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Short communication

Separation of chlorine-containing anions by ion chromatography and capillary electrophoresis[1]

Magdalena Biesaga[a,b], Małgorzata Kwiatkowska[a], Marek Trojanowicz[c,*]

[a]*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*

[b]*Institute of Environmental Protection, Krucza 5/11, 00-548 Warsaw, Poland*

[c]*Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland*

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Abstract

Chlorine is still commonly used as disinfectant in water and waste treatment and as bleaching agents in the paper industry. In these processes, numerous chlorine-containing anions are formed with different oxidation states, such as chloride, chlorite, chlorate and perchlorate. The present study is focused on the development of a single-column ion chromatography (SCIC) method and the use of capillary electrophoresis (CE) for the determination of chlorine anions in water at a concentration level up to 25 mg/l for IC and 20 mg/l for CE in the presence of nitrate and sulphate. © 1997 Elsevier Science B.V.

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1. Introduction

Chlorine is commonly used for disinfection of water and wastes and as a bleaching agent in the paper industry. In these processes various anions are formed containing chlorine at different oxidation states such hypochlorite, chlorite, chloride, chlorate and perchlorate. Chlorite and chlorate are considered as especially harmful and their concentration in tap water should not exceeded 1 mg/l [1].

Suppressed column ion chromatography was employed by several authors for determination of chlorite, chloride and chlorate [2–6]. Stahl [7] has reported a single-column ion chromatographic (SCIC) determination of chloride, chlorate and perchlorate in concentrated sulfuric acid with conductivity detection where detection limits of 0.23, 0.17 and 0.2 mg/l were obtained, respectively. Similar detection limit levels have been reported by Poovey and Rando [8] for determination of chlorite and chloride in bleaching solutions with the same method but using a different eluent.

A method alternative to high-performance ion chromatography for determination of inorganic and organic ions is capillary electrophoresis (CE). It usually offers better efficiency of separation, shorter analysis time and lower consumption of reagents, hence it has been successfully employed for analysis of various environmental samples such as waters, wastes and aerosols [9–17]. Jones and Jandik [18,19] have shown the possibility of CE separation of thirty-six different anions using chromate electrolyte with indirect UV detection, including some chlorine-containing anions. However, application of this

*Corresponding author.

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separation technique for the quantitative determination of anions containing chlorine at different oxidation states has not been shown.

The aim of the present work was to develop a CE method for the determination of chlorine-containing inorganic ions and to compare this method with single-column ion chromatography.

2. Experimental

2.1. Apparatus

SCIC measurements were performed using a HPLC setup from Knauer (Berlin, Germany) consisting of a pump Model 64, injection valve with 100-μl sample loop and variable-wavelength UV–Vis detector connected to potentiometric strip chart recorder Model TZ 4625 from Laboratorni Pristroje (Prague, Czech Republic). Indirect UV detection was carried out at 254 nm for 1 m*M* potassium phthalate eluent due to high background absorption of the eluent. Separations were carried out with a Vydac 302 IC column (Hesperia, USA) with silica-based stationary phase cross-linked with quaternary ammonium groups. Between measurements the column was conditioned with eluent at a flow-rate 0.2 ml/min.

CE measurements were performed using a Capillary Ion Analyzer from Waters (Milford, MA, USA) equipped with a UV detector, autosampler, hydrostatic sample injection system and data acquisition software Millenium 2010 Chromatography Manager. A fused-silica capillary Accusep 60 cm (52 cm effective length)×75 μm was conditioned overnight in water. CE measurements were carried out at 20 kV using 30-s hydrostatic injection with elevation 10 cm. A 2-min auto purge and indirect UV detection at 254 nm were applied. All measurements were carried out at ambient temperature.

2.2. Reagents

Sodium perchlorate was purchased from Fluka, sodium hypochlorite and chlorite from BDH. A 20 m*M* solution of electroosmotic flow modifier CIA-PAK OFM Anion BT was provided by Waters. All other reagents used were of analytical grade from POCh (Gliwice, Poland). All solutions used were prepared with deionized Milli-Q water from Waters.

Stock solutions of 1000 mg/l of individual analytes were stored in a refrigerator. Solutions of chlorite and chlorate were prepared once a week, whereas solutions of chloride and perchlorate were prepared once a month. All working solutions were prepared by appropriate dilution with freshly prepared eluent.

Eluents were prepared daily by dilution from concentrated solutions stored in a refrigerator, filtration through 0.45-μm filters from Cuno (Life Sciences Division, Meriden, USA) and ultrasonication. The pH of the eluents was adjusted with sodium tetraborate solution.

The concentrated electrolyte for CE measurements was prepared from sodium chromate and concentrated sulfuric acid. The working electrolyte solution of 4.6 m*M* sodium chromate, pH 8, containing 0.46 m*M* CIA-PAK OFM Anion BT was prepared daily from concentrated solutions, filtered through a 0.45-μm filter and degassed.

3. Results and discussion

3.1. Ion chromatography

In SCIC methods developed earlier with conductivity detection, phthalate [7] and 1-hexanesalfonate [8] eluents have been used. In the present work separation of chlorite, chloride, chlorate and perchlorate was investigated with indirect UV detection using as eluents solutions of sodium tartrate, sodium citrate and potassium hydrogenphthalate. With 2 m*M* sodium tartrate eluents of pH 3.24 and 4.4 no signal for perchlorate was observed, whereas for 1 m*M* sodium citrate of pH 4.9 no signal for chlorate was observed. The most satisfactory chromatographic response was found for phthalate eluent. For the optimization of separation its concentration was varied from 0.5 to 3.0 m*M* and its pH from 3.6 to 5.0. The most important task was to separate chloride from chlorite, chlorate from nitrate present in real samples, and perchlorate from sulfate, also present in natural samples. The effect of eluent concentration at pH 4.0 is shown in Fig. 1, whereas the effect of pH for 1 m*M* eluent can be seen in Fig.

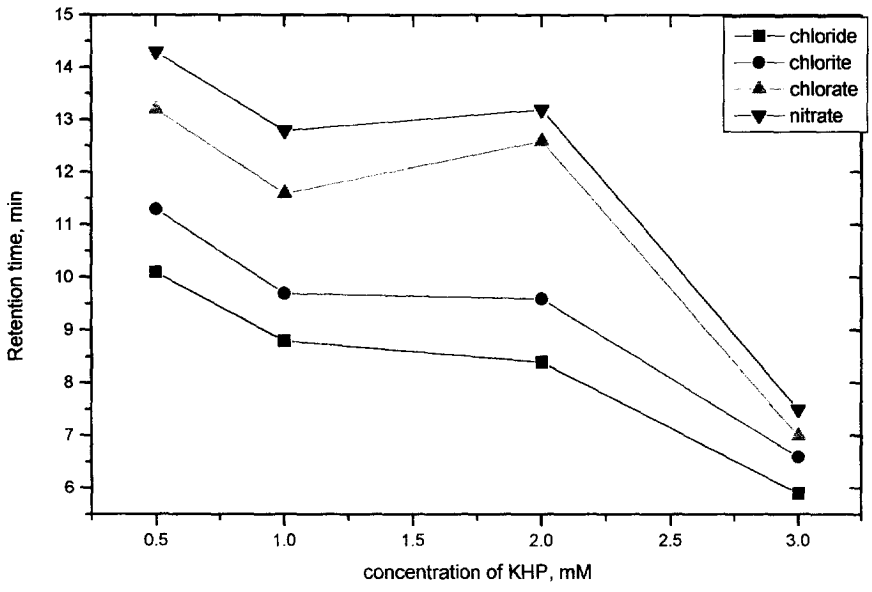

Fig. 1. Effect of potassium hydrogenphthalate concentration at pH 4 on retention times of anions. Flow-rate: 1 ml/min; detection: UV at λ=290 nm; column: Vydac 302 IC; sample injection volume: 100 μl.

2. The perchlorate was eluted at 111 min at 1 ml/min flow-rate and therefore it is not included in the figures. A 1 m*M* phthalate eluent of pH 4.0 was assumed as optimum. Much shorter retention time for perchlorate was observed at larger flow-rate without deterioration of separation of earlier eluted anions (at 41 min using flow-rate 2.5 ml/min). Fig. 3 shows the separation of the mixture of considered analytes at a flow-rate of 2.5 ml/min with detection at 254 nm.

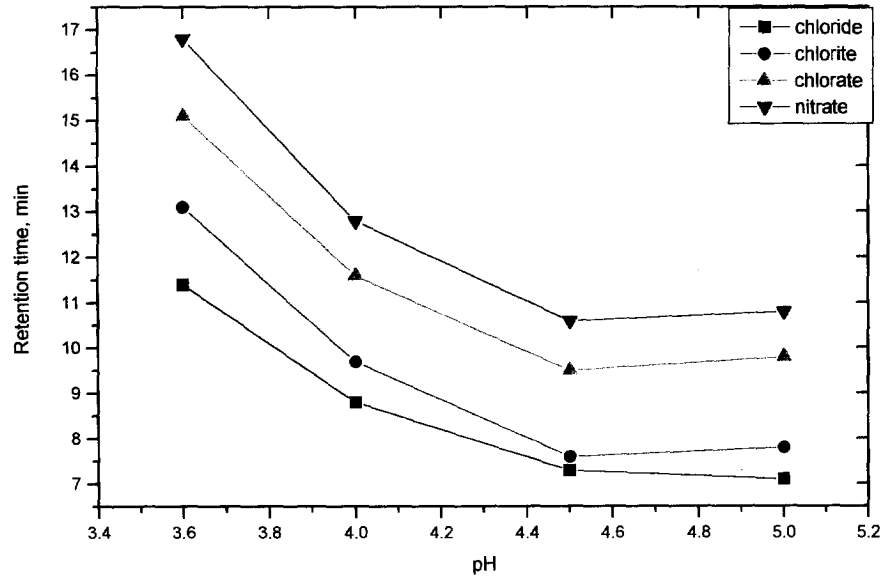

Fig. 2. Effect of pH of 1 m*M* potassium hydrogenphthalate on retention times of anions. Flow-rate: 1 ml/min; detection: UV at λ=254; column: Vydac 302 IC; sample injection volume: 100 μl.

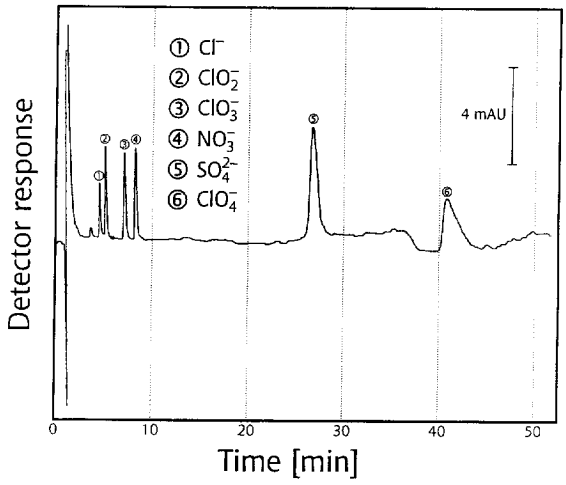

Fig. 3. Chromatogram of standard mixture of anions: Cl^-, 0.15 mg/l; ClO_2^-, 3 mg/l; ClO_3^-, 3.0 mg/l; NO_3^-, 2 mg/l; SO_4^{2-}, 10 mg/l; ClO_4^-, 10 mg/l. Eluent: 1 m*M* KHP; flow-rate: 2.5 ml/min; detection: UV at λ=254 nm; column: Vydac 302 IC; sample injection volume: 100 μl.

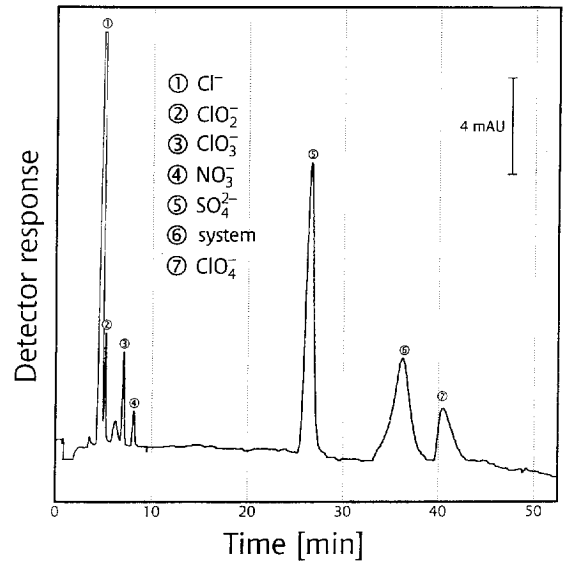

Fig. 4. Chromatogram of 5-fold diluted tap water spiked with 3 mg/l chlorite, 3 mg/l chlorate, 10 mg/l perchlorate. Eluent: 1 m*M* KHP; flow-rate: 2.5 ml/min; detection: UV at λ=254 nm; sample injection volume: 100 μl; column: Vydac 302 IC.

The quantitative response to chlorine-containing anions was evaluated by plotting peak heights (H) vs. concentration in injected samples (C). The results shown in Table 1 indicate satisfactory linearity of response, although the range of the linear response varied for different anions. The detection limit was estimated for signal-to-noise ratio equal to 3 [20]. Except for perchlorate the obtained values of the detection limit are better than reported earlier for SCIC with conductivity detection [7,8]. The estimated R.S.D. values for n=9 for solution containing 3 mg/l chlorite and chlorate, 0.2 mg/l chloride and 5 mg/l perchlorate were comparable to results reported earlier for chloride and chlorite [8]. The reason for this poor precision of SCIC measurements is unclear and most probably requires some improvements in the instrumentation used.

The effect of increasing concentration of chloride and nitrate above a certain level may affect to the same extent separation of chlorite and chlorate. At chloride concentration higher than 10 mg/l the peaks of chloride and chlorite are not completely resolved (R_s=1.14), however, the presence of excess of chloride does not affect the resolution of other solutes. The presence of 25 mg/l of nitrate does not affect the separation of chlorine-containing anions.

Fig. 4 shows the chromatogram obtained for a 5-fold diluted tap water spiked with chlorite, chlorate

Table 1
Characteristics of calibration plots $H=AC+B$ (peak height vs. concentration in mg/l) in SCIC measurements obtained with a Vydac 302 IC column and 1 m*M* potassium hydrogenphthalate eluent of pH 4.0 at a flow-rate of 2.5 ml/min, detection: UV at λ=254 nm

Parameter	Values for different analytes			
	Cl^-	ClO_2^-	ClO_3^-	ClO_4^-
A (mAU×l×mg^{-1})	3.21	1.04	0.87	0.17
B (mAU)	1.17	−0.31	0.02	−0.43
Limit of detection, mg/l	0.01	0.18	0.15	1.5
Upper linearity limit, mg/l	10	5	10	20
Correlation coefficient	0.978	0.9982	0.9991	0.9955
R.S.D., %	10	7	8	12

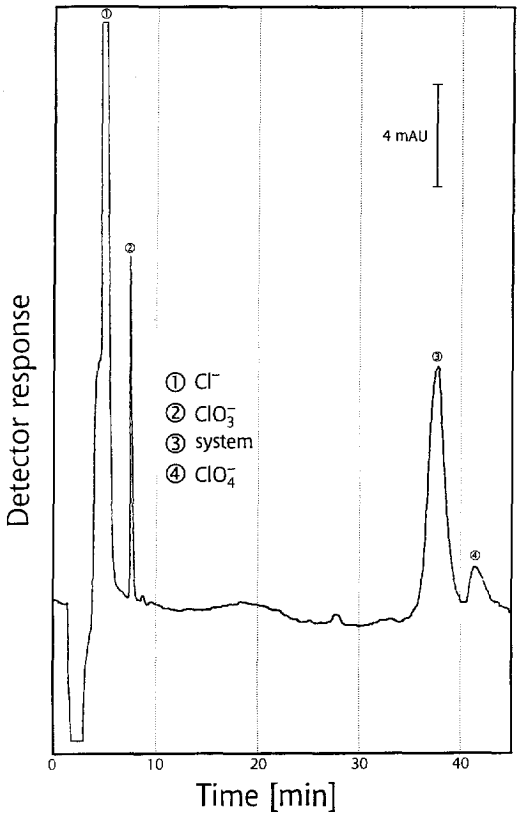

Fig. 5. Chromatogram of 1000-fold diluted commercial bleaching solution spiked with 5 mg/l chlorate, 5 mg/l perchlorate. Eluent 1 m*M* KHP; flow-rate: 2.5 ml/min; detection: UV at λ=254 nm; sample injection volume: 100 μl; column: Vydac 302 IC.

and perchlorate. The presence of a large excess of chloride does not disable the quantitation of chlorite. Fig. 5 shows the chromatogram of a 1000-fold diluted commercial bleaching solution also with known additions of chlorite, chlorate and perchlorate. In this case, however, in spite of the large dilution, the excess of chloride was too large to obtain a separation of chlorite and chloride. The results of recovery tests for chlorite, chlorate and perchlorate in natural samples are shown in Table 2. For the diluted tap water the obtained results are satisfactory except for a very large negative error for perchlorate for the sample water spiked with lower level of perchlorate. Five-fold dilution of water sample was not sufficient to determine the high concentration of chloride present. Larger deviations have been found for the determination of chlorate and perchlorate in diluted bleaching solution spiked with known amounts of analyte. In most cases the negative error was observed, which might be attributed to disproportionation reactions of chlorate and perchlorate with hypochlorite and free chlorine present in the analysed samples.

3.2. Capillary electrophoresis

CE measurements have been carried out using the electrolyte recommended earlier for determination of chloride, nitrate and sulfate in natural waters [21]. All considered chlorine-containing anions were baseline resolved with migration times below 5 min. The sequence of migration of chlorate, perchlorate and chlorite does not agree, however, with predictions which can be based on the mobilities of appropriate acids given by Hirokawa et al. [22] ($67.0 \cdot 10^5$, $69.8 \cdot 10^5$ and $53.9 \cdot 10^5$ $cm^2/V/s$ for chloric, perchloric and chlorous acids, respectively). This behavior may result from different associations of these ions with cations present in the running electrolyte. For the calibration plots a wider range of linear response of peak area vs. concentration was

Table 2
Results of SCIC determination of chlorine containing anions in natural samples in conditions as in Table 1

Analyte	Tap water, 5-fold diluted			Bleaching preparation, 1000-fold diluted		
	Found (mg/l)	Recovery (%)		Found (mg/l)	Recovery (%)	
		1st addition	2nd addition		1st addition	2nd addition
ClO_2^-	<0.18	100	100	–		
ClO_3^-	<0.15	107	100	4.5	82	120
ClO_4^-	<1.5	75	93	<1.5	75	81

Tap water: 1st addition: ClO_2^-, 1 mg/l; ClO_3^-, 1 mg/l; ClO_4^-, 5 mg/l; 2nd addition: ClO_2^-, 3 mg/l; ClO_3^-, 3 mg/l; ClO_4^-, 10 mg/l.
Bleaching solution: 1st addition: ClO_3^-, 3 mg/l; ClO_4^-, 5 mg/l; 2nd addition: ClO_3^-, 5 mg/l; ClO_4^-, 10 mg/l.

Table 3
Characteristics of calibration plots $y=Ax+B$ (peak area vs. concentration in mg/l) obtained for CE measurements

Parameter	Values for different analytes			
	Cl^-	ClO_2^-	ClO_3^-	ClO_4^-
A	717.65	497.68	257.86	284.44
B	436	−25.7	16.31	−69.05
Correlation coefficient	0.9982	0.9998	0.9992	0.9962
Limit of detection	0.1	0.2	0.2	0.6
Upper linearity limit, mg/l	50	10	20	10
R.S.D., %	2	0.6	0.4	1

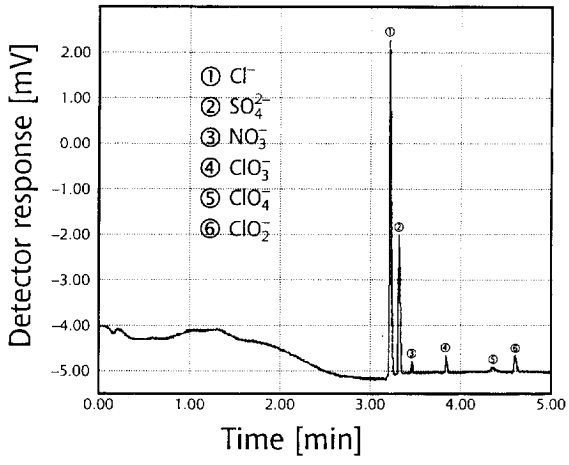

Fig. 6. Electropherogram of 5-fold diluted tap water spiked with 2 mg/l of each chlorine containing anions using as electrolyte 4.6 m*M* sodium chromate of pH 8.0 containing 0.46 m*M* CIA-PAK OFM Anion BT. Applied voltage: 20 kV (negative polarity). Indirect detection at 254 nm.

found (Table 3), and also much better precision for ten injections of standard solution containing 2 mg/l of each analyte, than was reported above for SCIC measurements. The detection limits obtained for CE determination are comparable to those estimated for SCIC except for a ten-times worse value obtained for chloride. The addition of excess of nitrate and sulfate up to 20 mg/l concentration does not affect the determination of chlorine-containing anions.

Fig. 6 shows an electropherogram obtained for 5-fold diluted tap water spiked with 2 mg/l of each chlorine-containing anions, whereas Table 4 shows the results of determination and recovery tests in three different natural samples. Very good separation of the chloride signal from those for other chlorine-containing anions also enables their quantitative determination in the presence of a large excess of chloride. The dilution applied for natural samples enabled the quantitative determination of chloride in all samples and chlorate in bleaching preparation.

Table 4
Results of CE determination of chlorine containing anions in natural samples

Analyte	Tap water, 5-fold diluted			Swimming pool water, 20-fold diluted			Bleaching preparation, 200-fold diluted		
	Concentration (mg/l)	Recovery (%)		Concentration (mg/l)	Recovery (%)		Concentration (mg/l)	Recovery (%)	
		I	II		I	II		I	II
Cl^-	18.8	90	105	2.4	115	106	37.4	103	108
ClO_2^-	<0.2	97	102	<0.2	103	96	<0.2	91	101
ClO_3^-	<0.2	92	99	<0.2	100	98	2.3	86	107
ClO_4^-	<0.6	86	98	<0.6	114	102	<0.6	–	105

Swimming pool water and bleaching preparation: 1st addition, 2 mg/l of each solute; 2nd addition, 4 mg/l of each solute.
Tap water: 1st addition, 1 mg/l of each solute; 2nd addition, 2 mg/l of each solute.

The level of other solutes was in all samples below the detection limit. With few exceptions only, the recovery tests yielded satisfactory results.

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References

[1] S. Regli, Environmental Protection Agency Status Report on Development of Regulation for Disinfectants and Disinfection By-Products, Washington, DC, June, 1991.
[2] D.P. Hautman, M. Bolyard, J. Chromatogr. 602 (1992) 65.
[3] M. Bolyard, P. Snyder Fair, D.P. Hautman, Environ. Sci. Technol. 26 (1992) 1603.
[4] L.C. Adams, G. Gordon, Anal. Chem. 67 (1995) 535.
[5] L.E. Vanatta, J. Chromatogr. A 671 (1994) 83.
[6] A.M. Dietrich, T.D. Ledder, D.L. Gallagher, M.N. Grabeel, R.C. Hoehn, Anal. Chem. 64 (1992) 496.
[7] R. Stahl, Chromatographia 37 (1993) 300.
[8] H.G. Poovey, R.J. Rando, J. Liq. Chromatogr. 18 (1995) 261.
[9] J.P. Romano, P. Jandik, W.R. Jones, P.E. Jackson, J. Chromatogr. 546 (1991) 411.
[10] J.P. Romano, J. Krol, J. Chromatogr. 602 (1992) 205.
[11] S.A. Oehrle, J. Chromatogr. A 733 (1996) 101.
[12] P. Jandik, W.R. Jones, J. Chromatogr. 546 (1991) 431.
[13] R. Kuhn and S. Hoffstetter-Kuhn, Capillary Electrophoresis – Principles and Practice, Springer Verlag, Berlin, 1993.
[14] J.P. Landers, Handbook of Capillary Electrophoresis, CRC Press, Boca Raton, FL, 1994.
[15] F. Foret, L. Krivankova and P. Bocek, Capillary Zone Electrophoresis, VCH, Weinheim, 1993.
[16] V. Sustacek, F. Foret, P. Bocek, J. Chromatogr. 545 (1991) 239.
[17] J. Pospichal, P. Gebauer, P. Bocek, Chem. Rev. 89 (1989) 419.
[18] W.R. Jones, P. Jandik, J. Chromatogr. 546 (1991) 445.
[19] W.R. Jones, P. Jandik, J. Chromatogr. 608 (1992) 385.
[20] J.P. Foley, J.G. Dorsey, Chromatographia 18 (1984) 503.
[21] Method N-601a, Waters Capillary Ion Analyzer Operator's Manual 153-02TP, Millipore, Milford, MA, July 1994.
[22] T. Hirokawa, M. Nishimo, N. Aoki, Y. Kiso, Y. Sawamoto, T. Yagi, J. Akiyama, J. Chromatogr. 271 (1983) D1.