Journal of Chromatography, 640 (1993) 27–31
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2772

Determination of inorganic and organic anions in one run by ion chromatography with column switching

C. Umile* and J. F. K. Huber

Institute of Analytical Chemistry, University of Vienna, Währingerstrasse 38, A-1090 Vienna (Austria)

ABSTRACT

A method for the simultaneous determination of low-molecular-mass organic and inorganic anions in aqueous solutions was developed using isocratic ion chromatography (IC) with suppressed conductimetric detection and column switching. Owing to the large differences in distribution coefficients between sulphate, nitrate and phosphate and the other species, these ions are separated in the first stage on a medium-capacity anion exchanger, whereas the other anions are led through a second column packed with a high-capacity anion-exchange resin via a column-switching valve. After optimization of the switching procedure a spiked drinking water sample was analysed. Fluoride, acetate, butyrate, formate, nitrate, nitrite and phosphate could be determined in addition to the main anions (chloride and sulphate). The time for a complete analysis is less than 20 min and the method can easily be automated. The precision and detection limit are as usual in IC with background suppression.

INTRODUCTION

In the last decade, ion chromatography (IC) has undergone significant changes. Initially IC was focused primarily on the determination of inorganic anions [1]. Nowadays it has a much wider scope, which ranges from the determination of inorganic and organic cations to that of inorganic and organic anions [1,2].

The introduction of a membrane suppressor [3] with improved suppression capacity and reduced void volume permitted the use of high concentrations of hydroxide as eluent and therefore the elution of more strongly retained anions. The high suppression capacity also opened the door to gradient elution in IC using suppressed conductivity detection [4]. This is one way to separate species with widely varying affinities (capacity factors, k') for the stationary phase in a reasonable time. Gradient elution starts with an eluent of low ionic elution strength for the resolution of the most weakly retained species. Increasing the concentration of the eluent during the run leads to the elution of the more strongly retained ions in a reasonable time. Using sodium hydroxide as an eluent component results in water as the suppression product. One example of the benefit of an ion strength gradient is the resolution of fluoride and early-eluting organic anions (most notably acetate and formate) under isocratic conditions, which caused serious problems in the routine determination of anions in environmental and power industrial samples [5,6].

Gradient elution is not without problems. One is the build-up of eluent impurities (mostly carbonate) in the separation column and their subsequent release as the eluent strength is increased. This problem can be minimized by using a trap column and very pure reagents (carbonate free sodium hydroxide and 18 MΩ cm water). Nevertheless, there remains a baseline drift caused by these impurities which complicates the integration of the peaks. Another drawback in gradient elution is that the column must be returned to its initial state, which leads to a longer analysis time.

An alternative to this technique resulted from the

* Corresponding author.

0021-9673/93/$06.00

introduction of a new high-capacity macroporous resin for anion exchange, which made it possible to separate fluoride from the early-eluting organic acids and to elute the more strongly retained anions isocratically. One drawback of this method is the long time of 40 min for the elution of nitrate and phosphate with a wide time window of non-used baseline. A final solution of the problem can be expected by applying column switching, combining this new high-capacity column with the low-capacity column used in previous work.

Column switching was first used in liquid chromatography in the low-pressure mode [7,8] and later in the high-pressure mode [9–21]. In IC one of the approaches to cation determination uses column switching to determine mono- and divalent ions in one isocratic run [22]. Another application of this technique in IC is the rapid analysis of pulping liquors [23].

This paper discusses the use of the column-switching technique for the determination of inorganic and organic anions by IC. After optimization of the system the method was tested with drinking water samples.

EXPERIMENTAL

Chemicals

All chemicals were of analytical-reagent grade: 50% sodium hydroxide (J. T. Baker, Deventer, Netherlands), sodium carbonate, sodium nitrate, sodium nitrite, 96% sulphuric acid, formic acid, acetic acid, butyric acid and sulphate, chloride, phosphate and fluoride Titrisol standards of 1000 mg/l (E. Merck, Darmstadt, Germany). All working standard solutions were prepared by appropriate dilutions of stock standard solutions. The eluents, regenerants and standards were prepared using ultra-pure 18 MΩ cm HPLC-grade water.

Apparatus

A Model 4500i ion chromatograph (Dionex, Sunnyvale, CA, USA) was used, equipped with an electrical conductivity detector with integrated background suppression via an anion micro membrane suppressor (Dionex). The instrument was modified by the plumbing of an additional high-pressure multi-port valve (Dionex) allowing column switching.

In position 1 of the switching valve the effluent is first led through the first column C_1 and then via the switching valve to the second column C_2 and finally, after suppression of the ion background, to the conductivity detector cell. In position 2 of the column switching valve the column sequence is reversed, maintaining the direction of flow within the columns. The chromatograms were monitored and processed by a Model AI-450 data station (Dionex). The injector and the switching valve were activated by the pump control.

The conditions for analysis were as follows: eluent, 75 m*M* NaOH solution; flow-rate, 1 ml/min; columns, C_1 = AS4A anion exchanger (Dionex) (250 × 4.6 mm I.D.) and C_2 AS10 anion exchanger (Dionex) (250 × 4.6 mm I.D.); column switching, 3 min after injection; injection volume, 50 μl; detector, electrical conductivity with chemical ion suppression; micro membrane suppressor continuously regenerated with 25 m*M* H_2SO_4 at 4 ml/min.

RESULTS AND DISCUSSION

Retention characteristics of columns C_1 and C_2

Table I compares the properties of the packing materials in the two columns. Owing to the higher capacity of column C_2 compared with C_1 the anions are generally eluted later under the same chromatographic conditions. Compared with the elution sequence with column C_2, there is a difference in selectivity. On column C_1 carbonate co-elutes with nitrite whereas on column C_2 there is co-elution of carbonate with chloride.

Column-switching sequence

Fig. 1 shows schematically the principle of separation. (a) The sample is injected on to column C_1 and the flow is directed from C_1 to C_2. (b) After a certain time the different species start to separate according to their differential retention. All inorganic anions, except fluoride, chloride and carbonate, have a higher affinity than the low-molecular-mass organic species for the anion exchanger. Therefore, they move slowly in column C_1, whereas the other anions elute from column C_1 and are directed via the switching valve to column C_2, where separation continues. (c) Now the switching valve is activated and the column sequence is reversed. The eluent flows first through column C_2

TABLE I

COMPARISON OF THE PROPERTIES OF THE PACKING MATERIALS IN COLUMNS C_1 AND C_2

Property	AS4A(C_1)	AS10(C_2)
Support	Pellicular	Macroporous
	Poly(styrene–divinylbenzene)	Ethylvinylbenzene–divinylbenzene
Diameter	15 μm	8.5 μm
Cross-Link	4%	55%
Pore Size	< 1 Å	2000 Å
Layer	Latex	Latex
Diameter	200 nm	65 nm
Cross-Link	0.5%	5%
Functional group	Alkanol	Alkanol
	Quaternary amine	Quaternary amine
Ion-exchange capacity	20 μequiv.	170 μequiv.
Column dimensions	250 mm × 4.6 mm I.D.	250 mm × 4.6 mm I.D.

and then through column C_1 without changing the flow direction within the columns. At first the more strongly retained anions, sulphate and nitrate, are eluted from column C_1 and detected (peaks 7 and 8 in Fig. 2). These species are separated only on column C_1. Phosphate as the most retained anion of the sample is passed by fluoride and the low-molecular-mass organic acids coming from column C_2 (peaks 1–3 in Fig. 2). The situation before the elution of phosphate is shown in Fig. 1d. Phosphate elutes from C_1, followed by chloride, carbonate and nitrite, which, like the organics, first pass through column C_1, then through C_2 and finally once again via the switching valve through column C_2.

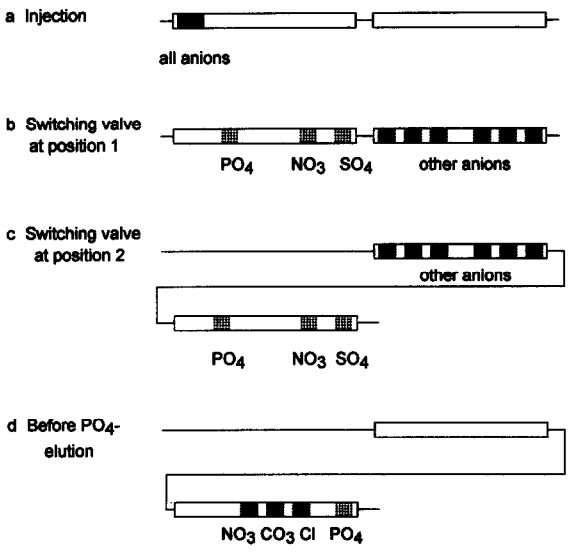

Fig. 1. Elution sequence during column switching

Switching time optimization

To find the optimum switching point first a chromatogram was monitored by injecting a nine-anion standard solution only using column C_1 (AS4A)

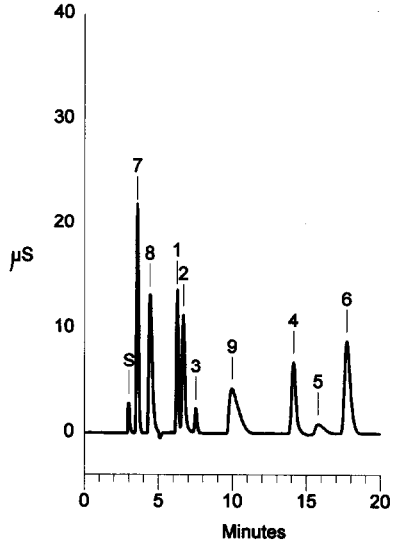

Fig. 2. Chromatogram of a nine-anion standard solution using column switching. Peaks: 1 = 2 mg/l fluoride; 2 = 10 mg/l acetate; 3 = 10 mg/l formate; 4 = 3 mg/l chloride; 5 = 100 mg/l carbonate; 6 = 10 mg/l nitrite; 7 = 5 mg/l sulphate; 8 = 10 mg/l nitrate; 9 = 15 mg/l phosphate; S = switching peak.

under the optimized mobile phase conditions for column C_2 (AS10). Compared with the conditions optimized for column C_1 ($NaHCO_3$–Na_2CO_3 eluent), different sensitivities and a different elution sequence can be observed. The inorganic anions elute in the order fluoride, chloride, nitrite, sulphate, nitrate, phosphate. Acetate and formate coelute with fluoride and carbonate interferes with nitrite. The complete elution of nitrite from column C_1 marks the earliest switching point, whereas the start of the elution of sulphate indicates the latest switching point.

The chromatograms obtained during the optimization of the switching point are shown in Fig. 3. Choosing the switching point between 3.1 and 2.8 min after injection (b to e), nitrite as the last-switched peak is transferred quantitatively on to C_2. Fig. 3a shows a decreased nitrite peak and an increase in the switching peak due to a non-quantitative transfer of the nitrite peak. The optimum switching point in this case is 3.00 min after injection.

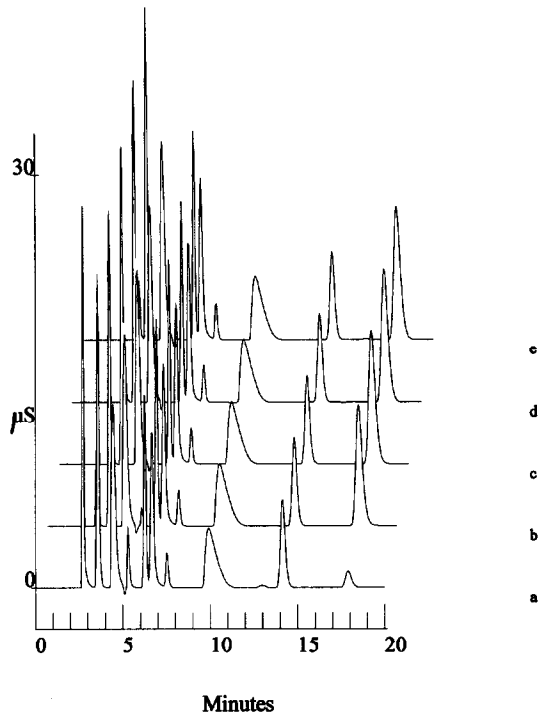

Fig. 3. Chromatograms of a nine-anion standard solution using column switching at different times. Switching point after (a) 2.7, (b) 2.8, (c) 2.9, (d) 3.0 and (e) 3.1 min.

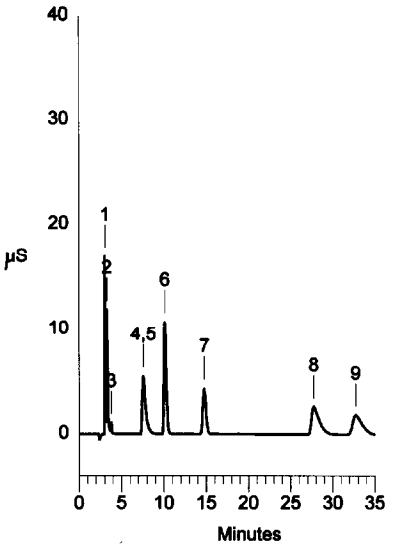

Fig. 4. Chromatogram of a nine-anion standard solution on column C_2. Peaks 1–9 as in Fig. 2.

One of the advantages of this method is that observing these limits there normally is a wide time window where the switching action can take place. Hence the control of this command does not need

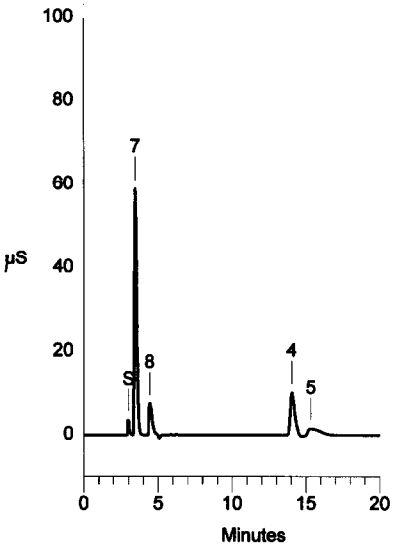

Fig. 5. Chromatogram of a drinking water sample using column switching. Peaks: 7 = sulphate; 8 = nitrate; 4 = chloride; 5 = carbonate; S = switching peak.

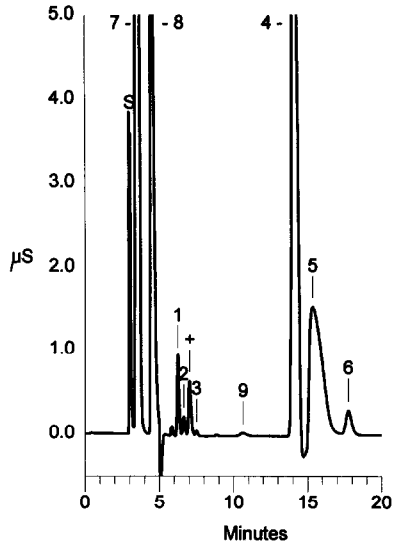

Fig. 6. Chromatogram of a spiked drinking water sample using column switching. Peaks: 7 = sulphate; 8 = nitrate; 4 = chloride; 5 = carbonate; S = switching peak. Spikes: 1 = 0.1 mg/l fluoride; 2 = 0.1 mg/l acetate; + = 0.1 mg/l butyrate; 3 = 0.1 mg/l formate; 6 = 0.3 mg/l nitrite; 9 = 0.1 mg/l phosphate.

to be very exact and can also be done manually just using a watch.

Compared with the separation on column C_2 alone (Fig. 4), there is a time saving of almost 50% and additionally the separation of chloride and carbonate, which may be very important, *e.g.*, in the application discussed in the following section.

Application

After optimization of the switching procedure, several drinking water samples were analysed. A representative sample is shown in Fig. 5. There is no interference between chloride (peak 4) and carbonate (peak 5). The spiked sample (Fig. 6) shows a good separation of fluoride (peak 1, 0.1 mg/l spike) from the organic acids acetate (peak 2, 0.1 mg/l spike), formate (peak 3, 0.1 mg/l spike) and butyrate (peak 2*, 0.1 mg/l spike). Phosphate (peak 9, 0.1 mg/l spike) and nitrite (peak 6, 0.3 mg/l spike) can also be measured with no problems in less than 20 min.

CONCLUSIONS

The example shown in this paper demonstrates the usefulness of column switching in ion chromatography. There are no significant adverse effects from the additional switching device and the very easy set-up, optimization and automation make this method very practical.

REFERENCES

1 H. Small, T. S. Stevens and W. C. Baumann, *Anal. Chem.*, 47 (1975) 1801.
2 H. Small, *Ion Chromatography*, Plenum Press, New York, 1989.
3 J. Stillian, *LC Mag.*, 3 (9) (1985) 802.
4 J. Weiss, *Ionenchromatographie*, VCH, Weinheim, 1991.
5 *Dionex Technical Note, No. 19*, Dionex, Sunnyvale, CA, 1986.
6 S. Harvey, *J. Chromatogr.*, 546 (1991) 125.
7 L. R. Snyder, *J. Chromatogr. Sci.*, 8 (1970) 692.
8 J. J. Lijama and A. A. Hallen, *J. Chromatogr.*, 57 (1971) 153.
9 J. F. K. Huber, R. van der Linden, E. Ecker und M. Oreans, *J. Chromatogr.*, 83 (1973) 267.
10 H. Oster and E. Ecker, *Chromatographia*, 3 (1970) 220.
11 I. Fogy, E. R. Schmid and J. F. K. Huber, *Z. Lebensm.-Unters.-Forsch.*, 173 (1981) 268.
12 I. Fogy, E. R. Schmid und J. F. K. Huber, *Z. Lebensm.-Unters.-Forsch.*, 169 (1979) 438.
13 I. Fogy, E. R. Schmid und J. F. K. Huber, *Z. Lebensm.-Unters.-Forsch.*, 170 (1980) 184.
14 J. F. K. Huber, I. Fogy and C. Fioresi, *Chromatographia*, 13 (1980) 408.
15 J. F. K. Huber and F. Eisenbeiss, *J. Chromatogr.*, 149 (1978) 127.
16 R. J. Dolphin, F. W. Willmott, A. D. Mills and L. P. J. Hoogeveen, *J. Chromatogr.*, 122 (1976) 259.
17 F. M. Willmott, I. Mackenzie and R. J. Dolphin, *J. Chromatogr.*, 167 (1979) 31.
18 F. Erni and R. W. Frei, *J. Chromatogr.*, 149 (1978) 561.
19 E. L. Johnson, R. Gloor and R. E. Majors, *J. Chromatogr.*, 149 (1978) 571.
20 H. Hulpke and U. Werthmann, *Chromatographia*, 12 (1979) 390.
21 H. Hulpke and U. Werthmann, *Chromatographia*, 13 (1980) 395.
22 *Dionex Product Information, Fast Cation*, Dionex, Sunnyvale, CA, 1986
23 S. Utzmann and D. Campbell, *LC · GC*, 9 (1991) 300.