Improvement of the performance of single-column ion chromatography by computerized detector signal processing and correlation chromatography

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ABSTRACT

The performance of medium-quality ion chromatographic equipment was improved by using pseudo-random sample introduction correlation chromatography (CC). The importance of the digital preprocessing of the detector signal prior to decorrelation was demonstrated for realization of the multiplex advantage of the CC method. The detection limits obtained for single-column ion chromatography using conductivity detection were 0.1, 0.12 and 0.17 ppm for Cl^-, NO_3^- and SO_4^{2-} ions, respectively. Using the same apparatus without CC the detection limits are in the range 1–3 ppm.

INTRODUCTION

Although various high-performance ion chromatographic (IC) products (columns, sampling valves and detectors), are commercially available, they may sometimes be too expensive, *e.g.*, in Eastern European laboratories. However, environmental monitoring in the regions concerned is even more necessary than in better developed countries because of their high levels of industrial waste pollution. To meet the demands of environmental monitoring, local manufacturers provide analytical instruments but these may provide much poorer performance than modern Western instruments.

The performance of less sophisticated local instrumentation can be improved by computerized measurement control and data processing. Mars and Smit [1] have demonstrated that the detection limit in HPLC can easily be improved by an order of magnitude. The same applies to single-column IC with UV detection [2]. Instead

of a common approach to trace enrichment and single injections, in both of these studies a sample was introduced into the column directly according to a pseudo-random binary sequence (PRBS), followed by computation of the chromatogram from a random function-like detector output by correlating the input signal pattern with the detector output. This technique is known as correlation chromatography (CC) [3].

Generally in single-column ion chromatography (SCIC), injection and system peaks are present. For anion determinations the injection peak is due to the passage of non-retained cations, water and eluent anions to the detector [4]. Their peak usually appears first on a single-injection chromatogram. The second system peak is due to the transport of the deficiency of the eluent cations and its position on the chromatogram depends on the eluent composition. The areas of the injection and system peaks are related to the total areas of the remainder of the peaks and are therefore the highest on the chromatogram [5]. Using UV detection, a suitable working wavelength can be selected to avoid detecting the injection peak. Using con-

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ductivity detection the injection and system peaks are usually neglected by being off the scale of the recorder. If the injection and system peaks are well separated from the other peaks, they have little effect on the determination of the analytes of interest.

In correlation IC, the injection and system peaks represent a serious problem. As in CC about 1000 injections are made during one measurement, variations in the sample amounts injected can disturb the resulting chromatogram (correlogram) obtained after transformation of the detector signal. This happens because the decorrelation operation converts all variations in the sample amounts introduced into a special type of noise that appears on the chromatogram, *i.e.*, correlation noise [3]. This noise frequently appears in the form of a "ghost" peak. It follows that the correlation noise due to variations in the cationic components of the injected sample (resulting in variations in the amplitudes of the injection peaks in anion IC) can mask small-amplitude peaks on the chromatogram On the other hand, the injection quality depends directly on the quality of the sampling device. In HPLC the only choice is the mechanical valve, whose performance depends strongly on the material of the valve rotor.

In addition to the injection reproducibility, there are other distortions of the detector signal that prevent the effective use of CC, such as baseline drift. This is a very frequent phenomenon in SCIC that cannot be neglected when working on detection limits. Also, power-line spikes and pump oscillations appear on the output signal. As the main aim of CC is to reduce the high-frequency noise power, the other detector signal distortions should be removed before applying the decorrelation procedure to ensure the ability of CC to establish detection limits.

In this work, effective means for decreasing the influence of baseline drift and pump oscillations on the decorrelation procedure were sought. The importance of preprocessing the detector signal by digital filtering prior to decorrelation is demonstrated. A special modification to the sample solution is provided to decrease the injection and system peak amplitudes

in order to lessen the influence of the irreproducibility of the injection device.

EXPERIMENTAL

The experimental set-up was the same as that described in a previous paper [2], except that the UV detector was replaced with a conductivity detector. The heart of the system is a six-port, two-position valve. The loop of the valve is continuously flushed with the sample solution by a peristaltic pump to waste. The other flow path of the sample valve is flushed with the eluent to the column. The sampling control and data recording are performed by an Apple IIe personal computer via laboratory-made interface electronics.

The equipment used in the measurements is as follows: sample pump, Zalimp peristaltic pump (Warsaw, Poland); eluent pump, Knauer Type 64.00 HPLC pump; sample valve, six-way mechanical rotary valve with an air actuator, a 140-μl loop and a PTFE rotor surface (Design Office, Estonian Academy of Sciences); column, anion-exchange column with sorbent RM, particle diameter 25–40 μm, phase ratio 1.1 (w/w), dimensions 150 × 4 mm I.D., with a capacity of 0.004 ± 0.002 mgeq/cm^3 (Institute of Chemistry, Estonian Academy of Sciences); detector, Knauer conductivity detector and a conductivity detector from the Design Office, Estonian Academy of Sciences (with the latter it is difficult to match the detector output voltage with the ADC input); analogue to digital converter (ADC), AKM-2, floating point (Design Office, Estonian Academy of Sciences); computer, Apple IIe; and valve actuator, a laboratory-made interface for converting the computer code into the corresponding air pulses.

The eluent was 1.3 mM phthalic acid (pH 4.36) at a flow-rate of 1.2 ml/min. Several sample solutions with concentrations of 0.1–10 ppm (w/w) were prepared in 1.3 mM phthalic acid.

Procedure

A continuous flow of sample through the valve loop was established by means of a peristaltic

pump. The flow-rate was about 7 ml/min, which ensured complete filling of the loop during a 1.95-s filling cycle. A pseudo-random injection sequence was generated by an Apple IIe computer using a 511-element pseudo-random binary sequence (PRBS) with a 1.95-s interval for each pulse. The detector signal was digitized with the same interval. During each experiment two sequences were generated, i.e., 512 injections were performed during each experiment. During each injection a 1.95-s time interval was left for valve loop filling. As the flow-rate through the column was lower than that set by the peristaltic pump, the sample volume introduced in each injection was $1.95 \text{ s} \cdot 1.2 \text{ ml/min} = 39 \ \mu l$ (not all of the 140-μl loop volume was used).

Experiment control and data processing software

The experiment control program was written in BASIC. This program generates PRBS and controls the sampling procedure via a laboratory-made digital valve interface and a pneumatic actuator. The program also records the digitized detector voltage. The detector signal after experiment was transported to an Olivetti M26 computer via cables using PROCOM software.

Detector signal preprocessing and decorrelation were performed by the Olivetti M26 computer. All this software was written in C language. Prior to decorrelation, the baseline drift was estimated by a piece-wise linear function on the monitor using the computer mouse and an interactive procedure, and subtracted from the detector signal. The occasional spikes were removed similarly. Ready-made computer programs also exist for this purpose. Decorrelation was done by a fast Hadamard transform [3]. The power spectrum of the correlogram was estimated using MATLAB software (Mathworks) to determine the cut-off frequency, applying digital filtering of the chromatograms. The cut-off frequency was determined at a point at which the standard deviation of the power spectrum amplitudes computed from higher to lower noise components remains constant. MATLAB provides several low-pass digital filters, of which we used the fifth-order Butterworth filter. After filtering the amplitudes peak areas were measured.

Injection and peak amplitude reduction

The eluent was 1.3 mM phthalic acid with the pH adjusted to 4.36 by adding sodium carbonate. The sample solution was prepared in phthalic acid (1.3 mM) without adding sodium carbonate. For such a sample the injection peak intensity is determined using two factors: the eluent anions displaced by sample anions on the ion-exchanger surface and the difference in cation concentrations between the sample and eluent solution. This gave rise to a negative system peak, as there is a deficiency of cations in the sample, unlike in the eluent. Then the sodium concentration in the sample solution was adjusted to be equal to that of the eluent solution by adding small portions of sodium carbonate to the sample vessel and registering the system peak area at the same time. This procedure was repeated until the system peak intensity was reduced to an acceptable level.

RESULTS AND DISCUSSION

Signal filtering

A typical detector output is shown in Fig. 1. Strong baseline drift is evident. Decorrelation of the detector output correlogram with and without baseline drift is shown in Fig. 2. The effect of the baseline subtraction before decorrelation is evident.

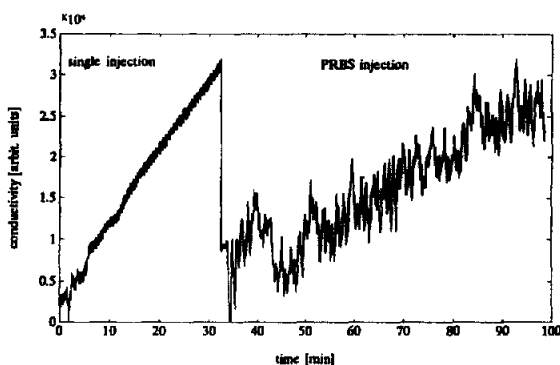The power spectrum of the ion correlogram illustrated in Fig. 2b is shown in Fig. 3a. The

Fig. 1. Conductivity detector output obtained by single injection and PRBS injection of sample. Concentrations: Cl⁻ 1 ppm, NO$_3^-$ 1.1 ppm and SO$_4^{2-}$ 1.6 ppm. The recorder signal has been attenuated four times for PRBS injection.
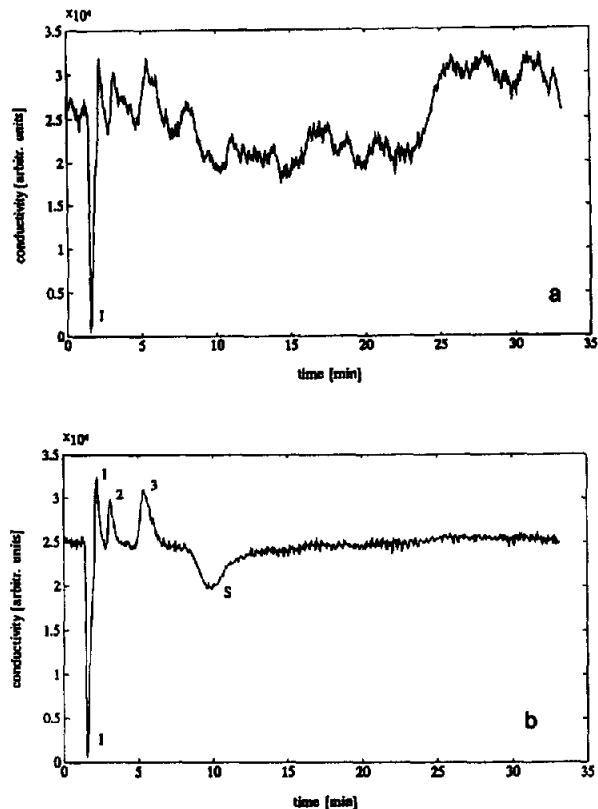
Fig. 2. Decorrelated detector outputs: (a) without and (b) with baseline subtraction before decorrelation. Peaks: I = injection; 1 = Cl$^-$; 2 = NO$_3^-$; 3 = SO$_4^{2-}$; S = system. Concentrations as in Fig. 1.

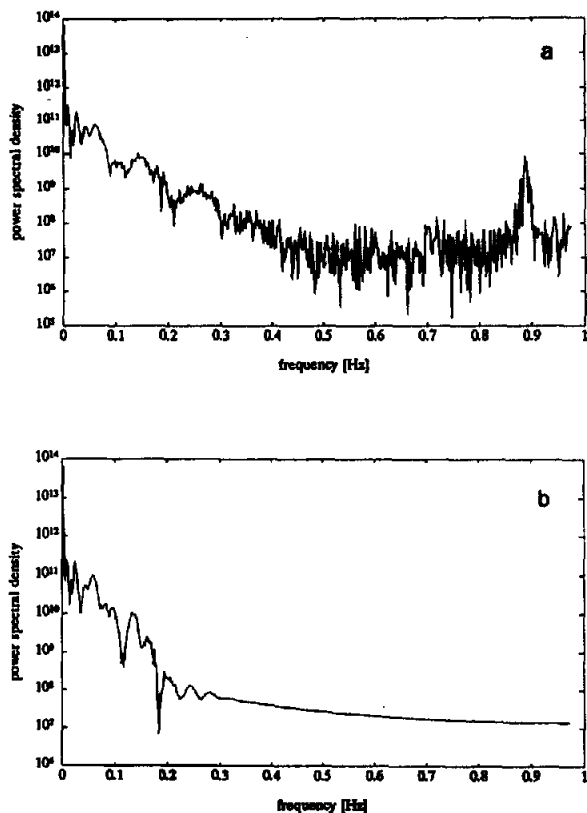

Fig. 3. Power spectrum of the chromatogram from Fig. 2b: (a) before and (b) after digital filtering with fifth-order Buttworth filter.

peak frequency components (peak information) are located at lower frequencies (from 0 to 0.3 Hz), whereas the noise components spread at higher frequencies. The cut-off point is around 0.3 Hz, as is clearly distinguishable. Also, the sharp-noise components present at 0.9 Hz are apparently related to the pumping system of the chromatograph used. They were present all of the power spectra. The presence of the peak that corresponded to the pump pulsations demonstrated that the efficiency of the laboratory-made damper is inadequate. The power spectrum of the same correlogram after applying the fifth-order Buttworth low-pass filter with a cut-off frequency of 0.25 Hz is shown in Fig. 3b.

The PRBS injection chromatogram after applying a low-pass filter is presented in Fig. 4. A comparison of Figs. 4 and 2b demonstrates that
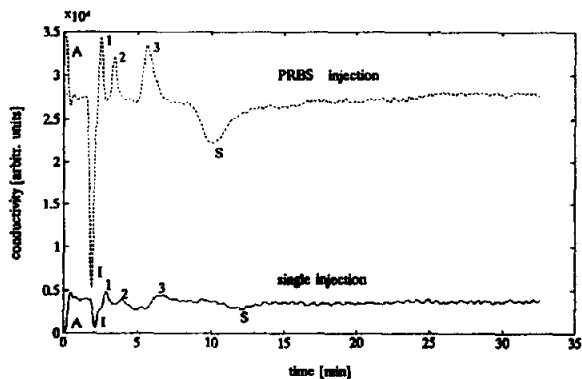

Fig. 4. Decorrelated chromatogram from Fig. 2b after filtering, and baseline-subtracted and filtered single-injection chromatogram from Fig. 1. A = artifact due to filtering procedure; other peaks and concentrations as in Fig. 2.

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the digital filtering was an efficient means of removing high-frequency components from the ion correlograms. This proved to be especially true of the removal of narrow-band deterministic signal components such as disturbances from pump oscillations. The same filtering procedure and baseline subtraction were also performed for the single-injection chromatogram shown in Fig. 1. The result shown in Fig. 4 demonstrates that CC can improve the signal-to-noise ratio of a chromatogram under the present experimental conditions. The improvement in the signal-to-noise ratio was *ca.* 10-fold, compared with the theoretical improvement of 11.3-fold.

Valve and column performance

Careful inspection of the correlogram in Fig. 4 reveals that the intensities of the ghost peaks are too low compared with those of real peaks to appear in the chromatogram as deviations distinguishable from the baseline. The low intensity of the ghost peaks demonstrates that the sampling valve performance is acceptable within one correlation experiment. However, after 8–10 correlation experiments the valve performance decreased significantly, being manifested by an increase in the ghost peak amplitude on the correlogram (Fig. 5). This was indicative of the need for valve rotor treatment. The position of a ghost peak should indicate the nature of the sampling system imperfection [6]. Inspection of the rotor flow paths used demonstrated that they are filled with PTFE rotor material. Evidently

the PTFE particles in the flow paths are scrubbed from the rotor surface by a stator.

An increase in the number of PTFE particles in rotor flow paths and their possible penetration into the sampling loop will apparently reduce the sampling loop and path volumes and one could therefore expect an increase in the restriction of the sample flow and a decrease in the sample flow-rate within the valve, which in turn would result in incomplete loop filling, leading to a specific ghost peak at the end of the correlogram [6]. Hence the behaviour of the sampling valve in our experiments seems to be in accordance with the predictions of CC theory. However, this explanation is a preliminary one and further studies are required in order to establish this fact exactly. After cleaning PTFE particles from the flow paths the ghost peak problems were eliminated.

In most specifications of IC columns, the column lifetime is given as the number of injections that the column is able to accept, which is in the range 5000–10 000. In ion CC this number is exhausted during only one or two experiments. No deterioration in column performance was observed during our experiments. This discrepancy with previous observations means that the column lifetime in IC probably depends on the volume and cleanliness of the eluent and samples that have passed through the column, which on the other hand can be related to the number of injections (as a measure of number of recorded chromatograms) in single-injection chromatography.
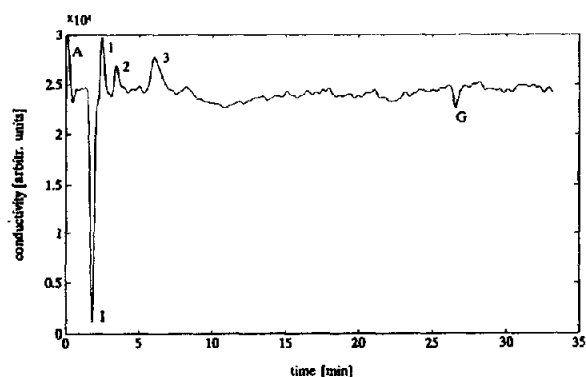
Measurement of sample concentrations near the detection limit

The calibration graph for common anions measured over a concentration range of about 1.5 decades is shown in Fig. 6. the limits of detection calculated for a signal-to-noise ratio for Cl^-, NO_3^- and SO_4^{2-} were 0.1, 0.12 and 0.17 ppm, respectively. The example chromatograms given in the Knauer detector manual for the Vydac column demonstrate that the detection limit for common anions for this detector is about 1–3 ppm in single-injection non-suppressed ion chromatography [7]. Thus, CC enables the detection limit to be decreased by
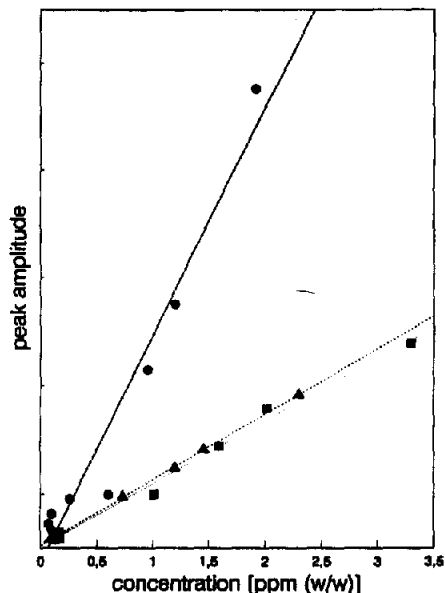

Fig. 5. A correlogram obtained with an imperfect input valve. G = ghost peak.

Fig. 6. Calibration graph. ● = Cl⁻ ; ▲ = NO₂⁻ ; ■ = SO₄²⁻ .

about one order of magnitude. The calibration points lie on the regression lines with correlation coefficients of 0.95, 0.996 and 0.993 for Cl^-, NO_3^- and SO_4^{2-}, respectively. The relatively low correlation coefficient for the Cl^- ion is due to the errors in Cl^- peak-area measurements because its peak badly interferes with the negative injection peak.

The detection limits obtained in this work reflect the possibilities achievable with the available equipment. By combining CC with eluent conductivity suppression the detection limit can be lowered by a further order of magnitude. Also, modern conductivity detectors allow work in the ppb region. Using the trace enrichment technique detection limits in the sub-ppb region have been obtained [8]. Hence CC provides an alternative to trace enrichment methods, the drawbacks of which are well known.

REFERENCES

1 C. Mars and H.C. Smit, Anal. Chim. Acta, 228 (1990) 193.
2 M. Kaljurand, E. Urbas and U. Haldna, Chromatographia, 34 (1992) 417.
3 M. Kaljurand and E. Kullik, Computerized Multiple Input Chromatography, Ellis Horwood, Chichester, 1989.
4 P.R. Haddad and P.E. Jackson, Ion-Chromatography—Principles and Application, Elsevier, Amsterdam, 1990.
5 R. Strassburg and J.S. Fritz, J. Chromatogr., 482 (1989) 343.
6 R. Mulder, P.J. Hoogerbrugge and H.C. Smit, Chemometr. Intell. Lab. Syst., 1 (1987) 243.
7 Knauer Conductivity Detector Operating Manual, No. 206.1106600, Knauer, Berlin, 1983.
8 G. Blo, M. Remelli, F. Pedrielli, L. Balconi and F. Sigon, J. Chromatogr., 556 (1991) 249.