysis is a consequence of contamination during sample preparation.

#### 4. Conclusions

With the new method of continuous melting and analysis of ice cores, lower blank values were achieved than with the conventional technique for most of the ionic species investigated. This is attributed to contamination occurring during the conventional sample preparation procedure by contact with laboratory air and with tools used for cutting, storing and melting the samples.

The application of the new method on a real ice core segment from Grenzgletscher in the Swiss Alps, which had already been analyzed before by the conventional technique, revealed that the method is well suited to quantify the overall amounts of ionic

impurities in the ice and to resolve their concentration patterns.

Thus, the newly developed method combines the advantages of the CFA technique — lower ice consumption, less time-consuming sample preparation, and a lower risk of contamination — with the potential of the multicomponent analytical ion chromatographic method. This method will consequently be used in future glaciochemical studies of ice cores.

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