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Short communication

Reduction of the detection limits of anions in polar ice core analysis using correlation ion chromatography with detector signal processing

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Abstract

Non-suppressed ion chromatography is usually a sensitivity deficit for polar ice core anionic content analysis. In the present study a method for signal improvement was tested. Ice core samples were injected into the chromatograph according to a pseudo-random binary sequence. The chromatogram was calculated by correlating the detector signal with the input sequence. The results demonstrated that the method used gives increased sensitivity and is applicable for performing ice core analysis but also requires high reproducibility of injection system, preliminary sample modification and relatively large sample volume. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Information about past climatic and atmospheric conditions has been stored in polar ice sheets. Determination of the ionic content of ice can be used for better understanding of the processes that have affected the atmosphere in the past and have lead to its final composition. Commonly the analysis of soluble impurities in the polar ice is performed using suppressed ion chromatography (IC) [1,2]. Further enhancement in sensitivity or improved detection limits for less sophisticated non suppressed IC instrumentation can be achieved by computerised sample input control with further data processing. This technique, known as correlation chromatography (CC) [3], includes multiple sample injection into the column according to a pseudo-random binary sequence (PRBS), followed by computation of the chromatogram by correlating the input signal with the detector output. While the main CC application area has been in gas chromatography [3], some initial studies has been made importing the CC method to HPLC [4,5].

In the present study a serial IC system was equipped with computer operated injection valve. Using valve control-detector signal acquisition software the system parameters and procedures were carefully optimised for the needs of CC. Finally the whole system was tested in term of sufficient de-

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tection limits for the determination of chloride, nitrate and sulphate 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 previously rinsed with ultrapure water (conductivity 0.06 μS/cm). Water was produced using the Millipore Milli-Q water system. All sampling procedures were performed in the cold clean room of the Estonian Biocentre at −20°C. The decontaminated samples were put in airtight bottles and kept frozen until the analysis.

2.2. Reagents and chemicals

All the reagents used were of analytical grade (Fluka, Switzerland). Standard solutions were prepared by dilution of individual stock 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.

2.3. Ion chromatography

The apparatus used was an IAK-12 analytical chromatograph equipped with conductivity detector and additional pump for sample injection (Inkrom Ltd., Estonia). The detector has 12-bit built in analog to digital converter that provides detector signal digital output directly to the PC memory via RS232 port. The separation column used was an IC anion column 3×150 mm (Tessek Ltd., Chechia), packed with resin synthesised in our laboratory. The resin matrix used for syntheses was Separon HEMA S 1000 with particle size 10 μm (Tessek Ltd., Chechia). The sample loop volume was 0.14 ml. The column and the cell of the conductivity detector were maintained at 35°C. Anion separation was performed with 2.0 m*M* potassium hydrogenphtalate eluent (pH=4.01).

2.4. Theory

In CC the samples are introduced into the separation column semi-continuously according to a PRBS, consisting of ones and zeros and generated using a special computer algorithm [3]. The whole run of the experiment is divided into intervals of equal duration (clock period) and the corresponding PRBS element is assigned to each of them. If a possible injection moment appears, the computer checks the corresponding sequence element value. If the sequence element is one, the sample is injected into the column, in the case of a zero value the sampling device is not activated. That effects the detector signal to build up from linear combinations of signals resulting from the single injection responses. As the injection sequence is known prematurely, the chromatogram can be found as a solution of linear equations by correlating the input sequence with the detector signal using three Fourier transformations. The important feature of CC is the reduced noise level on the correlogram compared with the single injection chromatogram giving the opportunity of reduction of detection limits of the analysis. From general statistical considerations it can be concluded that the noise amplitude reduction factor (multiplex advantage [3]) is about $\sqrt{n/2}$, where n is the number of injections made during the experiment. This multiplex advantage is valid only in the case if the detector noise spectrum is flat ('white' noise) which is usually not the case because of the base line drift, spikes, detector signal non-linearity and non-reproducibility of the injections. When two latter imperfections should be reduced as much as possible by the good design of the injection port and the whole correlation experiment itself, base line drift and spikes can be easily corrected using special software.

2.5. Sample injection, data acquisition and processing

The injection valve was controlled with a personal computer (PC) using the ADAM-4000 (Advantech Co. Ltd., USA) interface and a Labview 4.1 (National Instruments, USA) program. The overall length of the experiment is determined by the number and size of PRBS, by the intervals between injections and by

the injection length. The interval between two successive injections is determined by the sample flow-rate through the loop. During this study the sample flow rate was 3 ml/min and the loop filling time was chosen as 2.8 s – the theoretical minimal time for loop refilling. Analogously the injection length was chosen as 8.4 s allowing the use of the whole loop volume for injection. The detector digital output was simultaneously recorded in the PC with a sampling frequency of 5 Hz, chosen by careful consideration of the narrowest peak width possible on the chromatogram. The following signal processing included filtering for spike removal and baseline subtracting for drift removal whose importance was described in theoretical section. The final chromatogram was calculated correlating the resulting signal with the input sequence. All these procedures (through fully described in [5]) were performed using laboratory made subroutines in the Windows 3.1 version of Matlab 4.0 (MathWorks Inc., USA) or OS/2 version of Octave 2.0.11 (GNU public licence). According software is available upon request from authors.

The optimum length of the sequence is determined by the ratio of chromatogram length to the injection length. Contrary to the previous works [4,5], where larger sequences (with 511 or 1023 elements) were used to obtain improved S/N ratio, the PRBS was chosen to have an optimum length of 63 elements for our experimental setup. To achieve the same noise reduction rate as in case of longer sequences, several PRBS experiments were run in sequence and the results were averaged. Thus the overall S/N improvement was obtained as a simultaneous result of correlation experiment and averaging of correlograms.

3. Results and discussion

It has been demonstrated in previous publications [4,5], that CC gives expected results when all the parameters influencing the experiment are carefully optimised. The sample is continuously injected into the column after short time intervals, which causes significant dilution of eluent and thus reduces its elution strength. To avoid this, the sample should be prepared in eluent. This could be done by adding the equal amount of eluting ion to the sample. The difference between the cationic content of eluent and sample produced a large system peak on the chromatogram and lead to increased correlation noise on the final chromatogram. In a previous publication the cationic content in eluent and sample was equalised by adding the small portion of Na_2CO_3 stock solution to the eluent until the height of the system peak was tolerable [5]. However, this procedure caused a hydrocarbonate peak to appear on the chromatogram and badly interfered with the chloride peak. In the present study the eluent stock solution was used instead. That caused a small difference in the concentration of eluting ion in sample and eluent but as the sampling frequency is uniform during the experiment no effect on the final chromatogram was noticed. Calibration data were obtained using a series of ion standard solutions with concentration ratios chosen to be similar to those in Antarctic ice. The process of the detector signal processing is illustrated in Fig. 1. Calculated regression lines, estimation errors, correlation coefficients and detection limits are given in Table 1. Achieved detection limits demonstrate a significant increase in sensitivity by using CC. In comparison, the same IC system with single injection of 7 times larger (1 ml) sample volume had detection limits higher by about 2.5–6 times [6].

Determination of the ice core sample anionic content (Fig. 2) demonstrated that satisfactory detection limits were obtained, except for nitrate ions because of the total low ionic content in that depth interval [6]. The single injection of the same sample results only a small chloride peak to appear on the chromatogram.

4. Conclusions

The results, obtained during that study demonstrate that CC method combined with signal averaging could offer a significant increase in detection limits for the low ionic content samples such as polar ice analysis. Method requires improvement of conventional IC instrument with computer operated injection valve and with software controlling the injection sequence. The drawbacks are large sample volume needed, the need of pre adjusting sample-

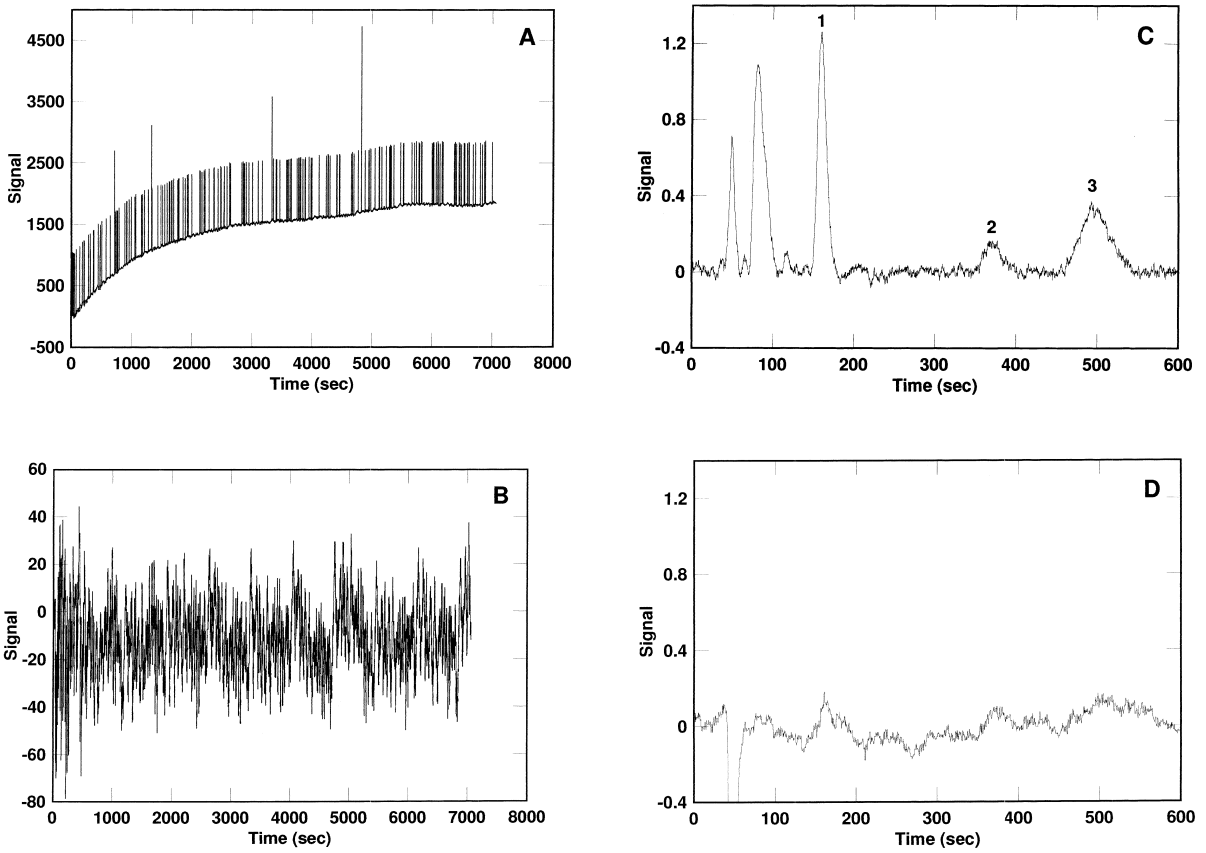

Fig. 1. Illustration of the detector signal processing and correlation procedure. Conditions as in text. Ions: 1=chloride; 2=nitrate; 3=sulphate. (A) detector signal resulting the CC experiment; (B) detector signal after removal of spikes and baseline subtraction; (C) final correlogram; (D) chromatogram resulting from single injection of the same sample.

and eluent contents and long analysis time per sample. However, the latter is not a substantial problem as the measurement is automated.

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Table 1
Calibration parameters for anion determinations[a]

Ion	Chloride	Nitrate	Sulphate
Range (ppb)	50–500	25–250	50–500
Regression line	$S=4.71+0.34C$	$S=-0.69+0.15C$	$S=8.67+0.11C$
Std. error of S est.	7.22	1.35	3.22
r^2	0.9925	0.9944	0.9856
DL (ppb)	2.7	13.1	17.1

[a] 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 $n=4$.

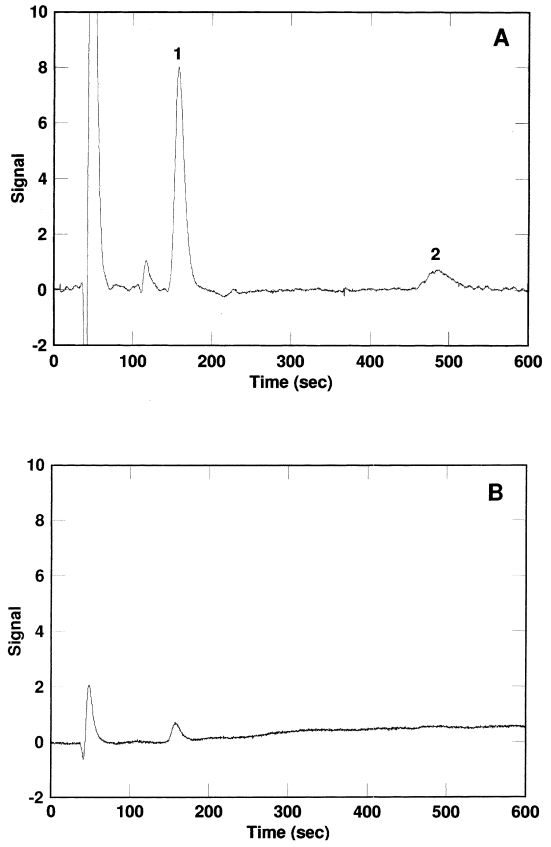

Fig. 2. Determinations of anions in the ice core section from a depth of 524.6 m at Dome B (East Antarctica). Conditions as in text. Ions: 1 = chloride (307 ppb); 2 = sulphate (87 ppb). (A) using CC method; (B) single injection.

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References

[1] M. Legrand, M. De Angelis, F. Maupetit, J. Chromatogr. 640 (1993) 251.
[2] C.F. Buck, P. Mayevski, M.J. Spencer, S. Whitlow, M.S. Twickler, D. Barrett, J. Chromatogr. 594 (1992) 225.
[3] M. Kaljurand, E. Küllik, Computerized Multiple Input Chromatography, Ellis Horwood, Chichester, 1989.
[4] M. Kaljurand, E. Urbas, Ü. Haldna, J. Chromatogr. A 660 (1994) 147.
[5] R. Kuldvee, M. Kaljurand, H.C. Smit, J. Chromatogr. A 789 (1997) 247.
[6] J. Ivask, J. Pentchuk, J. Cromatogr. 770 (1997) 125.