ELSEVIER

Journal of Chromatography A, 686 (1994) 143–148

JOURNAL OF CHROMATOGRAPHY A

Routine determination of anions by capillary electrophoresis and ion chromatography

R. Stahl

Nuclear Research Center Karlsruhe, Institut für Heisse Chemie, P.O. Box 3640, D-76021 Karlsruhe, Germany

First received 10 May 1994; revised manuscript received 8 August 1994

Abstract

Non-suppressed ion chromatography and capillary electrophoresis are used in routine analysis for the identification and determination of anions such as fluoride, formate, chloride, carbonate, bromide and nitrate in aqueous soil leachates and process solutions. Practical aspects of the analysis of samples that contain unknown components using these two orthogonal methods are discussed. The detection limits are found to be about 0.2 μg/ml for chromatography and about 2 μg/ml for electrophoresis. Both methods show linear calibration functions in the concentration ranges 1–50 and 5–50 μg/ml, respectively.

1. Introduction

Ion chromatography (IC) is an excellent method for the simultaneous determination of several inorganic anions in simple matrices such as drinking water and rainwater [1,2]. In complex sample matrices such as process solutions containing unknown components, waste water or soil leachates, one has to make sure that no co-eluting peaks appear. One possibility is to apply a coupled ion chromatograph with two chromatographic systems interconnected via an automatic column-switching valve [3]. On the other hand, capillary electrophoresis (CE) has recently been demonstrated to be a useful technique for the separation of different ions [4,5]. According to Jones and Jandik [6], who separated 30 anions, CE seems to be a very successful method for the determination of unknown components in solutions. In this paper, applications of CE and IC for the identification and determination of anions in routine analysis are discussed.

2. Experimental

2.1. Equipment and chemicals

The instrumental equipment used and the operating conditions for IC and CE are listed in Table 1. The IC analyses are performed under two different conditions using (a) phthalic acid (PA) [7] and (b) *p*-hydroxybenzoic acid (PHBA) as eluent. All eluents are filtered through a 0.45-μm membrane filter before use.

As most inorganic ions have a low or no absorbance in the high-energy UV region, a higher sensitivity in CE is attained with indirect detection. According to the results of Buchberger and Haddad [8], the carrier electrolyte (pH 8.2) is prepared from sodium chromate

0021-9673/94/$07.00
SSDI 0021-9673(94)00746-2

Table 1
Conditions for CE and IC

Method	Parameter	Conditions
CE	Instrumentation	Lauerlabs automated capillary electrophoresis system (Bischoff, Leonberg, Germany)
	Capillary	120 cm effective length × 75 μm I.D., uncoated (Scientific Glass Engineering, Weilerstadt, Germany)
	Temperature	30°C
	Buffer	5 m*M* chromate–0.2 m*M* TTAB, adjusted to pH 8.2 with 5 m*M* H_2SO_4
	Injection	25 mbar, 0.1 min
	Voltage	−30 kV
	Detection	275 nm, Lambda 1000 (Bischoff)
	Data acquisition	PC and Hyperdata software
IC	Instrumentation	Solvent degasser (ERC Alteglofsheim, Germany) Isocratic pump (Bischoff) Ion chromatograph including injection valve (100 μl) and conductivity detector (30°C) (Metrohm)
	Eluent 1	4 m*M* phthalic acid (pH 4.4) adjusted with Tris [7]
	Column 1	Vydac 302IC, flow-rate 2.5 ml/min, pressure 5.5 MPa
	Eluent 2	1.5 m*M* *p*-hydroxybenzoic acid (pH 8.4) adjusted with NaOH, stored under nitrogen
	Column 2	Alltech Anion R (100 mm × 4.1 mm I.D.), flow-rate 1.5 ml/min, pressure 6.4 MPa
	Data acquisition	PC and PE–Nelson software

tetrahydrate. As electroosmotic flow (EOF) modifier, a solution of tetradecyltrimethylammonium bromide (TTAB) is used after passing it through a column filled with a strong anion-exchange resin. Before each series of analyses, the carrier electrolyte is freshly prepared by mixing sodium chromate and TTAB solution; the pH is adjusted with sulfuric acid. The data acquisition of the electropherograms is started with a delay time of 8 min after the application of high voltage.

Standard solutions (1000 μg/ml) of all the investigated anions are prepared from the corresponding dried sodium salts. Before injection, suitable concentrations are obtained by dilution with distilled water. For the characterization of the methods, the concentration interval from 1 to 50 μg/ml is subdivided into eleven equidistant calibration points.

2.2. Sample preparation

Sample preparation is simple. All samples are filtered through a 0.45-μm membrane filter before use. Soil extracts are diluted 1:10 with eluent, if necessary, and process samples are diluted 1:5 with buffer solution.

3. Results and discussion

3.1. Process solution

Difluoromonochloromonobromomethane (CF_2BrCl; Halone), used in fire extinguishers, has been proved to cause severe damage in the atmosphere [9,10]. Therefore, it has to be replaced and disposed of by law in Germany [11]. One method that is being investigated is the chemical decomposition of Halone in solution [12]. The chromatogram of such a solution shows distinct signals for F^-, Cl^-, Br^- and $HCOO^-$ (Fig. 1). The emergence of a system peak is caused by the pH of the sample, which is not identical with the pH of the eluent. Identification of the anions is done by using standard chro-

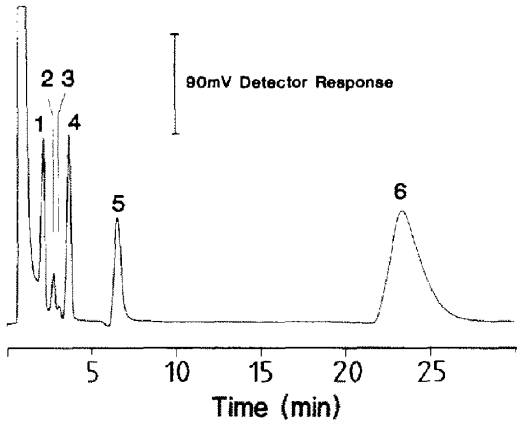

Fig. 1. Separation of a process solution. Conditions: 1.5 m*M* PHBA (pH 8.8); Alltech Anion R column; flow-rate = 1.5 ml/min. Peaks: 1 = fluoride; 2 = formate; 3 = carbonate; 4 = chloride; 5 = bromide; 6 = system peak.

matograms (Fig. 2) and spiking. The corresponding electropherogram (Fig. 3) is consistent with that of the standard mixture (Fig. 4). In both electropherograms the signals of the anions exhibit the same retention times, thus confirming the results.

3.2. Soil extracts

Two independent samples of soil extracts were investigated. The chromatograms of both samples are very similar and show, in addition to the sulfate and chloride signals, a third peak just

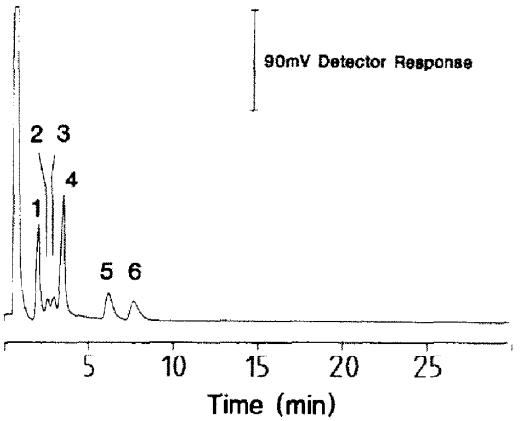

Fig. 2. Separation of a standard mixture. Conditions as in Fig. 1. Peaks: 1 = fluoride; 2 = formate; 3 = traces of carbonate; 4 = chloride; 5 = bromide; 6 = nitrate (5 μg/ml each).

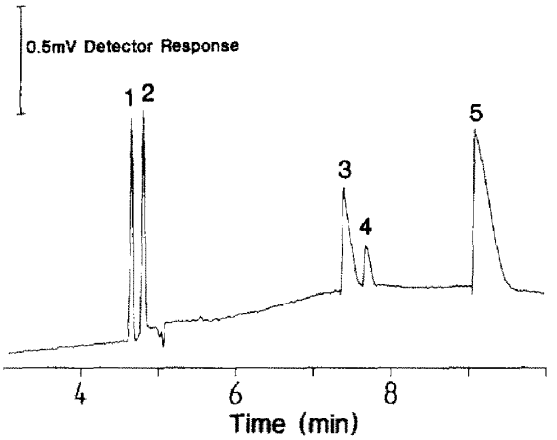

Fig. 3. Electropherogram of a process solution. Conditions: 5 m*M* chromate–0.2 m*M* TTAB (pH 8.2); −30 kV. Peaks: 1 = bromide; 2 = chloride; 3 = fluoride; 4 = formate; 5 = carbonate.

before the chloride signal when PA is used as the eluent. When PHBA is used instead, more signals appear in the same region. By using standard anion mixtures these peaks are identified in sample 1 to be (1) $HCOO^-$, (2) CO_3^{2-}, (3) Cl^- and (4) NO_3^- (Fig. 5). In sample 2 F^- is additionally identified (Fig. 6). Owing to the overlapping system peak, the quantification of sulfate is difficult. Again, the identification of the anions is confirmed by the results of CE without any problems (Figs. 7 and 8).

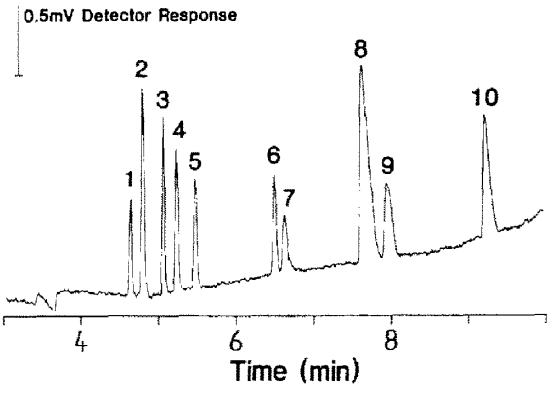

Fig. 4. Electropherogram of a standard mixture. Conditions as in Fig. 3. Peaks: 1 = bromide; 2 = chloride; 3 = sulfate; 4 = nitrite; 5 = nitrate; 6 = chlorate; 7 = perchlorate; 8 = fluoride; 9 = formate; 10 = carbonate (30 μg/ml each).

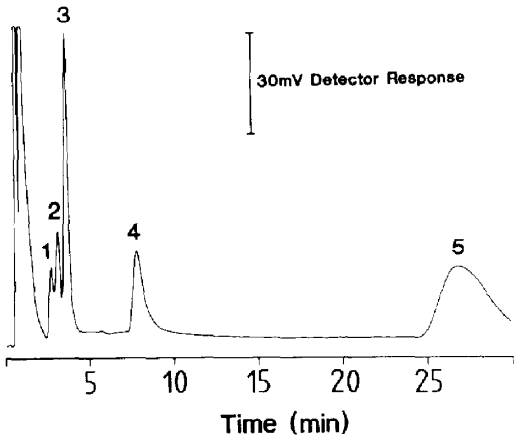

Fig. 5. Separation of extract of soil No. 1. Conditions as in Fig. 1. Peaks: 1 = formate; 2 = carbonate; 3 = chloride; 4 = nitrate; 5 = sulfate and system peak.

3.3. General aspects

The calibration graphs are obtained by injecting standard solutions. Each point of the calibration graph corresponds to the mean value obtained from six independent measurements. The resulting calibration functions show that the methods give a linear response. The corresponding parameters for the quality check are listed in Tables 2 and 3. From the standard deviation of the measurement of the lowest concentration, the detection limits are calculated

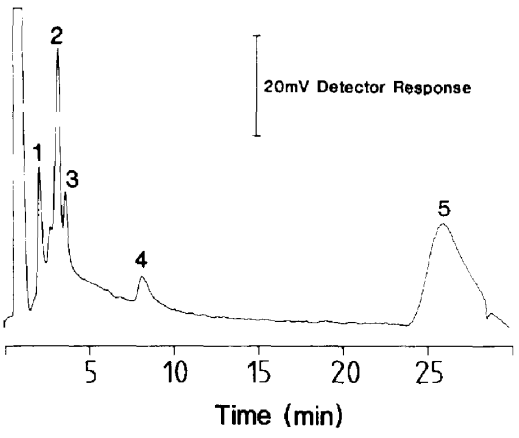

Fig. 6. Separation of extract of soil No. 2. Conditions as in Fig. 1. Peaks: 1 = Fluoride; 2 = carbonate (shoulder = formate); 3 = chloride; 4 = nitrate; 5 = sulfate and system peak.

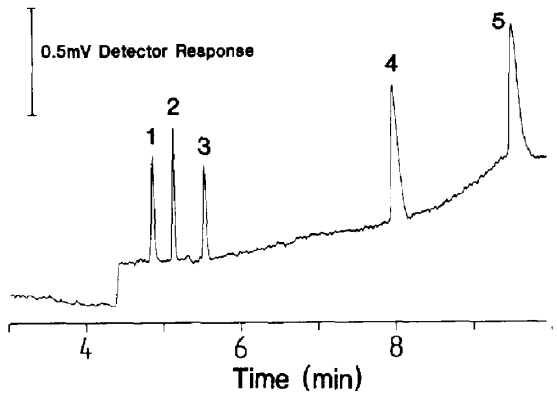

Fig. 7. Electropherogram of soil extract No. 1. Conditions as in Fig. 3. Peaks: 1 = chloride; 2 = sulfate; 3 = nitrate; 4 = formate; 5 = carbonate.

[13]. Under the given conditions the detection limit in CE is about ten times higher than that in IC. Increasing the injection time in CE only partially improves the detection limit, because the resolution of the fluoride and formate signals decreases significantly. With increasing age of the chromate buffer the retention times are steadily reduced. For that reason, in automated systems the integration parameters have to be chosen carefully.

Determination of the fluoride ion is not possible. The peak areas show a definite tendency towards higher values with increasing buffer age.

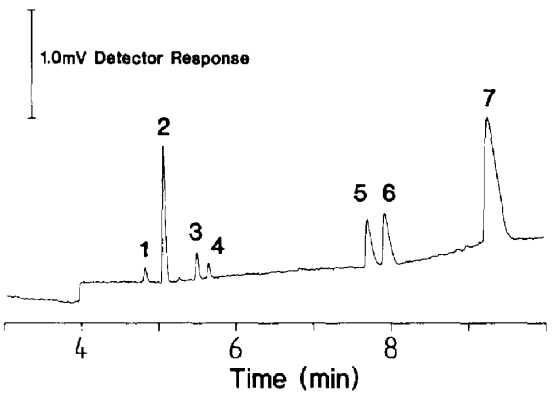

Fig. 8. Electropherogram of soil extract No. 2. Conditions as in Fig. 3. Peaks: 1 = chloride; 2 = sulfate; 3 = fluoride; 3 = nitrate; 4 = unknown; 5 = fluoride; 6 = formate; 7 = carbonate.

Table 2
Ion chromatography with PHBA: calibration parameters

Anion	Retention time (min)	Sensitivity (mV s ml/μg)	Blank (μg/ml)	S.D. (mV s)	Detection limit[a] (μg/ml)
F^-	2.3	301	−0.2	63	0.1
$HCOO^-$	2.9	112	−0.5	54	0.1
Cl^-	3.8	403	−0.1	73	0.2
Br^-	6.6	184	−0.6	36	0.2

[a] Detection limit = $3\sigma_{(1\ \mu g\ ml)}$/sensitivity.

Table 3
Capillary electrophoresis: calibration parameters

Anion	Retention time (min)	Sensitivity (mV s ml/μg)	Blank (μg/ml)	S.D. (mV s)	Detection limit[a] (μg/ml)
Br^-	5.0	31	−0.3	19	1.7
Cl^-	5.2	75	−0.3	33	1.1
SO_4^{2-}	5.5	56	−0.3	30	1.0
NO_2^-	5.7	56	−0.2	47	1.1
NO_3^-	5.9	44	−0.3	32	1.4
ClO_3^-	7.0	38	0.9	47	2.4
ClO_4^-	7.2	31	0.9	48	4.3
F^-	7.7	–	–	–	–
$HCOO^-$	8.7	93	0.6	101	1.6
CO_3^{2-}	9.2	–	–	–	–

[a] Detection limit = $3\sigma_{(5\ \mu g\ ml)}$/sensitivity.

This is confirmed by statistical tests (Wallis, Neuman, Cox–Stuart, Mann) [14].

The most important feature of CE is the distinct separation of the signals. Consequently, the quantification step is easier than in IC. Comparative analyses are reported in Tables 4 and 5. The scattering of the results and the confidence limits of the calibration have been taken into account [14]. In general, the results are comparable in accuracy and precision. Stan-

Table 4
Concentrations (μg/ml) of fluoride, chloride, sulfate, nitrate and formate in aqueous soil extracts (confidence level 90%)

Sample No.	Method	F	Cl	NO_3	$HCOO^-$	SO_4^{2-}
1	CE	–	8.4 ± 0.9	13.6 ± 1.4	10.2 ± 1.2	11.9 ± 0.6
	IC (PA)	–	9.8 ± 0.3	14.0 ± 2.6	–	12.3 ± 1.4
	IC (PHBA)	–	9.8 ± 0.2	13.4 ± 0.5	7.8 ± 0.4	–[a]
2	CE	–[b]	2.6 ± 0.5	8.2 ± 1.0	6.7 ± 1.6	29.9 ± 0.5
	IC (PA)	–	3.1 ± 0.2	7.0 ± 1.9	–	26.9 ± 2.0
	IC (PHBA)	4.9 ± 0.2	2.5 ± 0.2	7.9 ± 0.5	6.9 ± 0.4	–[a]

[a] Overlapping of system peak.
[b] Only qualitative.

Table 5
Concentrations (μg/ml) of fluoride, formate, chloride and bromide in a process solution (confidence level 90%)

Method	F	Cl	Br	HCOO
CE	–[a]	8.9 ± 0.5	20.9 ± 0.7	8.8 ± 1.2
IC (PHBA)	8.2 ± 0.2	8.1 ± 0.2	18.9 ± 0.4	6.1 ± 0.4

[a] Only qualitative.

dard additions to the analysed samples indicate that for these samples there are no substantial matrix interferences.

In routine operation it is important to use the chromate buffer freshly prepared just before each series of analyses. After not more than 15 injections the buffer must be replaced by a fresh solution. A 5-min capillary purge is performed prior to all injections to remove remaining constituents of the last sample from the capillary. The purge is accomplished by a pressure of 2 bar applied to the buffer vial. To check the validity of the calibration, three standards are analysed once before and after the measurement of the unknown samples. Each sample is measured three times.

4. Conclusions

The use of capillary electrophoresis combined with existing chromatographic methodology has been demonstrated to be an excellent analytical tool to confirm the identity and purity of ion chromatographic peaks. Especially with complex sample matrices CE is capable of separating simultaneously many more components than IC. Therefore, CE is an efficient technique for screening analysis. Studies on the determination of fluoride and other anions are in progress.

Acknowledgements

The cooperation and assistance of J. Scherwitzl, R. Durst and S. Fetzner is greatly appreciated.

References

[1] B. Rössner and G. Schwedt, *Fresenius' Z. Anal. Chem.*, 320 (1985) 566.
[2] F. Wagner, P. Valenta and H.W. Nürnberg, *Fresenius' Z. Anal. Chem.*, 320 (1985) 470.
[3] W.R. Jones, A.L. Heckenberg and P. Jandik, *J. Chromatogr.*, 366 (1986) 225.
[4] W. Beck, *Nachr. Chem. Tech. Lab.*, 41 (1993) M1.
[5] S.F.Y. Li, *Capillary Electrophoresis*, Elsevier, Amsterdam, New York, 1992.
[6] W.R. Jones and P. Jandik, *J. Chromatogr.*, 546 (1991) 445.
[7] R. Stahl, *Chromatographia*, 37 (1993) 300.
[8] W. Buchberger and P.R. Haddad, *J. Chromatogr.*, 608 (1992) 59.
[9] F.S. Rowland and D.G. Aldrich, *Environ. Conserv.*, 15 (1988) 101.
[10] G. Fellenberg, *Chemie der Umweltbelastung*, Teubner, Stuttgart, 1990, p. 99.
[11] *Bundesgesetzblatt*, Verordnung 662, 6 May 1991.
[12] U. Bauder, Nuclear Research Centre Karlsruhe, personal communication, 1993.
[13] R.A. Cochrane and D.E. Hillman, *J. Chromatogr.*, 241 (1982) 392.
[14] S. Ebel, *Statistik (Würzburger Skripten zur Analytik*, Reihe 1), Bayrische Julius-Maximilians Universität, Würzburg, 1992.