ELSEVIER

Journal of Chromatography A, 781 (1997) 457–466

JOURNAL OF CHROMATOGRAPHY A

Development of a capillary electrophoresis method with indirect photometric detection for the determination of anions related to anticaries

Tianlin Wang[a], Sam F.Y. Li[b,*]

[a]*Department of Chemistry, National University of Singapore, Singapore 119260, Republic of Singapore*

[b]*Department of Chemistry and Institute of Materials Research and Engineering, National University of Singapore, Singapore 119260, Republic of Singapore*

Abstract

There is a great need for simple, reliable and sensitive analytical methods for determination of anions, such as fluoride, monofluorophosphate, orthophosphate and polyphosphates, in both fundamental research on anticaries and quality control of dentifrices. To meet this need, we developed a capillary electrophoresis (CE) method for the determination of the anions by employing adenosine 5′-triphosphate (ATP) as UV chromophore for indirect photometric detection and cetyltrimethylammonium bromide (CTAB) as modifier to reverse EOF. Buffer pH, separation voltage and sample injection volume were optimised to obtain high-resolution separation and sensitive detection of the anions. All of the test solutes were better than baseline separated in less than 10 min. The method developed was successfully applied to determination of fluoride, monofluorophosphate, orthophosphate and pyrophosphate ions in a sample of commercial toothpaste. © 1997 Elsevier Science B.V.

Keywords: Inorganic anions; Dentifrices; Fluoride; Monofluorophosphate; Phosphate; Adenosine-5′-triphosphate

1. Introduction

The effectiveness of fluoridated dentifrices in caries prevention has been accepted for about four decades [1]. The reduction in caries experience following the use of topical fluorides applied in the form of toothpastes has been well documented. However, the precise mode of action of the fluoride agents most commonly found in toothpastes (monofluorophosphate and ionic fluoride) is not yet completely understood [2]. The enhancement of the process of remineralization is considered to be an important part of the mechanism of action of fluoride [3]. Other inorganic ions such as calcium and phosphorus (including orthophosphate and polyphosphate) will also play a role in this process [3,4].

Simple, reliable and sensitive analytical methods to determine the anions, such as fluoride, monoflurophosphate, orthophosphate and polyphosphates, related to anticaries are necessary for basic investigations of anticaries and quality control of dentifrices. For example, it is questioned that monoflurophosphate (MFP) provides a caries preventive effect that involves the conversion of hydroxyapatite to more caries resistant fluoroapatite by the action of the fluoride ion produced simply by the hydrolysis of MFP to orthophosphate, and advanced analytical techniques are needed to analyse not only inherent contaminants in MFP chemicals but also all reaction products for characterising the reactions of MFP [5].

*Corresponding author.

0021-9673/97/$17.00
PII S0021-9673(97)00375-0

Simple and reliable analytical methods are also needed for testing of competitive brands of dentifrices to keep up to date with emerging trends in the industry and monitoring product infringement in the marketplace [6].

There are currently several instrumental methods available for analysing the anions related to anticaries. Fluoride ions (F^-) can be determined by potentiometry with the use of a fluoride ion-selective electrode (ISE) [7,8]. Monofluorophosphate is hydrolysed with hydrochloric acid and fluorine species in toothpastes can be analysed by a gas chromatographic (GC) procedure [8]. Fluoride, monofluorophosphate, orthophosphate and polyphosphates are reported to be separated and determined by ion chromatography (IC) [5,6,9,10]. IC seems to be a technique suitable for the analysis of the above mentioned anions. However, some difficulties in practice exist when the anions are determined by IC [5,6,9]. Fluoride ion is weakly retained on common columns and is often eluted very close to the "dips" with many kinds of eluents. Some components of sample matrix, such as bicarbonate, can result in severe early baseline disturbances and a very large system peak, suppressed conductivity detection may be necessary for quantitation of fluoride in dentifrices by ion chromatography. Strong eluents are required to elute polyphosphates in a reasonable time due to high affinities of polyphosphates to anion exchangers. The strong eluents of high conductivity make conductivity detection of polyphosphates less useful. A post-column detection of derivatization with molybdate is more often used.

Capillary electrophoresis (CE) has the advantages of high separation efficiency, short separation time and low consumption of samples and reagents over conventional separation techniques [11]. Among many successful applications of CE [11,12] are the separation and determination of small anions with indirect photometric detection [13–15]. Jones and Jandik obtained remarkably successful separation of thirty anions with a carrier electrolyte consisting of chromate as UV chromophore and a hydrophobic quaternary ammonium ion as EOF modifier to reverse EOF [16]. The carrier electrolyte of chromate for the separation and indirect detection of inorganic anions has been widely used in CE due to its excellent UV absorbance characteristics and its high mobility [13–15]. However, chromate, an anion of large mobility, is less effective in the separation of anions of low mobilities, such as fluoride and phosphates. Asymmetric peak shape and low separation efficiency result when anions of low mobilities are separated in electrophoresis buffer containing co-ions of high mobilities [17]. It is difficult to decrease the effective mobility of chromate by only adjusting pH because the mobilities of both chromate (I) and chromate (II) have relatively large values and pK_{a1} is relatively small. The separation of anions related to anticaries by CE with chromate-based buffer was less successful. A noisy baseline was observed when temperature was manipulated to improve resolution [18] and only partial separation of interesting anions was obtained when 1-butanol was used as additive [19]. Shamsi and Danielson [20] reported the results of the separation of anions in toothpastes with adenosine 5′-monophosphate-based carrier electrolyte near neutral pH. Fluoride and monofluorophosphate were not separated. The separation time was long. For example, migration time of pyrophosphate was longer than 24 min. The method was not quantitatively evaluated. So far, the potential of CE for the separation of the anions related to anticaries has not yet been fully explored. In this paper another CE approach is described for the analysis of the anions related to anticaries. Its application is demonstrated for the separation and determination of fluoride, monofluorophosphate, orthophosphate and pyrophosphate ions in a sample of commercial toothpaste. The method is simple, reliable and sensitive.

2. Experimental

2.1. Chemicals

Cetyltrimethylammonium bromide (CTAB), disodium monoflurophosphate (MFP, FPO_2^{2-}) and sodium pyrophosphate (P_2, $P_2O_7^{4-}$) were purchased from Aldrich (Milwaukee, WI, USA). Adenosine 5′-triphosphate disodium salt (ATP), tripolyphosphate pentasodium salt hexahydrate (P_3, $P_3O_{10}^{5-}$) and trisodium trimetaphosphate (cP_3, $P_3O_9^{5-}$) were products of Sigma (St. Louis, MO, USA). Disodium

hydrogen phosphate anhydrous (P_i, PO_4^{3-}) and sodium fluoride (F^-) were purchased from Fluka (Buchs, Switzerland) and Merck (Darmstadt, Germany), respectively. Other chemicals used were of analytical grade. Deionized water used throughout the experiments was prepared with a Milli-Q system (Millipore, Bedford, MA, USA).

CE buffer solutions composed of 5 m*M* ATP and 0.02 m*M* CTAB were prepared freshly on a daily basis. pH adjustment was accomplished by adding 0.1 *M* sodium hydroxide until the required pH was obtained. The solutions were filtered through a 0.45-μm Nylon syringe filter before use.

Total ionic strength adjustment buffer (TISAB) contained appropriate amounts of acetic acid, sodium chloride and citrate sodium. pH was controlled at about 5.2 by adding sodium hydroxide.

2.2. Apparatus

CE was performed with a laboratory built CE system, equipped with a Spellman CZE1000R power supply (Spellman, Plainview, NY, USA) and a Linear UVIS 200 detector (Linear Instruments, Reno, NV, USA). Electropherograms were recorded with a HP 3390A integrator (Hewlett-Packard, Avondale, PA, USA) connected with a switch for changing the polarity of the input signal. Polyimide coated fused-silica capillaries of an inner diameter (I.D.) of 50 μm and an outer diameter (O.D.) of 362 μm (Polymicro Technologies, Phoenix, AZ, USA) were used. The total length was 50.0 cm and the effective length was 40.0 cm. On-column indirect UV detection was conducted at 260 nm. The hydrostatic sample injection mode was employed for sample introduction into the capillary at the cathodic side, with injection time of 40 s, unless otherwise stated, at a height difference of 3.0 cm between the liquid levels of the sample vial and the buffer reservoir at the grounded electrode. Temperature was maintained at 25±1°C.

Chromatographic separation and determination of MFP and P_i was carried out on a Waters IC-PAK A HR column connected to a Waters 510 HPLC pump and a Waters 413 conductivity detector (Milford, MA, USA). Sodium borate–gluconate eluent flowed at 1.0 ml/min.

Potentiometric measurements to determine fluoride ions were completed by using an HI 8417 microprocessor bench pH meter (Hanna Instruments, Limena, Italy) with a pF electrode (Shanghai Dianguang Device Factory, Shanghai, China) against a Ag/AgCl reference electrode.

2.3. Sample preparation and procedure

A commercial toothpaste of about 0.4 g was accurately weighed and dissolved in about 40 ml water to prepare 50.00 ml of sample solution. The solution was stirred with magnetic stirrer for 20 min and transferred to a 50 ml flask. It was topped up to 50.00 ml. The solution was centrifuged for 2 min. After being passed through a 0.45-μm Nylon filter, the sample solution was ready for IC and CE. When necessary, the sample solution was appropriately diluted before sample injection. Sample solutions for potentiometric measurements were prepared in a similar way to the above procedure. 25.00 ml of sample solution containing 0.4 g toothpaste was first prepared and an equal volume of the TISAB was added before the determination.

The capillary was first flushed with 0.1 *M* NaOH for 5 min, then with water for 3 min, and finally with buffer for 10 min everyday before starting the CE experiments. Between two successive runs, the capillary was flushed with buffer for 1 min. When not in use, the capillary was flushed with water for about 5 min before being kept in storage.

3. Results and discussion

3.1. Effects of buffer pH and applied voltage on separation

Our previous study has shown that P_1, P_2 and P_3 can be well separated and sensitively detected in ATP–CTAB based electrophoresis buffer at pH 3.5 [21]. So, separation of a standard mixture of P_1, P_2, P_3, cP_3, F^- and MFP was first conducted in ATP–CTAB based electrophoresis buffer at pH 3.5 and at different separation voltages. The electropherograms obtained are shown in Fig. 1a Fig. 1b Fig. 1c. The tested compounds of orthophosphate and polyphosphates were well separated, but the peak pair of F^- and MFP was not sufficiently separated for quantita-

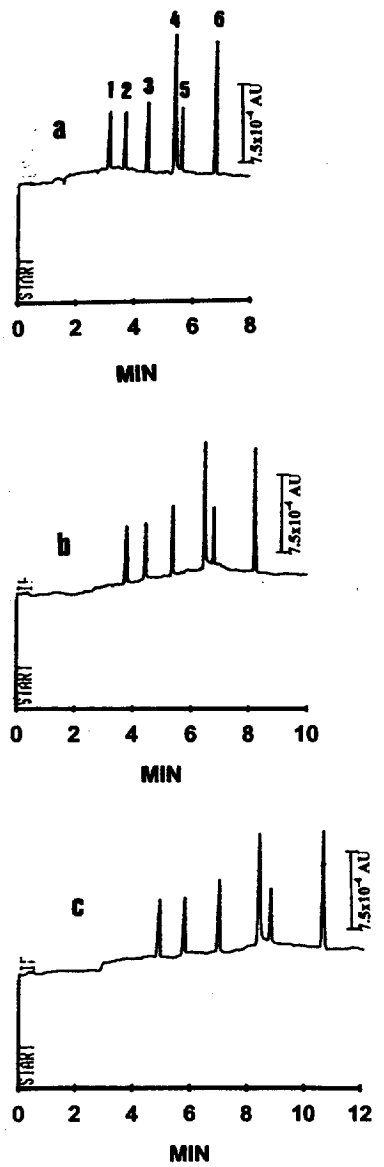

Fig. 1. CE separation of a standard mixture of P_1, P_2, P_3, cP_3, F^- and MFP in an electrophoresis buffer of 5 m*M* ATP–0.02 m*M* CTAB at pH 3.5 and at different voltages. (a) −15 kV; (b) −12.5 kV; (c) −10 kV. Peaks: 1 = cP_3 (28 ppm); 2 = P_3 (25 ppm); 3 = P_2 (17 ppm); 4 = F^- (10 ppm); 5 = MFP (10 ppm); 6 = P_1 (20 ppm). For other experimental conditions see Section 2.

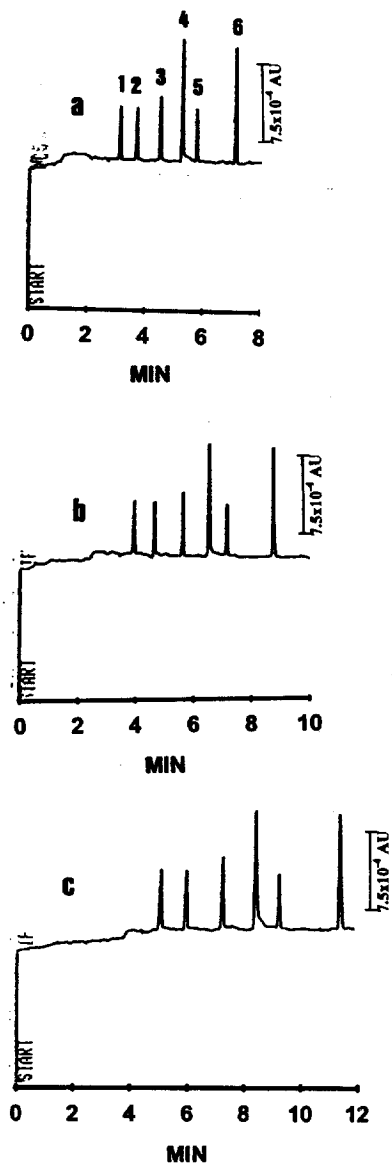

Fig. 2. CE separation of a standard mixture of P_1, P_2, P_3, cP_3, F^- and MFP in an electrophoresis buffer of 5 m*M* ATP–0.02 m*M* CTAB at pH 3.6. (a) −15 kV; (b) −12.5 kV; (c) −10 kV. All other experimental conditions as in Fig. 1.

tion purpose. It was noted that the baseline noise was at lower level in this work than that in the previous study. Such lower baseline noise might be due to the use of capillaries of smaller I.D. and buffers of lower concentrations of ATP and CTAB. The problems of decomposition of ATP and convection of electrophoresis buffer due to Joule heating effect would be alleviated under these conditions. Lower noise levels would be beneficial to an improvement of detection limit. Another advantage of using low concentrations

of ATP and CTAB in the buffer was that precipitation was no longer a problem in preparation and storage of the buffers.

Fluoride ion (F^-) is an anion of a weak acid ($pK_{a1}=3.18$) and monofluorophosphate (MFP) ion is an anion of an acid containing at least one weakly dissociable group ($pK_{a2}=5.12$) [22]. As the two compounds in this standard mixture are partially dissociated at about pH 3.5, it was expected that pH would be an important experimental parameter to be optimised for their separation. Fig. 2a Fig. 2b Fig. 2c show electropherograms obtained under the same conditions as those for Fig. 1 but at pH 3.6. The resolution between the peak pair of F^- and MFP was significantly improved and the resolutions between all adjacent peaks were much greater than unity. The effective mobility of a solute which can dissociate is the weighted sum of the mobilities of all the ionic and non-ionic forms in which the solute can exist at equilibrium. Effective mobility of F^- was increased from $3.77 \cdot 10^{-4}$ $cm^2/V/s$ to $4.03 \cdot 10^{-4}$ $cm^2/V/s$ when pH of the buffer increased from 3.5 to 3.6. Similarly, effective mobility of MFP was increased from $3.62 \cdot 10^{-4}$ $cm^2/V/s$ to $3.65 \cdot 10^{-4}$ $cm^2/V/s$. There were little changes in effective mobilities of the other test compounds with the pH change. The electroosmotic mobility was measured with water peak and it was corrected when the effective mobilities of the test compounds were calculated. pH was the most prominent experimental parameter affecting the resolution of the test compounds through changing the effective mobilities. Buffer of higher pH resulted in co-migration of phosphate and an unidentified anion in the separation of a commercial toothpaste sample.

Voltage was one of the instrumental parameters which could be most conveniently controlled to enhance separation efficiency, especially in a laboratory-built CE system. Fig. 3 shows effect of voltage on separation efficiency and baseline noise level.

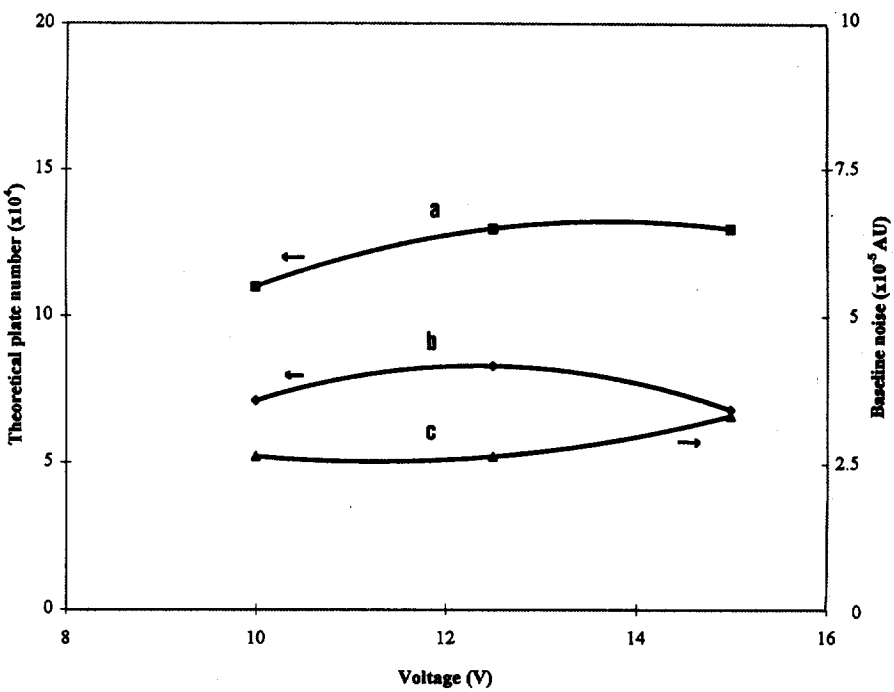

Fig. 3. Effect of applied voltage on separation efficiency and baseline noise. (a) Theoretical plate numbers were measured with MFP at different voltages (refer to ordinate on the left hand side). Injection volume was 1.0 nl and injection length was 0.51 mm. Buffer: 5 m*M* ATP–0.02 m*M* CTAB at pH 3.6. Sample: 34 ppm MFP in buffer. (b) Theoretical plate numbers were measured with MFP (refer to ordinate on the left hand side). Injection volume was 4.1 nl and injection length was 2.1 mm. (c) Baseline noise was measured at different voltages (refer to ordinate on the right hand side).

When injection volume was 1.0 nl, i.e., 0.51 mm injection length, separation efficiency increased with separation voltage although not proportionally. When injection volume increased to 4.1 nl, i.e., 2.1 mm injection length, separation efficiency showed a maximum value at −12.5 kV. It indicated that the separation efficiency was limited by injection volume in the latter case [23].

It was noted that baseline noise started to increase when voltage was higher than −12.5 kV due to Joule heating [24,25] as our CE equipment was operated without a cooling device. It was also noted that poor reproducibility in terms of peak area arose when injention volume was smaller than 4.1 nl with our manually operated laboratory-built CE system. As we know, reproducible sample injection and low baseline noise are essential to quantitative analysis. Separation voltage of −12.5 kV and injection volume of 4.1 nl were chosen for real sample analysis. In addition, it was noted that there was an improvement on the reproducibility of migration times under the chosen experimental conditions. The run-to-run reproducibility of the migration times was at a nearly constant level for all of the test solutes and in a range between 0.5–0.8% (0.67 for cP_3, 0.73 for P_3, 0.68 for P_2, 0.58 for F^-, 0.69 for MFP, 0.63 for P_1) in terms of relative standard deviation (R.S.D.) for triplicate measurements in the present work while the run-to-run reproducibility of the migration times was in a range between 1–2% R.S.D. for most of the test solutes and late migrating peaks showed poorer reproducibility than early ones [21]. These facts might indicate better stability of the ATP–CTAB based electrophoresis buffer under the present experimental conditions, which could be attributed to reduced Joule heating effect as a result of the use of lower buffer concentrations, lower electric field strength and capillaries of smaller diameter. Such a good reproducibility was beneficial to facilitating both peak identification and quantitation.

3.2. Optimization of injection volume for high efficiency separation and sensitive detection

Theoretical studies on the effect of injection volume or injection zone length on CE separation efficiency were conducted with experimental verification [23,26,27]. Nevertheless, few quantitative experimental data in this aspect from an CE system with indirect detection mode were reported. The effect of injection volume was examined to make a reasonable compromise between sensitive detection and high efficiency separation. The results are shown in Fig. 4. For hydrodynamic injection, the volume of sample solution injected by the hydrodynamic flow due to the pressure difference across the capillary is described by the Poiseuille equation:

$$V = \frac{\Delta P \pi d^4 t}{128 \eta L} \quad (1)$$

When using gravity, the pressure difference (ΔP) is determined by the difference in the heights of the surfaces of the liquids in the inlet vial and the outlet vial (ΔH) and the density of the liquid (ρ). The pressure difference (ΔP) can be calculated by the following equation.

$$\Delta P = g \rho \Delta H \quad (2)$$

where g is the acceleration of gravity, approximately being equal to 9.80 m/s^2. In our experiments, a 50.0 cm × 50 μm I.D. capillary was used. The difference in the heights (ΔH) for injection was set at 3.0 cm. Simply assuming that the density and viscosity of the buffer and the sample solution of MFP approximate the values for water at 25°C ($\rho = 997.045$ kg/m^3, $\eta = 0.8903$ cP). The injection volume and injection length for a known injection time can be calculated by using the above equations.

When injection volume was less than 1.0 nl or injection length less than 0.51 mm, it was not a predominant factor affecting separation efficiency. It was indicated by the fact that peak area was proportionally decreased when injection volume was reduced to 0.51 nl, but theoretical plate number remained the same as that with injection volume of 1.0 nl. Once injection volume exceeded the critical value of 1.0 nl, separation efficiency decreased considerably with injection volume increase. Peak area was proportional to the injection volume in the examined injection volume range. An injection volume of 4.1 nl or an injection length of 2.1 mm resulted in about a 35% reduction of theoretical plate number. Separation efficiencies measured through the experiments agreed well with the theoretically predicted ones [27] when injection volume was no

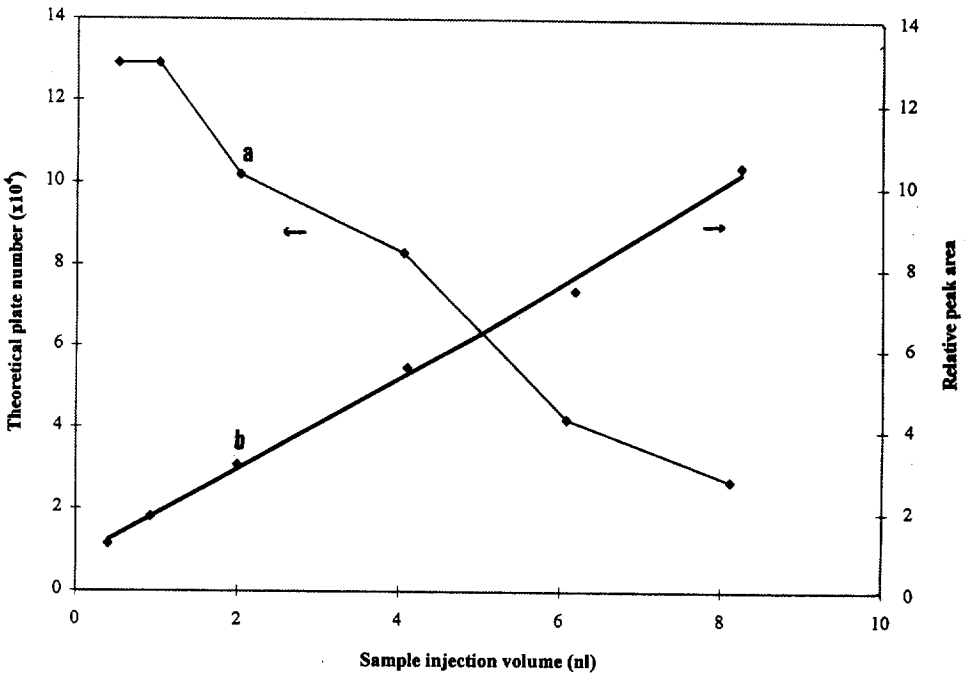

Fig. 4. Effect of injection volume on separation efficiency and relative peak area. (a) Theoretical plate numbers measured with different injection volumes (refer to ordinate on the left hand side). Voltage: −12.5 kV. (b) Relative peak area measured with different injection volumes (refer to ordinate on the right hand side).

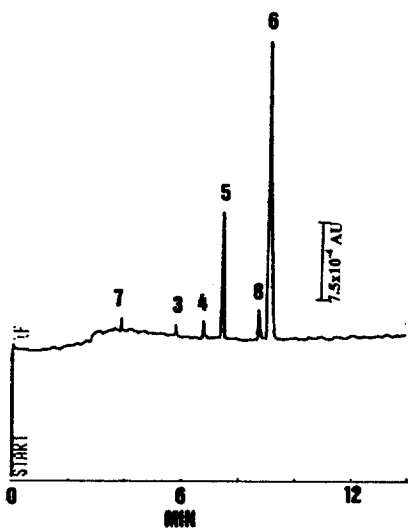

Fig. 5. A typical electropherogram obtained with a sample of commercial toothpaste. Voltage: −12.5 kV. Injection: 40 s at 3.0 cm. Peaks: 3=P_2; 4=F^-; 5=MFP; 6=P_1; 7=SO_4^{2-}; 8=unidentified.

larger than 4.1 nl. An injection volume of 6.1 nl or an injection length of 3.1 mm resulted in about 65% reduction of theoretical plate number. Separation efficiencies measured through the experiments were

Table 1
Results of analysis of fluoride (F^-), monofluorophosphate (MFP), orthophosphate (P_1) and pyrophosphate (P_2) in a commercial toothpaste by CE and other methods

	Amount of fluoride and phosphates (w/w, %)	
	CE (%R.S.D.)[a]	Other methods (%R.S.D.)[a]
F^-	0.019 (4.0)	0.021 (6.0)[c]
MFP	0.39 (2.8)	0.36 (1.7)[d]
P_1	1.3[b] (2.4)	1.4 (1.4)[d]
P_2	0.033 (3.6)	–[e]

[a] The values in parentheses in this table are the relative standard deviations (%) for triplicate measurements.
[b] 3.00 ml of the sample solution was diluted with water to 25.00 ml.
[c] Ion selective electrode (ISE).
[d] Ion chromatography (IC).
[e] Not available.

much lower than the theoretically predicted ones when injection volume was larger than 4.1 nl. For further experiments in this work, injection volumes of 4.1 nl were used. Baseline separation for all of the compounds in the standard mixture and the real sample were still obtained. It was found that such a relatively large injection volume was necessary in our manually operated laboratory-built CE system to obtain reproducibility of peak area of the test compound better than 3% of the relative standard deviation for triplicate measurements. Detection sensitivity or the peak area (the integral response of the detector as a function of time) with injection volume of 4.1 nl was accordingly about 4 times higher than that obtained with injection volume of 1.0 nl. When injection volume was increased to 6.1 nl, reproducibility of the peak area of the test compound better than 2% of the relative standard deviation was

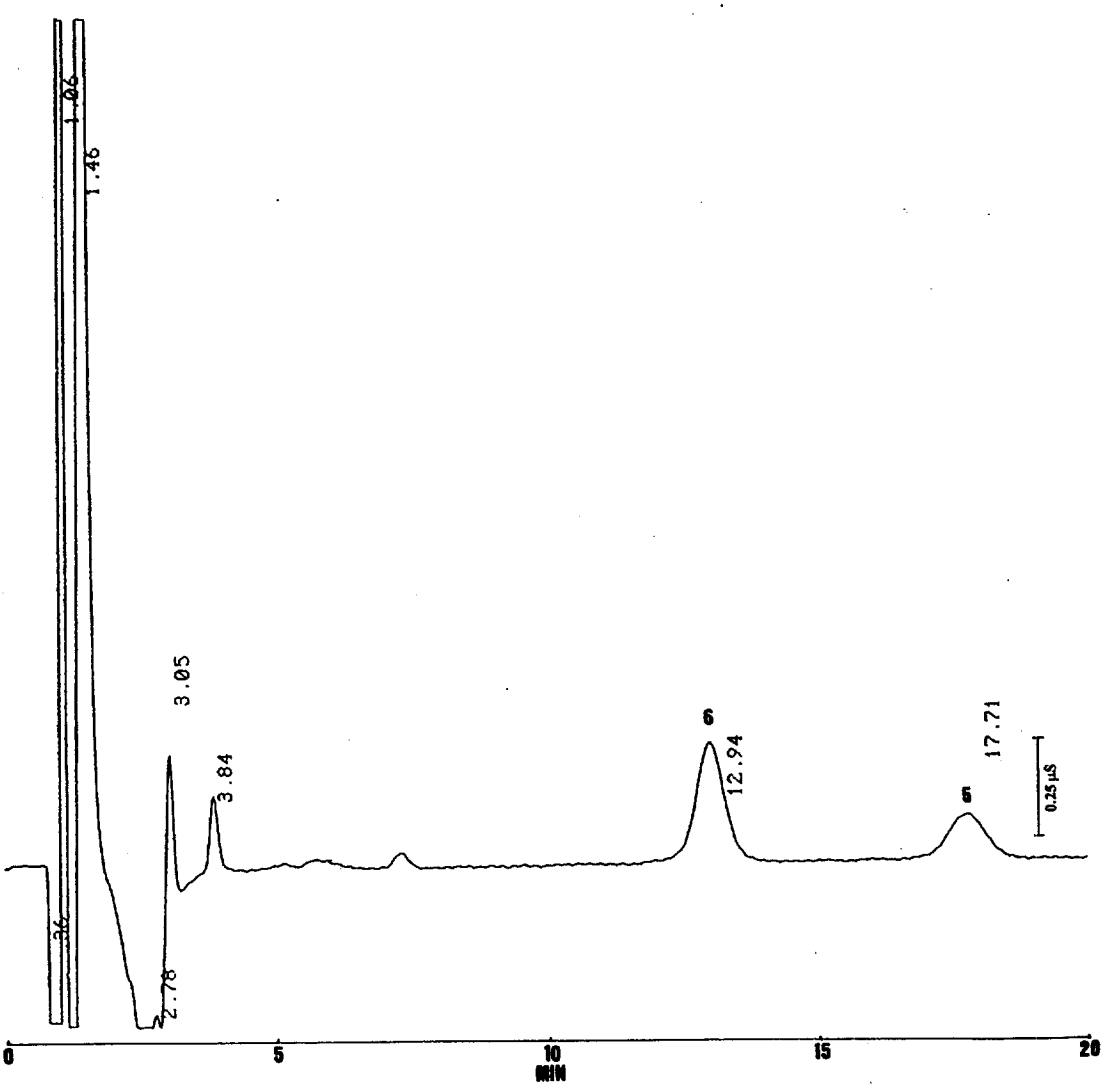

Fig. 6. A typical chromatogram obtained with a sample of commercial toothpaste. For experimental conditions see Section 2. Peaks: 5=MFP; 6=P_1.

achievable. But resolution in real sample analysis was not sufficient for quantitative analysis due to a great loss of separation efficiency.

3.3. Detection limits for the anions

Yeung [28] has shown that in indirect detection, the concentration limit of detection (C_{lim}) can be related to the concentration of background coionic chromophore (C_m), the dynamic reserve (DR) and the transfer ratio (TR) as follows:

$$C_{lim} = \frac{C_m}{DR \times TR} \quad (3)$$

The lower the concentration of background coionic chromophore and the larger the dynamic reserve is, the lower the concentration limit of detection is. In the present work, the dynamic reserve (DR) was calculated to be $2.8 \cdot 10^3$ as ratio of background absorbance to background noise.

Detection limits for cP_3, P_3 and P_2 were found to be $5.0 \cdot 10^{-6}$ *M* and detection limits for F^-, MFP and P_1 to be $2.1 \cdot 10^{-5}$ *M*, $1.0 \cdot 10^{-5}$ *M* and $5.6 \cdot 10^{-6}$ *M*, respectively ($S/N \geq 2$). The detection limits for P_1, P_2 and P_3 in this work were lower than previously reported ones which ranged from $2.0 \cdot 10^{-5}$ to $5.0 \cdot 10^{-5}$ *M* [21].

3.4. Application to the separation and determination of F^-, MFP, P_1 and P_2 in a commercial toothpaste sample

The method developed was applied to the separation and determination of F^-, MFP, P_1 and P_2 ions in a sample of commercial toothpaste. Fig. 5 illustrates a typical electropherogram obtained. Peak identification was carried out by comparing the migration times with those of the standards and by spiking the sample with standards. Table 1 gives quantitative results of the above sample obtained by CE. The CE results are compared with those obtained by other established methods (e.g., ion selective electrode and IC). The CE results generally agree well with the results obtained from the other methods, with comparable precision.

Fig. 6 shows a typical chromatogram of the sample of the commercial toothpaste on an IC-PAK A HR column with borate–gluconate eluent. Fluoride peak was masked by an early eluting "dip" and pyrophosphate was either not yet eluted out within the elution time range or not detected by the conductivity detector.

Based on results shown in Figs. 5 and 6, it was noted that the CE method provided higher efficiencies and shorter analysis time compared with the IC method.

Acknowledgments

The authors thank the National University of Singapore for financial support.

References

[1] J.R. Mellberg and L.W. Ripa, Fluoride in Preventive Dentistry, Chicago, Quintessence, 1983, pp. 215–233.
[2] A.D. Sidi, Caries Res. 23 (1989) 268.
[3] S.A. Leach (Editor), Factors Relating to Demineralisation and Remineraalisation of Teeth, IRL Press, Oxford, 1986.
[4] J.R. Mellberg, I.D. Petrou, R. Fletcher, N. Grote, Caries Res. 25 (1991) 65.
[5] N. Yazo, S. Nakashima, T. Nakazato, N. Ueda, H. Kodama, A. Tateda, Anal. Chem. 64 (1992) 1499.
[6] D. Murawski, J. Chromatogr. 546 (1991) 351.
[7] W.P. Venetz, C. Mangan, I.W. Siddiqi, Anal. Biochem. 191 (1990) 127.
[8] Official Journal of the European Communities, No. L 291 (1983) 37–40.
[9] J.S. Fritz, D.T. Gjerde, C. Pohlandt, Ion Chromatography, Huehtig, Heidelberg, 1982, pp. 69–72.
[10] R.H. Stehl, Anal. Chem. 42 (1970) 1802.
[11] S.F.Y. Li, Capillary Electrophoresis: Priciples, Practice and Applications, Elsevier, Amsterdam, 1992.
[12] C.A. Monning, R.T. Kennedy, Anal. Chem. 66 (1994) 280R.
[13] P. Jandik, W.R. Jones, A. Weston, P.R. Brown, LC·GC 9 (1991) 634.
[14] P.E. Jackson, P.R. Haddad, Trends Anal. Chem. 12 (1993) 231.
[15] W. Buchberger, S.M. Cousines, P.R. Haddad, Trends Anal. Chem. 13 (1994) 313.
[16] W.R. Jones, P. Jandik, J. Chromatogr. 546 (1991) 445.
[17] F.E.P. Mikkers, F.M. Everaerts, T.P.E.M. Verheggen, J. Chromatogr. 169 (1979) 18.
[18] E. Skocir, A. Pecavar, A. Krasnja, M. Prosek, J. High Resolut. Chromatogr. 16 (1993) 243.
[19] A.H. Harakuwe, P.R. Haddad, J. Chromatogr. A 734 (1996) 416.
[20] S.A. Shamsi, N.D. Danielson, Anal. Chem. 67 (1995) 1845.
[21] T. Wang, S.F.Y. Li, J. Chromatogr. A 723 (1996) 197.
[22] J.A. Dean (Editor), Langes Handbook of Chemistry, McGraw-Hill, New York, 13th ed., 1985, pp. 5-14–5-15.

[23] X. Huang, W.F. Coleman, R.N. Zare, J. Chromatogr. 480 (1989) 95.
[24] T. Wang, S.F.Y. Li, J. Chromatogr. A 707 (1995) 343.
[25] F. Steiner, W. Beck, H. Engelhardt, J. Chromatogr. A 738 (1996) 11.
[26] E. Grushka, R.M. McCormick, J. Chromatogr. 471 (1989) 421.
[27] K. Otsuka, S. Terabe, J. Chromatogr. 480 (1989) 91.
[28] E.S. Yeung, Acc. Chem. Res. 22 (1989) 125.