Analysis of size-classified ice crystals by capillary electrophoresis

B. Tenberken-Pötzsch[a], M. Schwikowski[a,*], H.W. Gäggeler[a,b]

[a]*Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[b]*Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland*

Abstract

In order to analyse the main inorganic cations (NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}) as well as carboxylic and dicarboxylic acids in ice crystals by capillary electrophoresis, electrolyte systems were developed and optimised with respect to limits of detection, resolution, reproducibility and analysis time. We applied indirect UV detection, which enables the simultaneous detection of multiple components. Salicylic acid and 4-methylaminophenolsulfate were used as UV-active co-ions for analysis of anions and cations, respectively. The special features of these systems were low limits of detection in the range 0.3–0.9 μmol L^{-1}, i.e. absolute limits of detection were in the fmol range, and short analyses times. Separations of cations as well as anions including carboxylic and dicarboxylic acids were completed within 4 min allowing a high sample throughput. Furthermore, the applicability of the newly developed electrolyte systems was demonstrated by comparative analyses with ion chromatography and by first field experimental studies. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ice crystals; Inorganic anions; Inorganic cations; Organic acids

1. Introduction

The main aim of atmospheric research is the examination of anthropogenic influences on natural processes. Within this scope the investigation of precipitation (rain, snow, etc.) as the most important cleansing mechanism of the troposphere is of particular interest.

The formation of precipitation in the moderate climate of Europe is closely related to the existence of mixed-phase clouds, i.e. clouds containing both supercooled cloud droplets and ice crystals. Although ice nuclei catalyse the formation of ice in supercooled clouds, great uncertainty exists as to which aerosol particles serve as ice nuclei, what are

their typical atmospheric concentrations and how do their concentrations depend on temperature, supersaturation, and cloud conditions. We therefore investigated the chemical composition of ice crystals and supercooled cloud droplets in precipitating clouds [1–3].

For that purpose, techniques were developed to collect and analyse size-classified ice crystals [4] as well as to separate cloud droplets and ice crystals [5] (see Section 2.2). Since the developed sampling techniques result in small absolute sample volumes (<100 μL) and the concentrations of the main solutes in ice crystals are in the low μmol L^{-1} range (1–10 μmol L^{-1}), small injection volumes and low absolute limits of detection are required. Furthermore, for comprehensive interpretation of atmospheric processes the simultaneous determination of various components and a high sample throughput are necessary.

*Corresponding author. Tel.: +41-56-310-4110; fax: +41-56-310-4435.
E-mail address: margit.schwikowski@psi.ch (M. Schwikowski)

Normally, ion chromatography (IC) is used for the analysis of the main cations and anions in ice samples due to the low concentration limits of detection. However, for the analysis of sample volumes smaller than 100 μL, IC is not suitable. In order to analyse various species in small volumes, capillary electrophoresis (CE) in particular is well suited because of the low absolute limits of detection, low sample requirements, high resolution and fast separations. As the method for analysis we therefore chose CE, which has already been used for similar problems of analysis, such as, for example, the investigation of raindrops and fogdrops [6–9].

However, for the analysis of ice crystals the existing methods cannot be applied directly, because the concentrations of the main anions and cations in ice crystals are a factor of 10 less concentrated than in raindrops. Hence, the application of CE to ice crystal samples requires the development of electrolyte systems with reduced limits of detection and which are especially optimized with respect to a high sample throughput to enable comprehensive atmospheric interpretations, i.e. the separation time has to be reduced. To reduce limits of detection the signal-to-noise ratio has to be optimised. Within this scope the co-ion concentration and the pH of the electrolyte solution are the most important optimization parameters. For indirect UV detection the concentration of the UV-active co-ion should be as high as possible; limiting effects are detector linearity and Joule heating [10]. In order to reduce the analysis time for separation of anions it is necessary to use reversed electroosmotic flow (EOF) and to separate the anions coelectroosmotically [11,12]. It is further possible to increase the mobility of anions by increasing the pH of the electrolyte solution, as the effective charge of ions is determined by the degree of ionization, which is influenced by the pK_a value of the analyte. Furthermore, the EOF increases with increasing pH, resulting in shorter analysis times. For cations the separation time can also be reduced by increasing the pH of the electrolyte, but restricting the influence is the pK_a of the analyte.

In this paper we present the development and optimization of electrolyte systems for analysing the main cations and anions, including carboxylic and dicarboxylic acids, as a special application for size-classified ice crystal samples.

2. Experimental

2.1. Equipment and chemicals

Analysis was performed by CE with the CES-1 system from Dionex (Olten, Switzerland). Separations were carried out in conventional fused-silica capillaries (Dionex) of 66 cm length and 50 μm and 75 μm inner diameter followed by indirect UV detection. Samples were injected by hydrostatic injection. All separations were carried out at room temperature and a high voltage of 30 kV. The electrolyte constituents 4-methylaminophenolsulfate, salicylic acid, hexadimethrin bromide, and tris-(hydroxymethyl)aminomethane were obtained from Fluka (Buchs, Switzerland), 18-crown-6 and methanol from Merck (Dietikon, Switzerland), 2-hydroxy-isobutyric acid from Aldrich (Steinheim, Germany), triethanolamine from Sigma (St. Louis, MO, USA), and sodium hydroxide from Merck (Darmstadt, Germany). Stock standard solutions of anions and cations were prepared from analytical-grade reagents from Merck (Darmstadt, Germany).

All solutions were prepared using ultra-pure water (18 MΩ cm) produced by means of a Milli-Q system (Millipore, Molsheim, France).

2.2. Sampling of ice crystals and sample preparation

For sampling of size-classified ice crystals we used a modified version [4] of the Guttalgor method, originally developed for the size-classified sampling of raindrops by Bächmann et al. [13]. Ice crystals were collected into a dewar vessel containing liquid nitrogen and a cascade of stainless steel sieves, 10 cm in diameter, with mesh diameters of 25, 100, 212, 560, and 1000 μm. Because the density of ice is greater than that of liquid nitrogen, the crystals sink upon impact and are separated according to their sizes by the sieves. After sampling, each sieve fraction was transferred into 0.5–1.9 mL polyethylene vials and kept frozen until chemical analysis by CE was performed. Sample volumes were about 100–500 μL.

Furthermore, ice crystals were sampled by means of an inertial impaction system [5]. This method is based on the different sticking properties of ice

crystals and supercooled cloud droplets and enables the simultaneous sampling and separation of these two cloud compartments. Sample volumes and preparation were as described for size-classified sampling of ice crystals.

All field experiments were performed at the High-Alpine Research Station Jungfraujoch.

3. Results and discussion

3.1. Optimization of the separation of the main anions occurring in ice crystals

In order to achieve optimal peak symmetries in CE separations the mobility of the electrolyte co-ion has to be comparable to the mobilities of the analyte ions. For separation in one run of inorganic anions with high electrophoretic mobility as well as of carboxylic and dicarboxylic acids, which have low electrophoretic mobilities, we selected salicylic acid as electrolyte co-ion, which has an average mobility [8,14,15]. It further enables indirect UV detection due to its high molar absorptivity of 1259 L mol^{-1} cm^{-1} at a wavelength of 232 nm [16]. To analyse even the slow mobile analytes (e.g., propionate) the EOF was reversed and anions were separated coelectroosmotically. As EOF modifier, hexadimethrin bromide (HDB) was chosen, which reverses the EOF at concentrations of about 0.001% [8,11,12]. The use of reversed EOF reduced the analysis time and separations were completed within 3 min. We further

used 2% of methanol to reduce the EOF and to improve resolution. Methanol interacts with the modifier HDB and therefore is able to influence the coating of the capillary surface which is, without addition of methanol, very stable and results in a very fast EOF.

The system was optimised regarding limits of detection, resolution and reproducibility. As the limits of detection are given by the signal-to-noise ratio, which is influenced by the electrolyte concentration, we optimised the concentration of salicylic acid (Fig. 1). The maximum signal-to-noise ratio for all anions was found to be between a concentration of 8 and 9 mM salicylic acid. Therefore, the optimum electrolyte concentration was fixed at 8.5 mM salicylic acid.

Fig. 2a and b show the optimization of the electrolyte pH, which was adjusted by changing the concentration of tris(hydroxymethyl)aminomethane. The mobilities of all anions vary only slightly at different pH values (Fig. 2a). It can be observed that, with decreasing pH, the resolution of formate and malonate decreases, until these two species comigrate at pH 7.2. Furthermore, the resolution of nitrate and sulfate decreases with increasing pH. These effects are due to the different dissociation steps of single-charged and double-charged anions. The effective mobilities of double-charged anions increase stronger than the effective mobilities of single-charged anions. Fig. 2b shows the dependence of the signal-to-noise ratio on pH. As malonate and formate comigrate at pH 7.2 there are no data points for
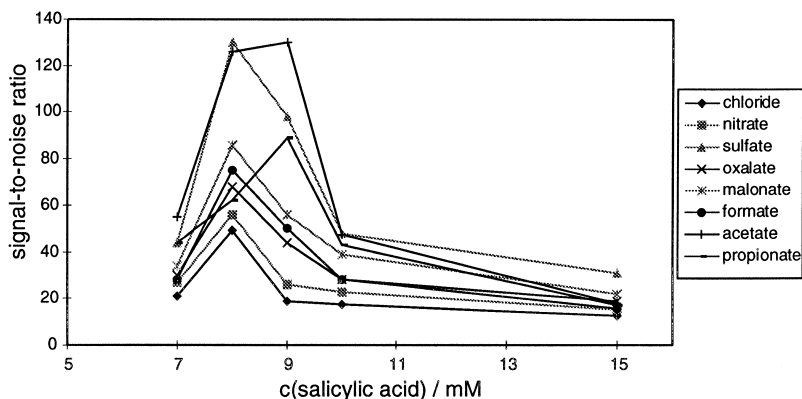

Fig. 1. Optimization of the co-ion concentration for separation of inorganic anions as well as carboxylic and dicarboxylic acids (for conditions, see Fig. 3).
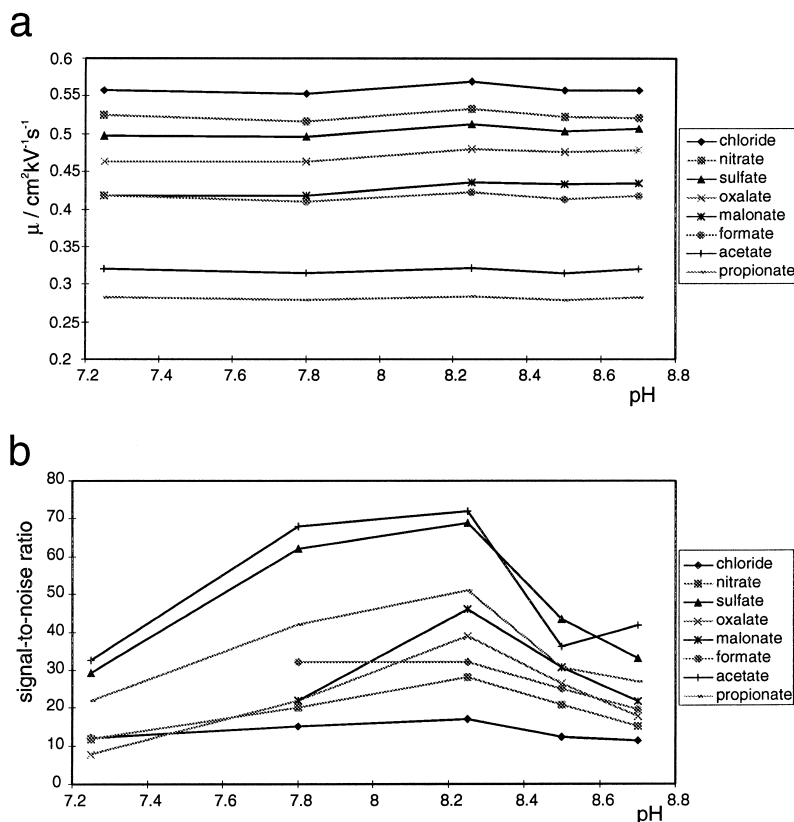
a

b

Fig. 2. Optimization of electrolyte pH for separation of inorganic anions as well as carboxylic and dicarboxylic acids (for conditions, see Fig. 3): (a) influence of pH on the electrophoretic mobility of anions; (b) pH-dependence of the signal-to-noise ratio.

malonate and formate at this pH. It can be seen that the signal-to-noise ratios are optimum between pH 7.8 and pH 8.4. We selected pH 8.25 as the most favourable electrolyte pH.

The reproducibility of the optimised system for corrected peak areas and retention times is 6–11% and about 1%, respectively. Limits of detection are 0.3–0.8 μmol L^{-1}.

A typical electropherogram of a size-classified ice sample is shown in Fig. 3. Detailed separation conditions are given in the figure caption. The anions chloride, nitrate, sulfate, formate, acetate, and propionate were detected.

To test the applicability of the method to real samples, ice crystal samples should also be analysed by a second method of analysis. However, as sample volumes of ice crystal samples are only about 100

μL it is impossible to analyse all analytes using a different method. We therefore tested the method by analysing the same standard solution of anions by CE and IC [17]. The results of both methods were in good agreement within the range of analytical error.

3.2. Optimization of the separation of the main inorganic cations in ice crystals

Since alkaline and alkaline earth metals as the main cations in ice crystals do not absorb UV light, indirect UV detection as for the analysis of anions has to be used. For the analysis of inorganic cations we selected 4-methylaminophenolsulfate as co-ion and UV-active background electrolyte [6,7]. We further used the complexation agent 18-crown-6 for separation of ammonium and potassium.
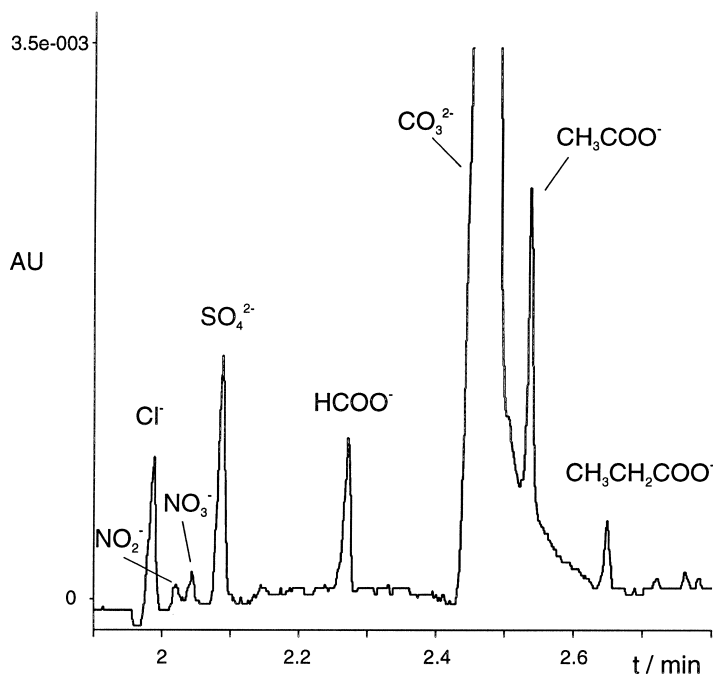
Fig. 3. Typical electropherogram of anions in a sample of size-classified ice crystals with diameters of 25 μm (chloride, 29 μM; nitrite, not quantified; nitrate, 2.3 μM; sulfate, 24 μM; formate, 23 μM; acetate, 21 μM; propionate, 5.5 μM). Electrolyte, 8.5 mM salicylic acid, 21 mM tris(hydroxymethyl)aminomethane, 0.001% HDB, 2% methanol, 2 mM sodium hydroxide (pH 8.25); capillary, 66 cm (60 cm to detector)$\times$50 μm I.D.; voltage, 30 kV; detection, indirect UV detection (232 nm); injection, 10 cm, 60 s; separation temperature, room temperature.

The optimization of the concentration of 4-methylaminophenolsulfate is demonstrated in Fig. 4. In this plot the dependence of the signal-to-noise ratio on the co-ion concentration for each cation is shown. As magnesium and lithium comigrate at a co-ion concentration of 8 mM there are no data points for magnesium and lithium at this concentration. The best signal-to-noise ratios were clearly found at a concentration of 5 mM 4-methylamino-phenolsulfate.
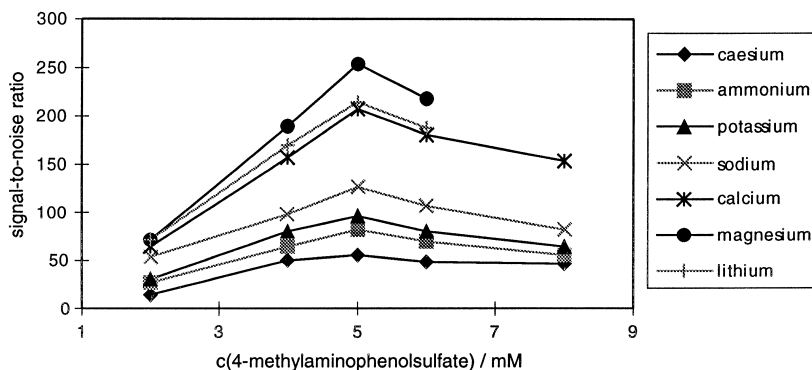
Fig. 4. Optimization of the co-ion concentration for separation of inorganic cations (for conditions, see Fig. 6).

Fig. 5a and b illustrates the optimization of electrolyte pH, which was adjusted by tri-ethanolamine. It can be seen that the mobilities of caesium, ammonium, potassium, sodium, calcium, magnesium and lithium vary uniformly and only slightly (Fig. 5a). The signal-to-noise ratio is highest at pH 4.2, as can be seen from Fig. 5b. We therefore chose pH 4.2 as the optimum separation condition. Limits of detection of the optimised system were 0.4–0.9 μM. The reproducibility of retention times and corrected peak areas are 2–3% and 2–5%, respectively.

Fig. 6 shows a typical electropherogram of cations in a size-classified ice sample. The separation is completed within 4 min. Comparing the analyses of cation standard solutions analysed by CE and IC [17,18] shows good agreement between both methods within the range of analytical errors.

3.3. Field experimental studies

The newly developed electrolyte systems were further successfully applied during the first field experimental studies to investigate the scavenging processes of ice crystals as well as the chemical properties of ice nuclei and cloud condensation nuclei. These field experimental results will be discussed in detail in future publications [4,5].

Table 1 shows an example of the analysis of size-classified ice crystals collected during a precipitation event on the Jungfraujoch using the sampling
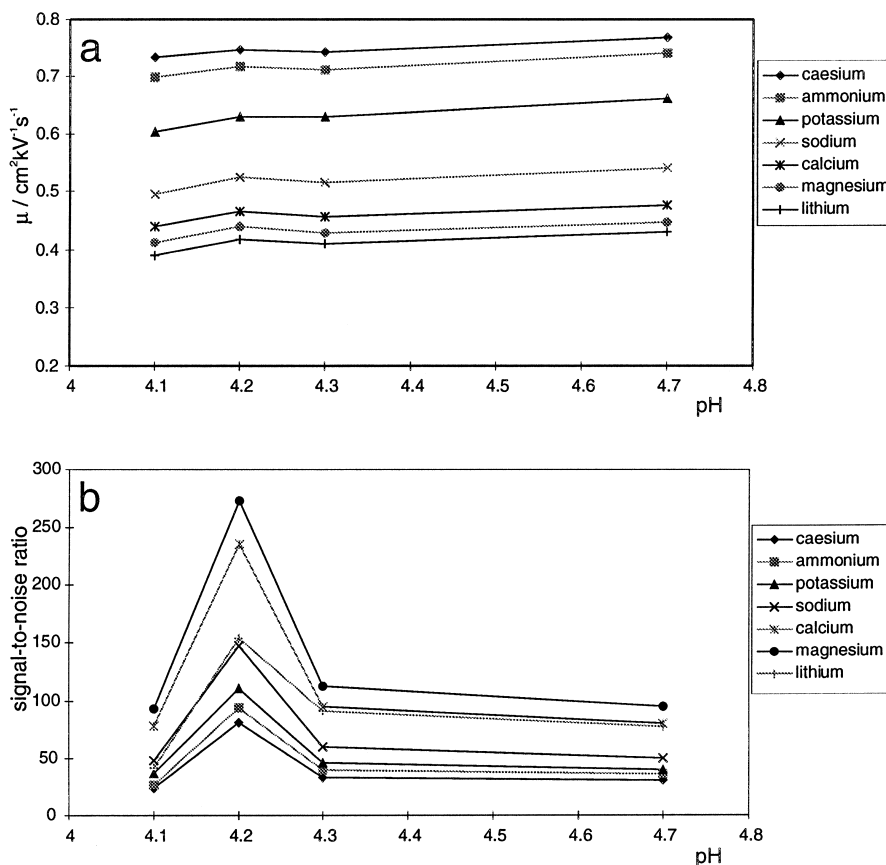

Fig. 5. Optimization of electrolyte pH for separation of inorganic cations (for conditions, see Fig. 6): (a) influence of pH on the electrophoretic mobility of cations; (b) pH-dependence of signal-to-noise ratio.
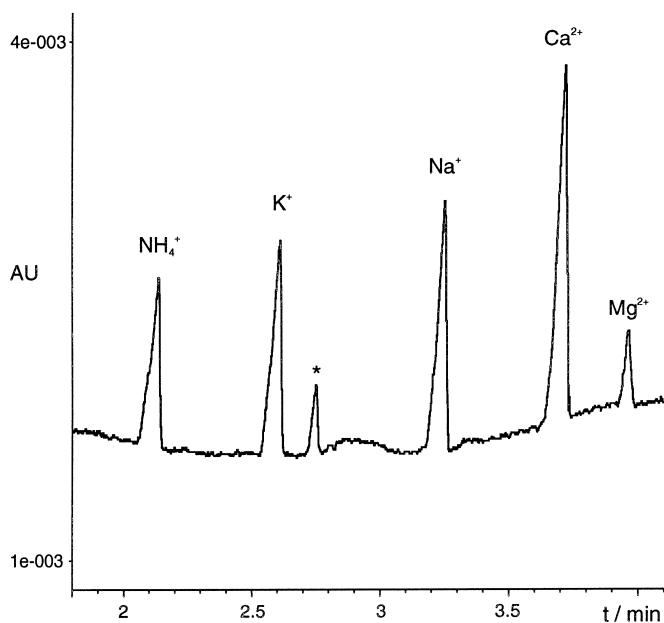
Fig. 6. Typical electropherogram of cations in a sample of size-classified ice crystals with diameters of 25 µm (ammonium, 58 µM; potassium, 59 µM; sodium, 49 µM; calcium, 35 µM; magnesium, 8 µM; *, degradation product of 4-methylaminophenolsulfate). Electrolyte, 5 mM 4-methylaminophenolsulfate, 4 mM 18-crown-6, 5 mM 2-hydroxyisobutyric acid, 2.5 mM triethanolamine (pH 4.2); capillary, 66 cm (60 cm to detector)×75 µm I.D.; voltage, 30 kV; detection, indirect UV detection (220 nm); injection, 10 cm, 45 s; separation temperature, room temperature.

procedure described in Section 2.2. The calcium concentration shows a strong dependence on the size of the ice crystals and decreases with increasing crystal size.

Table 2 shows the first results for the simultaneous sampling and separation of ice crystals and super-cooled cloud droplets collected during the same precipitation event on the Jungfraujoch. The concentrations of the cations ammonium, potassium, sodium, calcium and magnesium were in the µM range. Cloud droplets clearly showed higher con-

centrations of cations than large ice crystals. For the small ice crystals sampled on the PET sieve the concentrations were usually higher than those for large ice crystals.

These first experiments demonstrate the applicability of the newly developed methods for sampling and analysis of ice crystals and open up interesting perspectives for future field experimental studies.

Table 1
Field experimental data for a precipitation event on 17 February 1999, 5:15–6:00 p.m., Jungfraujoch, Switzerland: dependence of calcium concentration on ice crystal size

	d (µm)				
	25	100	212	560	1000
c (Ca^{2+}) (µM)	13.27	13.79	10.72	8.36	7.08

Table 2
Field experimental data for a precipitation event on 17 February 1999, 5:15–6:00 p.m., Jungfraujoch, Switzerland: concentration of water-soluble cations in different cloud compartments

	c (µM)				
	NH$_4^+$	K$^+$	Na$^+$	Ca^{2+}	Mg^{2+}
Cloud drops	58.62	59.33	49.15	34.96	8.56
Large ice crystals	18.27	0.69	12.05	9.76	0.35
Small ice crystals	137.10	13.89	26.74	25.94	6.90

4. Conclusion

Special electrolyte systems for the analysis of the main inorganic cations, anions and carboxylic and dicarboxylic acids in ice crystals have been developed. These systems were optimised with respect to limits of detection, reproducibility, analysis time and resolution.

A special feature of these systems is the very low limits of detection (0.3–0.9 μmol L^{-1}), which enable for the first time the analysis of various components in size-classified ice crystal samples. Additional properties of these systems were the short analyses times of about 4 min, resulting in a high sample throughput, which is essential for comprehensive atmospheric interpretation.

The newly developed electrolyte systems were successfully applied during first field experimental studies and will be used in future field experiments to investigate scavenging processes of ice crystals as well as the chemical properties of ice nuclei and cloud condensation nuclei.

References

[1] M. Schwikowski, U. Baltensperger, H.W. Gäggeler, O. Poulida, Atmos. Environ. 32 (1998) 4001–4010.

[2] U. Baltensperger, M. Schwikowski, D.T. Jost, S. Nyeki, H.W. Gäggeler, O. Poulida, Atmos. Environ. 32 (1998) 3975–3983.

[3] O. Poulida, M. Schwikowski, U. Baltensperger, J. Staehelin, H.W. Gäggeler, Atmos. Environ. 32 (1998) 3985–4000.

[4] B. Tenberken-Pötzsch, M. Schwikowski, H.W. Gäggeler, Atmos. Environ. (in preparation).

[5] B. Tenberken-Pötzsch, M. Schwikowski, H.W. Gäggeler, Atmos. Environ. (submitted for publication).

[6] B. Tenberken, P. Ebert, M. Hartmann, M. Kibler, A. Mainka, T. Prokop, A. Röder, K. Bächmann, J. Chromatogr. A 745 (1996) 209–215.

[7] B. Tenberken, K. Bächmann, J. Chromatogr. A 755 (1996) 121–126.

[8] B. Tenberken, K. Bächmann, J. Chromatogr. A 775 (1997) 372–377.

[9] B. Tenberken, K. Bächmann, Atmos. Environ. 32 (1998) 1757–1763.

[10] J.R. Landers, Handbook of Capillary Electrophoresis, CRC Press, Boca Raton, FL, 1994.

[11] S.M. Masselter, A.J. Zeeman, O. Bobleter, Electrophoresis 14 (1993) 36–39.

[12] S.M. Masselter, A.J. Zeeman, Anal. Chem. 67 (1995) 1047–1053.

[13] K. Bächmann, I. Haag, A. Röder, Atmos. Environ. 27A (1993) 1951–1958.

[14] A. Mainka, P. Ebert, M. Kibler, T. Prokop, B. Tenberken, K. Bächmann, Chromatographia 45 (1997) 158–162.

[15] A. Röder, K. Bächmann, J. Chromatogr. A 689 (1995) 305–311.

[16] D.G. Grasselli, W.M. Ritchey, Atlas of Spectral Data and Physical Constants for Organic Compounds, CRC Press, Cleveland, OH, 1975.

[17] M. Schwikowski, Chimia 51 (1997) 786–789.

[18] A. Döscher, M. Schwikowski, H.W. Gäggeler, J. Chromatogr. A 706 (1995) 249–252.