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Modified field amplification sample injection for micellar electrokinetic chromatography of neutral compounds with amino-substituted cyclodextrin as carrier and 1-adamantanecarboxylate as displacer

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Abstract

A modified field amplification sample injection method was proposed and evaluated by using positively mono charged cyclodextrin (CD) as carrier and 1-adamantanecarboxylate as displacer for on-capillary preconcentration of neutral compounds and improvement of the concentration limit of detection in micellar electrokinetic chromatography. In modified sample injection mode a displacer plug was introduced before sample injection to reduce the length of the concentrated sample zone and increase the peak height by slowing down the forward movement of the neutral sample associated with β-CD-NH2 and the backward movement of the neutral sample partitioned in the micelles of sodium dodecyl sulfate. Stability of the inclusion complexes formed between the carrier and the solute was found to be an important factor affecting stacking efficiency in both the conventional field amplification sample injection mode and the modified one. However, further enhancement of the stacking efficiency in the modified mode rested on the relative stability of the displacer–carrier complex to that of the solute–carrier complex. Practical limits to the stacking efficiencies in both modes were discussed as well.

Keywords: Injection methods; Field-enhanced sample stacking; Cyclodextrin; Adamantanecarboxylic acid

1. Introduction

Micellar electrokinetic chromatography (MEKC) has gained popularity in analytical separation of neutral compounds as well as charged ones since it was introduced by Terabe and his coworkers [1] in 1984. Separation in MEKC is based primarily on the partitioning of the solutes between the micellar phase and the aqueous phase. This technique shows advantages of high separation efficiency, short analysis time, easy operation and low reagent and sample consumption.

The main shortcoming of MEKC, which is common to most of other capillary electrophoresis (CE) formats, lies in the high concentration limit of detection, due to small dimension of the capillary, minute volume of sample loaded and poor concentration sensitivity of the UV detector. Development of concentration techniques is of necessity for expanding its applications. On-capillary concentration techniques are of highly preferred since off-line

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concentration techniques are usually tedious and vulnerable to sample loss and contamination.

The simplest and most intensively studied on-capillary concentration approaches to improve the limit of detection in MEKC were those based on stacking [2–8] which was adapted from capillary zone electrophoresis (CZE) [9–11]. Sample stacking arises from abrupt reduction in electrophoretic velocity of samples when crossing the boundary and entering the separation buffer. Thus, more samples can be loaded without compromising high separation efficiency. Extremely large range of enrichment factors were reported by different researchers for different stacking systems. Nevertheless, readers should be cautious about adopting those enrichment factors reported. In practice, the upper limit to the enrichment factor does exist in an on-capillary concentration approach based on stacking. When peak area is concerned, value of the concentration enrichment factor should not be greater than the ratio of total injected amount of the sample to the injected amount of the reference (usually such a ratio would be equal to the zone length of the injected sample for stacking divided by the zone length of the injected reference material) in accordance with material conservation. When peak height is concerned, value of the concentration enrichment factor should not be greater than the ratio of the zone length of the injected sample for stacking to the width of the detector window because signal for any narrower peak will be averaged with respect to the width of the detector window. We prefer to use concentration factor (CF) defined as the ratio of the peak height of the concentrated sample to the reference peak height with sample prepared in the separation buffer and injected in a zone of standard length in hydrodynamic mode.

Neutral compounds cannot be stacked directly since they lack intrinsic mobilities. To facilitate stacking, charged carriers should be introduced to impart electrophoretic mobilities to the neutral compounds. Charged carriers reported are mainly ionic surfactants [2–8,12]. There were two reports on the use of negatively charged cyclodextrin derivatives [13,14]. In the present work, we evaluate a positively charged cyclodextrin derivative, mono(6-amino-6-deoxy)-β-cyclodextrin (β-CD-NH_2), for stacking neutral compounds for MEKC. Especially, we report here for the first time the introduction of a plug of displacer to enhance shortening the zone length of the concentrated neutral compounds at stacking boundary, which consequently improves CF. This approach was demonstrated with the model compounds of 1-naphthalenemethanol (NM1), 1-naphthaleneethanol (NE1) and 2-naphthalenemethanol (NM2).

2. Materials and methods

2.1. Materials and solutions

Sodium dihydrogen phosphate and sodium monohydrogen phosphate were purchased form Fluka (Buchs, Switzerland). Sodium dodecyl sulfate (SDS) and formamide were obtained from Sigma (St Louis, MO, USA). 1-Adamantanecarboxylic acid (AC) and sodium acetate were products of Merck (Darmstadt, Germany). Sudan III was obtained from BDH ((Poole, UK). 1-naphthalenemethanol (NM1), 1-naphthaleneethanol (NE1) and 2-naphthalenemethanol (NM2) were provided by Aldrich (Milwaukee, WI, USA). Mono(6-amino-6-deoxy)-β-cyclodextrin (β-CD-NH_2) was supplied by Cyclolab (Budapest, Hungary). Fused silica capillaries (50 μm I.D.) were products of Polymicro Technologies (Phoenix, AZ, USA). Total length of the capillaries was 65.6 cm, and effective length from the injection end to the detection window was 51.7 cm. Water (≥18 MΩ) used throughout the experiments was supplied by a NANOpure ultrapure water purification system (Barnstead, IA, USA).

Separation buffer of 50 m*M* SDS in 25 m*M* phosphate buffer (pH=7.0) was prepared weekly. A concentration of 100 m*M* 1-adamantanecarboxylate was prepared by dissolving 1-adamantanecarboxylic acid with 500 m*M* sodium hydroxide and then diluting to the required volume. Stock solutions (1.0 mg/ml) of model compounds were prepared in methanol. Sample solutions for injection were made by appropriate dilution of the stocks as specified.

2.2. Instruments

All CE experiments were carried out using the CE-L1 capillary electrophoresis system (CE Re-

sources, Singapore) with a UV–Vis spectrophotometric detector of SPD-10AV (Shimadzu, Kyoto, Japan). Detection was made at 210 nm. Data acquisition and recording of electropherograms were accomplished with a CSW chromatography station (CE Resources). Conductivity was measured with a Conductivity Meter CM-115 (Kyoto Electronics, Japan).

2.3. Procedure for CE experiments

A new capillary was rinsed with 0.1 *M* NaOH for 10 min, and then followed by the run buffer for another 10 min. Sample introduction was made in either electrokinetic or hydrodynamic mode as specified. After sample introduction, 15 kV voltage was applied for separation. When a displacer plug of 1-adamantanecarboxylate was employed, its introduction was accomplished by applying pressure to the solution located at the injection end of the capillaries for a preset time just before sample injection. The CE experiments were carried out at a temperature of 24.5±0.5 °C.

3. Results and discussion

3.1. Basic consideration

Comparing SDS and charged CDs, one readily realizes that the former solubilizes neutral molecules in collective effect but the latter interacts with a neutral molecule individually. Use of negatively charged CD derivatives have been reported for stacking neutral compounds in MEKC [13,14]. Introduction of CDs helps improve solubility of many neutral compounds [14]. Mono(6-amino-6-deoxy)-β-cyclodextrin (β-CD-NH_2) was chosen for this study based on an expectation of least disturbance to electroosmotic flow (EOF) and steric hindrance to solutes [15,16] among positive-charged CDs commercially available. Using positively charged carriers, stacking can be easily performed without requirements on delicately manipulating EOF and switching the power polarity. In addition, such an experimental arrangement, i.e. using β-CD-NH_2 for stacking and SDS for separation, markedly reduced consumption of β-CD-NH_2 which was expensive.

To understand stacking of the neutral compounds in the presence of β-CD-NH_2, we assume that the model compounds form 1:1 inclusion compounds with β-CD-NH_2. The general equation for the equilibrium of the 1:1 complex formation is given by Eq. (1).

$$S + \beta\text{-CD-NH}_2 \quad S\text{-}\beta\text{-CD-NH}_2 \tag{1}$$

in which S refers to a solute and S-β-CD-NH_2 refers to an inclusion complex formed between the solute and the β-CD-NH_2. The apparent stability constant for the above process is denoted by *K* and is defined as:

$$K = [\text{S-}\beta\text{-CD-NH}_2] / ([\text{S}][\beta\text{-CD-NH}_2]) \tag{2}$$

The square brackets indicate corresponding molar concentration terms.

Effective mobilities of the neutral compounds in the presence of β-CD-NH_2 can be represented by Eq. (3):

$$\mu_{\text{eff}} = \mu_{\beta\text{-CD-NH}_2} [\text{S-}\beta\text{-CD-NH}_2]) / ([\text{S}] + [\text{S-}\beta\text{-CD-NH}_2]) \tag{3}$$

where $\mu_{\beta\text{-CD-NH}_2}$ is electrophoretic mobility of β-CD-NH_2. Combining Eq. (2) and Eq. (3), we obtain Eq. (4):

$$\mu_{\text{eff}} = \mu_{\beta\text{-CD-NH}_2} K[\beta\text{-CD-NH}_2] / (1 + K[\beta\text{-CD-NH}_2]) \tag{4}$$

Optimization of CF can be achieved by maximizing the velocity ratio of the neutral compounds moving towards the boundary between the sample zone and the separation buffer to that moving away from the boundary.

3.2. Modified field amplification sample injection

The outlines of the steps involved in field amplification sample injection (FASI) and its modification in the present work can be depicted as Fig. 1. The capillary was first filled with the separation buffer. Then, sample solution containing a low concentration of β-CD-NH_2 and the anode electrode were placed at the injection end of the capillary. Samples were introduced into the capillary in the electrokinetic mode. After the preset injection time, the

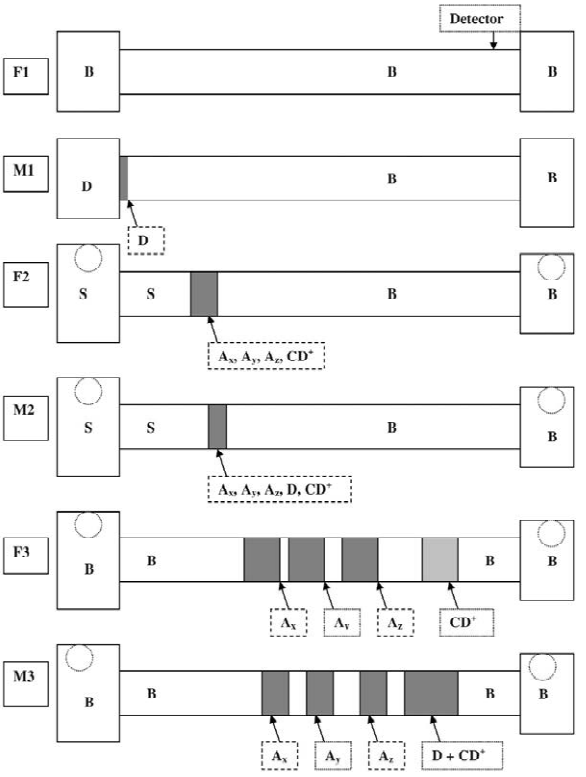


Fig. 1. Schematic illustration of field amplified sample injection (FASI) and modified field amplified sample injection (mFASI). In FASI, F1: before sample injection; F2: during sample injection; F3: Sample separation. B: separation buffer; S: sample solution containing the carrier of β-CD-NH_2, A: model compounds with retention factor in order of $k_{Ax} > k_{Ay} > k_{Az}$; CD^+: β-CD-NH_2. In mFASI, M1: before sample injection; M2: during sample injection; M3: sample separation. D: displacer of 1-adamantanecarboxylate.

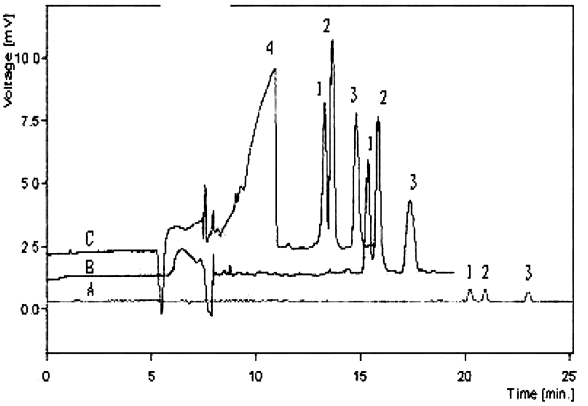


Fig. 2. Typical electropherograms obtained using the model compounds of 1-naphthalenemethanol (NM1), 1-naphthaleneethanol (NE1) and 2-naphthalenemethanol (NM2). The same separation buffer (50 m*M* SDS in 25 m*M* phosphate of pH 7.0) and the high voltage of 15 kV for separation were employed in obtaining Traces A, B and C. Trace A was obtained with the sample (1 ppm each) prepared in the separation buffer and injection made at 0.3 p.s.i. (1 p.s.i. = 6894.76 Pa) for 14 s (equivalent to zone length of 5 mm). Trace B was obtained using field amplified sample injection (FASI). Trace C was obtained using modified field amplified sample injection (mFASI). In both FASI and mFASI modes, the sample solution (1 ppm each) was prepared by diluting the 1 mg/ml stock solution with 4 m*M* β-CD-NH_2 (acidified to pH 5 with acetic acid) and electrokinetic injections of the samples were completed by applying the voltage of 15 kV for 120 s. Peak identification: 1. NM1; 2. NM2; 3. NE1; 4. displacer. Both Trace B and Trace C have been shifted up for clarity.

sample solution was replaced with the separation buffer. Finally, the high voltage was applied for the separation. In modified field amplification sample injection (mFASI), a plug of the displacer of 1-adamantanecarboxylate (AC) was hydrodynamically introduced into the capillary just before sample injection.

Typical electropherograms are shown in Fig. 2 obtained using the model compounds NM1, NM2 and NE1. Trace A in Fig. 2 was obtained with the sample prepared in the separation buffer and injection made at 0.3 p.s.i. (1 p.s.i. = 6894.76 Pa) for 14 s (equivalent to zone length of 5 mm). Trace B was obtained using FASI. It was found that peak heights of NM1, NM2 and NE1 in Trace B were 9.2, 14 and 7.2 times those in Trace A. Trace C was obtained using modified FASI. It was found that the peak heights of NM1, NM2 and NE1 in Trace C were 12, 18 and 13 times those in Trace A. A moderate improvement on CF was achieved in FASI and mFASI. The mFASI was better in terms of CF.

3.3. Effect of stability of inclusion complexes on concentration factor

From Eq. (4), we know the stability of inclusion complex formed between a model compound and β-CD-NH_2 will affect the effective electrophoretic velocity of the model compound and consequently its CF. To understand the different concentration factors for different model compounds shown in Fig. 2, we attempted to measure the apparent stability constants

of the inclusion complexes formed between the model compounds and β-CD-NH_2. Effective mobilities were measured for the model compounds at two concentrations of β-CD-NH_2 at pH 7.0. The corresponding electropherograms are shown in Fig. 3. A reported procedure [17] for calculating the apparent stability constant was adopted. Eq. (4) can be rearranged in terms of effective mobility as in Eq. (5):

$$\mu_{\beta\text{-CD-NH}_2} = \mu_{\text{eff}}\,(1 + K[\beta\text{-CD-NH}_2])\,/\,(K[\beta\text{-CD-NH}_2]) \quad (5)$$

From Eq. (5), one obtains Eq. (6):

$$\mu_{\text{eff1}}\,(1 + K[\beta\text{-CD-NH}_2]_1)/(K[\beta\text{-CD-NH}_2]_1) = \mu_{\text{eff2}}\,(1 + K[\beta\text{-CD-NH}_2]_2)/(K[\beta\text{-CD-NH}_2]_2) \quad (6)$$

K could be solved when effective mobilities were experimentally measured at two concentrations of β-CD-NH_2. The apparent stability constant was determined to be 6.8×10^2 M^{-1} for NM2. The apparent stability constants for NM1 and NE1 were significantly smaller than that for NM2 and could not be accurately determined in the manner above. Nevertheless, from the peak order in Fig. 3 we knew stability increased in the order NE1 < NM1 < NM2. This order was parallel to the order of the peak heights in Trace B and Trace C in the Fig. 2. It indicated that stability of inclusion complexes was a key factor affecting stacking efficiency in the systems investigated.

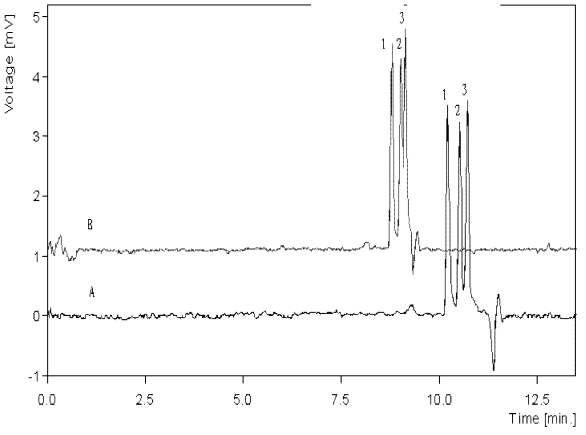


Fig. 3. Electropherograms obtained for evaluating interaction of 1-naphthalenemethanol (NM1), 1-naphthaleneethanol (NE1) and 2-naphthalenemethanol (NM2) with β-CD-NH_2. Trace B: obtained in 4 mM β-CD-NH_2 and 25 mM phosphate (pH = 7.0); Trace A: obtained in 10 mM β-CD-NH_2 and 25 mM phosphate (pH = 7.0). Sample: mixture of NM1, NE1 and NM2 (10 ppm each) in the separation buffer. Peak identification: 1. NM2; 2. NM1; 3. NE1. Trace B has been shifted up for clarity. Other experimental conditions were the same as those for Trace A in Fig. 2.

3.4. Effect of displacer plug on concentration factor

As discussed in Section 3.1, concentration factor is dependent on the effective electrophoretic mobilities in both sample zone and in the separation buffer zone. The effective electrophoretic mobilities for individual model compounds in the sample zone were the same in both the FASI and the mFASI modes. Thus, the different concentration factors resulted from different situation of the concentrated samples in the vicinity of the boundary between the sample zone and the separation buffer zone in the two stacking modes.

In FASI, the front parts of the zones of the concentrated samples were determined by the forward movement of the model compounds due to their interaction with β-CD-NH_2; while the rear parts were determined by the backward movement due to partition in micelles of SDS. The question is still open to us about how much of each contributes to the zone length of the concentrated sample during FASI. The former was strongly dependent on the stability of the inclusion complexes; but the latter on the retention factor (k') which was defined as the molar ratio of the solute incorporated into the micelles to the solute in the aqueous phase [1]. The retention factors were determined, using the procedure described in Ref. [1], to be 4.17, 4.96 and 8.62 respectively for NM1, NM2 and NE1 in the separation buffer. Since the retention factors for these model compounds were not high, the concentration factors (ca. five-fold) obtained for the model compounds were rather low when SDS was used as the carrier in FASI [4].

The displacer plug of 1-adamantanecarboxylate introduced played a role in reducing the zone length

of the concentrated sample in mFASI. On the one hand, the high concentration displacer interacting with β-CD-NH_2 could strongly compete with the model compounds for β-CD-NH_2. The apparent stability constant of the inclusion complex formed by the displacer of 1-adamantanecarboxylate and β-CD-NH_2 was estimated to be in the order of 10^4 M^{-1} [18]. It was about 100 times greater than that of NM2. The forward movement of the model compounds due to interaction with β-CD-NH_2 was slowed down in the displacer plug. In addition, high pH and high conductivity may slow down the forward movement of β-CD-NH_2 and the model compounds too. The conductivities were measured to be $3.1\cdot10^{-4}$ Ω^{-1} cm^{-1}, $4.4\cdot10^{-3}$ Ω^{-1} cm^{-1} and $8.9\cdot10^{-3}$ Ω^{-1} cm^{-1}, respectively for the sample solution, the separation buffer and the displacer solution. On the other hand, the backward movement of the model compounds due to the partition in the micelles of SDS may also slow down in the displacer plug of high conductivity. When the displacer plug was replaced with a sodium acetate plug of high pH, no enhancement in CF was observed compared with the results obtained in FASI. The displacement of 1-adamantanecarboxylate for the model compounds is the essential part for the enhancement of CF in mFASI. Enhancement in CF, i.e. difference in CF for each peak in mFASI and in FASI, was dependent on relative stability of the inclusion complex of displacer-β-CD-NH_2 to the inclusion complex of the solute-β-CD-NH_2, i.e. $K_{\text{displacer-β-CD-NH}_2}/K_{\text{solute-β-CD-NH}_2}$.

Length of the displacer plug was experimentally optimized for enhancement of CF. Fig. 4 shows the resultant peak height versus length of displacer plug. Peak heights at zero length of the displacer plug referred to FASI without modification. There was a general trend that there was one optimal length of the displacer plug for each of the model compounds. The optimal length for NM2 was the longest one. It seemed that the more stable inclusion complex formed by NM2 and β-CD-NH_2 required a longer displacer zone for full displacement of NM2 out of β-CD-NH_2 by the displacer of AC although other interactions might also have an influence on the optimal length of the displacer plug. When length of the displacer plug was shorter than the optimal length, the front part of the zones of the concentrated sample was determined by the forward movement of the model compounds due to their interaction with β-CD-NH_2; while the rear part was determined by the backward movement due to the partition in the micelles of SDS. When the length of the displacer plug was optimal, the part of the zone of the concentrated sample determined by the forward movement of the model compound due to the interaction with β-CD-NH_2 roughly overlapped with the other part determined by the backward movement due to partition in micelles of SDS. When the length of the displacer plug was longer than the optimal length, the front part of the zones of the concentrated sample was determined by the backward movement due to partition in micelles of SDS; while the rear part was determined by the forward movement of the model compounds due to their interaction with β-CD-NH_2.

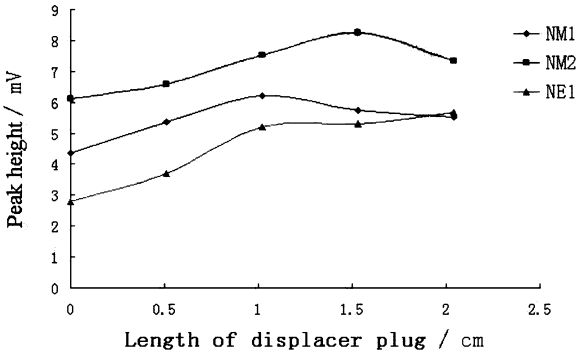
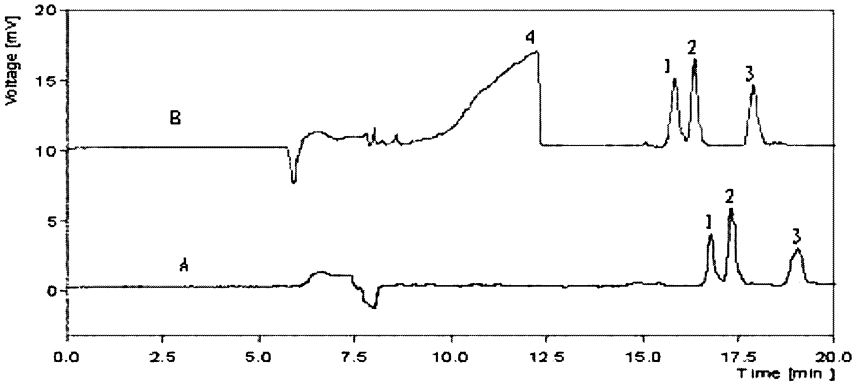


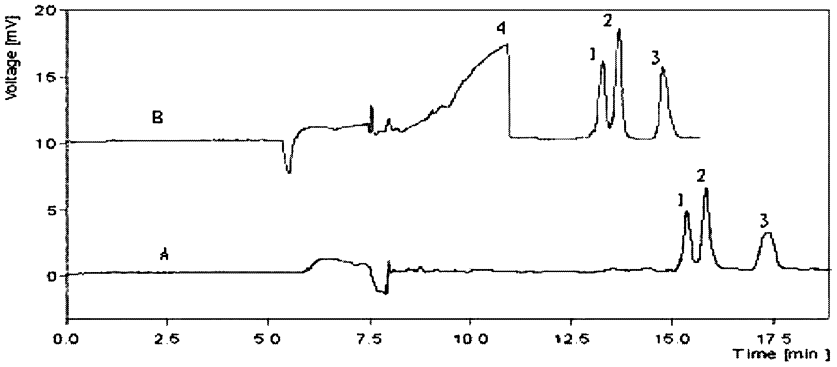
Fig. 4. Effect of length of the displacer plug on peak height. Other experimental conditions were the same as those for Trace B and Trace C in Fig. 2.

3.5. Optimization of injection time

Electropherograms were obtained with different injection time in both FASI and mFASI as shown in Fig. 5. CF increased with injection time duration in a range of 90 s to 150 s. But the separation efficiency and resolution deteriorated with the injection time of 150 s. The reason for the deterioration might be due to strong laminar flow resulting from the mismatch of electroosmotic flow in different regions and the reduced effective capillary length for the separation [9–11]. Thus, injection time of 120 s for mFASI was adopted for the remaining part of this work.



(a)



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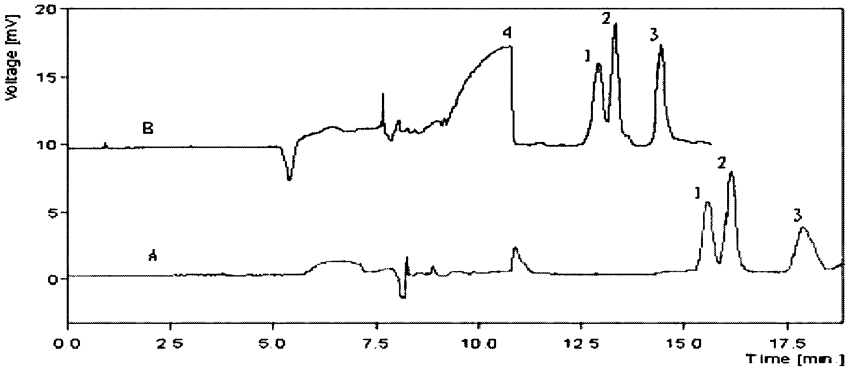

(c)

Fig. 5. Electropherograms were obtained with different injection times in both FASI and mFASI. Trace A: FASI. Trace B: mFASI. Injection time: (a) 90 s; (b) 120 s; (c) 150 s. Peak identification: 1. NM1; 2. NM2; 3. NE1; 4. displacer. Other experimental conditions were the same as those for Trace B and Trace C in Fig. 2.

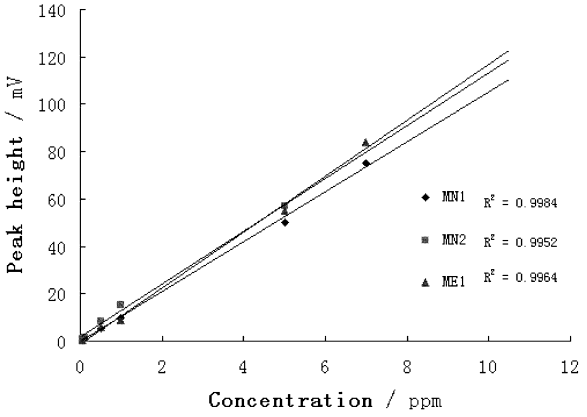

Fig. 6. Dependence of peak height on sample concentration using modified field amplification sample injection (mFASI). Other experimental conditions were the same as those for Trace C in Fig. 2.

3.6. Evaluation of analytical performance of modified field amplification sample injection

The detection limits were 10 ppb for NM2 and 20 ppb for NM1 and NE1 in mFASI. In comparison, the detection limits obtained with samples prepared in the separation buffer in hydrodynamic injection mode were 200 ppb for all the three model compounds. Using the mFASI, the concentration limits of detection were improved by 10 to 20 times in the present work.

The plot of peak height versus sample concentration in mFASI is shown in Fig. 6. The dependence of peak height on the sample concentration showed good linearity in a concentration range of 40 ppb to 7 ppm. The square of correlation coefficients (r^2) for all the three lines were greater than 0.99. Samples of higher concentration than 7 ppm generated hyperbolic plots of the peak height versus the sample concentration. When a sample of the three model compounds (at 40 ppb each) were repeatedly analyzed using mFASI, run-to-run reproducibilities of peak height obtained were 2.4%, 1.9% and 1.0% ($n=5$) for NM1, NM2 and NE1 in terms of the relative standard deviation.

4. Conclusions

A modified field amplification sample injection was proposed and evaluated for improving the detection limit of neutral compounds in micellar electrokinetic chromatography on the basis of using positively mono charged cyclodextrin as carrier and 1-adamantanecarboxylate as displacer. The modified field amplification sample injection moderately further improved the detection limit compared with the field amplification sample injection without the use of the displacer plug. The displacer plug reduced the length of the concentrated sample zone and increased the peak height by slowing down the forward movement of the neutral sample associated with β-CD-NH_2 and the backward movement of the neutral sample partitioned in the micelles of SDS. Stability of the inclusion complexes formed between the carrier and the neutral sample was a key factor for concentration factor in both the field amplification sample injection and modified one. But compared with the field amplification sample injection, the further enhancement of the concentration factor in modified field amplification sample injection was mainly dependent on the relative stability of the displacer–carrier complex to the stability of the neutral solute–carrier complexes, i.e. $K_{\text{displacer-β-CD-NH}_2}/K_{\text{solute-β-CD-NH}_2}$. There was an optimal length of the displacer plug for every solute. The more stable the solute–carrier complex, the longer the optimal displacer plug. The modified field amplification sample injection showed the detection limit being more than 10 times lower for the model compounds compared with that obtained with the sample dissolved in separation buffer in the hydrodynamic injection mode. The method is potentially useful in expanding applications of micellar electrokinetic chromatography.

5. Nomenclature

β-CD-NH_2	mono(6-amino-6-deoxy)-β-cyclodextrin
AC	1-adamantanecarboxylic acid
NM1	1-naphthalenemethanol
NE1	1-naphthaleneethanol
NM2	2-naphthalenemethanol
FASI	field amplification sample injection
mFASI	modified field amplification sample injection
CF	concentration factor

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References

[1] S. Terabe, K. Otsuka, K. Ichihara, A. Tsuchiya, T. Ando, Anal. Chem. 56 (1981) 111.
[2] Z. Liu, P. Sam, S.R. Sirimanne, P.C. McClure, J. Grainger, D.G. Patterson, J. Chromatogr. A 673 (1994) 125.
[3] K.R. Nielsen, J.P. Foley, J. Chromatogr. A 686 (1994) 283.
[4] T. Wang, in: Proceedings of HIT Summer Seminar 95 in Eng. and Sci, 1995, p. 26.
[5] J.P. Quirino, S. Terabe, J. Chromatogr. A 781 (1997) 119.
[6] J.P. Quirino, S. Terabe, J. Chromatogr. A 791 (1997) 255.
[7] J.P. Quirino, S. Terabe, Anal. Chem. 70 (1998) 149.
[8] J. Palmer, N.J. Munro, J.P. Landers, Anal. Chem. 71 (1999) 1679.
[9] R.-L. Chien, D.S. Burgi, Anal. Chem. 63 (1991) 2042.
[10] R.-L. Chien, D.S. Burgi, J. Chromatogr. 559 (1991) 141.
[11] R.-L. Chien, D.S. Burgi, Anal. Chem. 64 (1992) 489A.
[12] J.B. Kim, J.P. Quirino, K. Otsuka, S. Terabe, J. Chromatogr. A 916 (2001) 123.
[13] J.P. Quirino, S. Terabe, K. Otsuka, J.B. Vincent, G. Vigh, J. Chromatogr. A 838 (1999) 3.
[14] N.J. Munro, J. Palmer, A.M. Stalcup, J.P. Landers, J. Chromatogr. B 731 (1999) 369.
[15] R. Ivanyi, L. Jicsinszky, Z. Juvancz, Chromatographia 53 (2001) 166.
[16] F. Lelievre, P. Gareil, A. Jardy, Anal. Chem. 69 (1997) 385.
[17] F. Lelievre, P. Gareil, J. Chromatogr. A 735 (1996) 311.
[18] E.-S. Kwak, F.A. Gomez, Chromatographia 43 (1996) 659.