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Short communication

Analysis of ions in polar ice core samples by use of large injection volumes in ion chromatography

Jüri Ivask*, Jaan Pentchuk

Institute of Chemical Physics, Tartu University, Jakobi 2, EE2400 Tartu, Estonia

Abstract

In the present study a non-suppressed ion chromatography system with conductivity detection was tested in terms of sampling effects, the effects on the ion separation efficiency and analysis detection limits to find optimum conditions for the determination of chloride, nitrate, sulfate, sodium, ammonium, potassium, calcium and magnesium ions in polar ice core samples.

Keywords: Inorganic anions; Inorganic cations

1. Introduction

Archives of numerous environmental parameters are recorded in polar ice sheets. Snow, accumulating in polar areas buries atmospheric impurities, which are then preserved for millennia in the ice layers. Analysis of the ionic content of ice can be used to improve the understanding of the processes that have affected the atmosphere in the past and lead to the final composition of atmosphere.

Ion chromatography (IC) is a multispecies technique and is well suited for analyses of soluble impurities in ice. Such studies have been performed using suppressed IC with sample preconcentration and gradient elution [1,2] or using large sample volumes [3]. The detection limits of the process were as much as one order of magnitude lower than the mean content in polar ice [1], but the equipment is complicated and the suppressor system decreases ion separation efficiency. Non-suppressed methods allow comparable detection limits to be achieved if sample

preconcentration methods or large injection volumes are employed [4,5]. In these studies the authors suggested photometric detection. Use of large injection volumes requires less complicated instrumentation and is possible if analysis conditions are optimized to minimize the interference of the large injection peak with the peaks of early eluting ions [4]. In the present study a non-suppressed IC system with conductivity detector and 1-ml sample loop was tested to find optimum analysis conditions for the determination of chloride, nitrate, sulfate, sodium, ammonium, potassium, calcium and magnesium ions in polar ice core samples.

2. Experimental

2.1. Sample preparation

The ice core decontamination was performed by shaving off the outer part of the core with a special knife that had been previously rinsed with ultrapure water (conductivity 0.06 μS/cm). Water was produced using the Millipore Milli-Q water system. All

*Corresponding author. Present address: Institute of Geology, Estonia Ave 7, EE0001 Tallinn, Estonia.

sampling procedures were performed in the cold clean room of the Estonian Biocentre at −20°C. The decontaminated samples were put in air-tight bottles kept frozen until the injection into the chromatograph.

2.2. Ion chromatography

The apparatus used was an IAK-12 analytical chromatograph with conductivity detector (Inkrom, Estonia). The separation columns used were IC cation and anion columns 150×3 mm, packed with resins synthesized in our laboratory. The resin matrix used for syntheses was Separon HEMA S 1000 with particle size 10 μm (Tessek, Czech Republic). The chromatographic experiment was performed with a flow-rate of 1.0 ml/min. The sample volume used was 1.0 ml. The column, loop injector and the cell of the conductivity detector were maintained at 35°C. Cation separation was performed with 7.5 mM tartaric acid+0.8 mM pyridine-2,6-dicarbonic acid eluent [6] and anion separation with 2.0 mM potassium hydrogenphtalate eluent (pH 4.01). All the reagents used were of analytical grade (Reakhim, Russia). Standard solutions were prepared by dilution of individual standard solutions at 1000 ppm (μg/g) with concentration ratios chosen to be similar to those in ice samples. Standard solutions for calibration were prepared a few minutes before usage.

3. Results and discussion

The ability of an IC system to perform ion separations using large injection volumes is determined by the interference of a large injection peak with the peaks of some rapidly eluted ions (fluoride,

Table 2
Analytical quality of the ice core analyses

Ion	Estimate of precision (%)	
	Low	High
Chloride	32	7
Nitrate	48[a]	22
Sulfate	18	5
Sodium	11	1
Ammonium	73	2
Potassium	42	3
Calcium	8	1
Magnesium	23[a]	2

Estimate of precision denotes the relative standard error of IC measurement at the upper and lower values of the respective ion in the ice core.
[a] Values corresponding to the detection limit.

chloride, sodium) [5]. Preliminary experiments demonstrated that when a 1-ml sample loop was used the peaks of the studied ions were well separated and not affected by the injection peak, therefore the tested injection volume was applied in further studies. Calibration data were obtained using a series of ion standard solutions with concentration ratios chosen to be similar to those in Antarctic ice. Calculated regression lines, estimation errors, correlation coefficients and detection limits are given in Table 1. Blank samples with Milli-Q water did not cause the appearance of any measurable peaks on the chromatograms. Determination of the ionic content of the ice core samples demonstrated that satisfactory sensitivity was obtained, except for nitrate and magnesium ions in some ice core sections whose total ionic content was low. The precision of the analyses is summarized in Table 2. The chromatography equipment and elution conditions used allowed good separation of all determined ions to be achieved (Fig.

Table 1
Calibration parameters for anion and cation determinations

Ion	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Na$^+$	NH$_4^+$	K$^+$	Ca^{2+}	Mg^{2+}
Range (ppb)	100–1000	50–500	100–1000	50–500	50–500	10–100	50–500	20–200
Regression line	$S=2.22+0.08C$	$S=0.96+0.04C$	$S=0.77+0.05C$	$S=10.00+0.37C$	$S=8.54+0.38C$	$S=4.31+0.15C$	$S=10.17+0.29C$	$S=5.07+0.34C$
Std. error of S est.	2.32	0.68	0.93	3.36	4.19	1.64	1.90	2.29
r^2	0.9947	0.9915	0.9973	0.9979	0.9968	0.9358	0.9988	0.9927
DL (ppb)	19	38	43	5	5	13	28	29

C represents the concentration [ppb (ng/g)] and S the peak area expressed in relative units, DL denotes the detection limit defined as the amount of solute producing a signal-to-noise ratio of 3 ($S/N=3$), r is the correlation coefficient and $n=6$.

Fig. 2. Long-term variations in sulfate concentrations in the ice core sections between the depths 346–606 m.
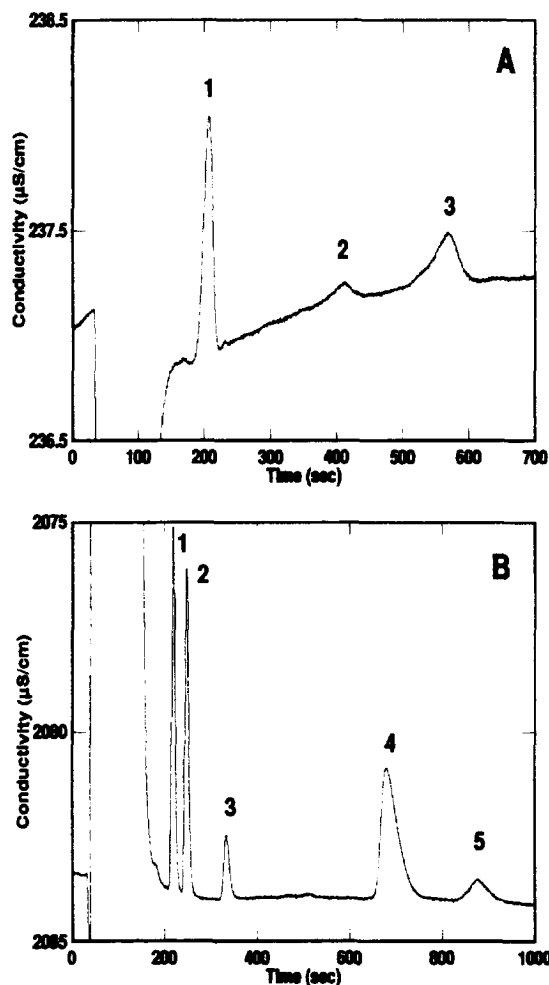
Fig. 1. Determination of anions (A) and cations (B) in the ice core section from a depth of 525 m at Dome B (East Antarctica). Conditions as in text. Ions: A: 1=chloride (153 ppb); 2=nitrate (76 ppb); 3=sulfate (221 ppb). B: 1=sodium (175 ppb); 2= ammonium (176 ppb); 3=potassium (106 ppb); 4=calcium (407 ppb); 5=magnesium (48 ppb).

onstrates the variation of sulfate concentration in the ice core between the depths 346–606 m. Results show that there is an increase in the sulfate concentration in ice core sections collected deeper than 525 m, corresponding to the climatic change between the last ice age and the present interglacial period [7].

1) and this technique offers an alternative approach to sample preconcentration methods or indirect photometric detection methods and it requires only a simple modification of conventional IC instrumentation. Long-term variations in the ionic species concentrations in the polar ice core provide information for paleoclimatologic studies. Fig. 2 dem-
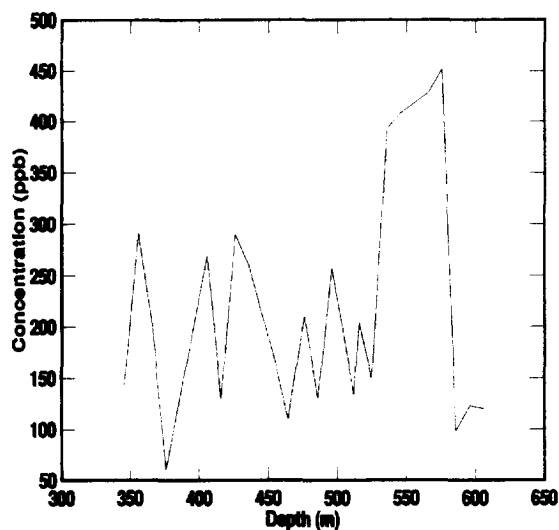
References

[1] M. Legrand, M. De Angelis and F. Maupetit, J. Chromatogr., 640 (1993) 251.
[2] M.E. Hansson, Tellus, 46B (1994) 390.
[3] C.F. Buck, P. Mayevski, M.J. Spencer, S. Whitlow., M.S. Twickler and D. Barrett, J. Chromatogr., 594 (1992) 225.
[4] A.L. Heckenberg and P.R. Haddad, J. Chromatogr., 299 (1984) 301.
[5] T. Okada and T. Kuwamoto, J. Chromatogr, 350 (1985) 317.
[6] J. Ivask and J. Pentchuk, Proc. Estonian Acad. Sci. Chem., 43 (1994) 86.
[7] J. Jouzel, R. Vaikmäe, J.R. Petit, M. Martin, Y. Duclos, M. Stievenard, C. Lorius, M. Toots, M.A. Melieres, L.H. Burcle, N.I. Barkov and V.M. Kotlyakov, Climate Dynamics, 11 (1995) 151.