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Research Article

Fast CEC-MS using poly(dimethylsiloxane) microinjector, short packed column, and low-sheath-flow interface

A fast CEC-MS approach based on a microinjector and a short CEC column was developed. Poly(dimethylsiloxane) was used as the substrate for microinjector fabrication. A short capillary column (~5 cm) packed with 5 μm octadecyl silica particles was inserted into the microinjector. The microinjector CEC device was interfaced to ESI-MS using a low-flow sheath liquid interface. The device delivers the advantages of sample introduction, pre-concentration, elution, and fast analysis as in chip-CEC yet avoids the difficulty of packing stationary material into the chip. The online pre-concentration and CEC-MS analysis capabilities of this device were demonstrated by analysis of a six-triazine mixture. A signal enhancement of 20–99-fold was achieved with a sample loading time of 180 s.

Keywords: CEC-MS / Low-sheath-flow interface / Online pre-concentration / Packed CEC / PDMS
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1 Introduction

Capillary electrochromatography (CEC), which combines the high separation efficiency of capillary electrophoresis (CE) and the high selectivity of high-performance liquid chromatography (HPLC), has been a powerful analytical tool in separation science. In the recent years, CEC has been extended to a microchip format to have a rapid and sensitive analysis. Using in situ stationary phase synthesis methods, both monolithic CEC [1–6] and open-tubular CEC (OT-CEC) [7–11] have been demonstrated in microchips. Unfortunately, OT-CEC suffers from limited sample capacity. Although monolithic CEC has an expanded sample capacity, extensive trial-and-error optimization is needed to sort out the proper conditions for polymerization.

Likewise, packed CEC has also been widely used [12]. A clear advantage of packed CEC is its potential to utilize a large variety of high-quality stationary phases, which are already available for HPLC. However, in contrast to column-based packed CEC, chip-based packed CEC has faced the great challenge of introducing a stationary phase into the chip and the difficulty of fabricating a sintered frit into the channel. Despite the difficulties, several groups have succeeded in the packing of ODS particles into a chip, although these packing approaches were in general not so effortless [13–16].

While several methods of detection can be used with CEC, mass spectrometry (MS) is an increasingly popular choice owing to its high sensitivity and high specificity [17]. The additional mass dimension is quite useful for the analysis of complex mixtures, as it is possible to separate the analytes from interfering compounds in unresolved peaks based on *m*/*z* values. Unlike column-based CEC-MS system, the coupling of CEC chip with MS is not a simple task because it is difficult to fabricate and connect an ESI sprayer to a CEC chip. An integrated approach has been published on a chip-based monolithic CEC with ESI-MS [4]. Nevertheless, the microfabrication process was complicated and required expensive equipment for the fabrication [18].

An alternative to chip-based packed CEC-MS is the use of a short packed CEC column coupled to MS. However, it is difficult to be achieved using typical CEC-MS instruments because a minimum CEC column length of ~27–40 cm (depending on the setup) was needed for bending and insertion the column tips into the sample vial and CEC-MS interface. By using an in-house constructed valve, Walhagen et al. have reported a valve-integrated CEC-MS interface [19] and that a CEC column of 15 cm length could be successfully employed.

In this study, a new approach for fast CEC-MS analysis is proposed. By incorporating a 5-cm fritless packed CEC column into a polydimethylsiloxane (PDMS) microinjector, a simple short column CEC-MS device is presented. The microinjector packed CEC column device was interfaced to ESI-MS using a flat low-sheath-flow interface [20]. With the proposed approach, the difficulties of packing commercial stationary phase into the chip and the fabrication of chip-CEC-MS interface were alleviated.

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Abbreviations: ODS, octadecyl silica; **PMMA**, poly(methyl methacrylate); **PC**, polycarbonate; **PEEK**, polyether ether ketone; **SEF**, signal enhancement factor

Triazine, a common herbicide for weed control, has been a great concern in the environment and water control. Triazines analysis using LC [21, 22], CE [23–26], and CEC [27] coupled to MS have been reported. In this study, low-level triazines were selected to perform the pre-concentration and separation behavior on our device.

2 Materials and methods

2.1 Chemicals

PDMS prepolymer was purchased from Dow Corning (Sylgard 184, Midland, MI, USA). Poly(methyl methacrylate) (PMMA) plates were obtained from Chi Mei (Tainan, Taiwan). Ammonium acetate was obtained from Wako (Osaka, Japan), and 48% HF was obtained from Sigma-Aldrich Chemical (St. Louis, MO, USA). Methanol, acetonitrile, and acetic acid of HPLC grade were purchased from J. T. Baker (Phillipsburg, NJ, USA). Simazine, atrazine, ametryn, prometon, propazine, and simetryn were obtained from Supelco (Bellefonte PA, USA). Deionized water (Milli-Q Water System, Millipore, Bedford, MA, USA) was used for the preparation of the samples and buffer solutions. The C18 stationary phase (5 μm, 100-Å pore size) was purchased from Macherey-Nagel (Düren, Germany).

2.2 Preparation of a fritless 5 cm packed CEC capillary column

To prepare a short (~5 cm) packed CEC capillary column, a fused-silica capillary column (~10 cm) of 50 μm id, 365 μm od (Polymicro Technologies, Phoenix, AZ, USA) was drawn manually using a vertically suspended section of capillary to which a small weight (45 g) had been attached. The capillary was slowly heated to the melting stage using a butane/oxygen micro-torch (Pro-Iroda Industries, Taiwan) and then quickly withdrawn. A tip of ~10 μm id was obtained by removing the end of the tip using a ceramic cutter aided by visual inspection with a microscope. This tapered tip was etched in 48% HF for the duration to make the dimension of the tip about 25 μm od and 15 μm id.

The tapered (~15 μm id, 25 μm od) capillary column (~10 cm) was then mounted on a homemade pressure vessel that served as a packing reservoir. A slurry of 2 mg, 5 μm ODS in 1 mL methanol was sonicated for 5 min to prevent aggregation of particles and subsequently transferred into the reservoir. The pressure vessel was connected to a nitrogen cylinder. Once the high pressure nitrogen (1500 psi) was provided, the ODS particles were pumped into the capillary and retained in the tapered column. After packing to 5 cm, the nitrogen was turned off and the packed CEC column was quickly pulled out from the vessel. Because the packing material could be loosen during this procedure, the column was then flushed with methanol at 500 psi pressure for 5 min.

2.3 The fabrication of a PDMS-based microinjector

To construct a PDMS microinjector, the method reported by Bergquist et al. [28] was modified and utilized in this study. In comparison with the design reported by Bergquist et al., a 50-μm id instead of a 180-μm id channel was used as the injection and waste channel to minimize the Joule heating effect during electrokinetic injection. In addition, a 30-μm id channel instead of a 50-μm id channel was used for connecting to a CEC column to prevent the negatively charged packing material moving back to the microinjector. A PMMA mold is shown in Fig. 1. Two pairs of 1.7 mm holes were drilled into the sidewalls of the mold. Tungsten wires with an od of 50 and 30 μm (S.I.S., Ringoes, NJ) were inserted into two 100 μm id × 375 μm od and two 50 μm id × 375 μm od fused-silica capillaries, respectively. The polyimide at the head of a capillary corresponding to channel e (Fig. 1) was removed by a flame to reduce the size from 375 to 365 μm id. Each capillary was further inserted into a 1/16-in. PEEK tubing, with an id of 400 μm. Finally, two such arrangements were fitted into the mold in a two-leveled cross structure as illustrated in Fig. 1. To ensure that two tungsten wires could contact to each other for making a cross section, the holes for the lower channel were positioned 0.4 mm above the holes for the upper channel. The position of the peek tubings was adjusted to provide the desired channel lengths ($a = 3$ mm, $b = 2$ mm, $c = 3$ mm, $d = 1$ mm). Channel e (1.5 mm in length, 365 μm id) was fabricated for the insertion of a packed CEC column. PDMS prepolymer was mixed with its curing agent in the volume ratio of 9:1 and then degassed for 30 min. The PDMS prepolymer was then poured into the mold, covering the wires and PEEK tubings. The microinjector was cured at 70°C for 48 h to reduce unpolymerized material. After curing, the wires, capillaries, and PEEK tubings were removed. The large channels (1.6 mm id, 1.5 cm in length) formed by PEEK tubings were served as buffer vials. The PDMS microinjector was ready for coupling

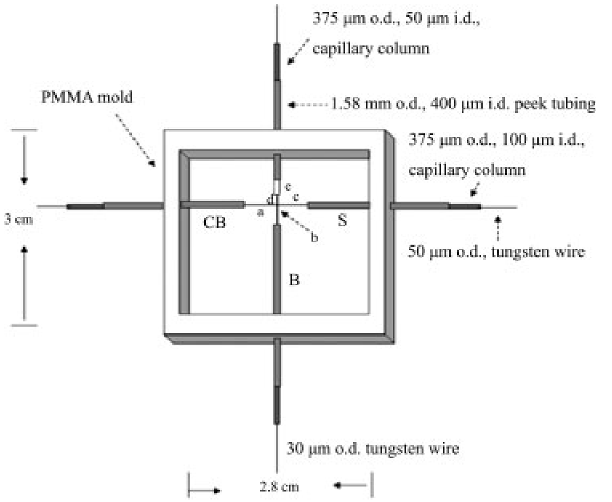

Figure 1. Schematic diagram of the PMMA mold for microinjector.

to a fritless CEC column that could be directly inserted into channel e. Two reservoirs of the upper channel served as a condition buffer vial (CB) and a sample vial (S), respectively. The reservoir of the lower channel served as a separation buffer vial (B).

2.4 CEC-MS interface

A flat low-sheath-flow interface was fabricated using the method described by Li et al. [20]. Briefly, the interface consisted of a PMMA-based sheath liquid reservoir (10 mm × 1.5 mm × 2 mm), an ESI sprayer, and a PMMA plate (1 mm × 30 mm × 60 mm). The liquid reservoir was created using a 3-mm od driller to a depth of ∼1 cm. Two channels of different dimensions were created across the liquid reservoir. The larger channel (∼870 μm id) was used for the insertion of an ESI sprayer, a 2 cm × 700 μm id × 860 μm od fused-silica capillary (Polymicro Technologies, Phoenix, AZ) with a tapered tip of ∼15 μm orifice. The smaller channel (∼400 μm id) was drilled for insertion of the CEC column.

2.5 CEC-MS operation

Ammonium acetate buffer solutions (20 mM) were prepared with two different ACN concentrations (30 and 90% v/v). The pH of each solution was adjusted to 7.0. The buffer with 30% ACN was used as the CB and the buffer with 90% ACN was used as the CEC separation buffer. Sample solutions were prepared in the CB. The sheath liquid consisted of methanol, water, and formic acid (50/50/1, v/v/v). The experimental configuration is shown in Fig. 2. A platinum electrode was inserted into each reservoir for electrical contact. The CEC voltage was supplied by two high-voltage power supplies (CZE1000R and CZE2000, Spellman, Hauppauge, NY, USA) and the ESI voltage was supplied by the LTQ mass spectrometer. All high-voltage control was carried out using a high-voltage relay arrangement through an in-house-written LabVIEW^{TM} program (National Instruments, TX, USA). For CEC experiments without pre-concentration, the sample was injected electrokinetically into the column with 3 kV applied from reservoir S to SL for 5 s, with reservoirs B and CB floated. The sample was then eluted with 3.5 kV applied from reservoir B to SL and detected by MS, with reservoirs S and CB floated. For online pre-concentration CEC experiments, four steps were performed. Briefly, the CB (30% ACN in 20 mM ammonium acetate) was introduced with 3 kV applied from reservoir CB to SL for 30 s, with reservoirs B and S floated. Then sample was then loaded onto the CEC column with 3 kV applied from reservoir S to SL for a specified time (10–180 s), with reservoirs B and CB floated. The CB was introduced again with 3 kV to wash the remaining sample within channel e onto the CEC column, with reservoirs B and S floated. Sample retained on ODS particles was finally eluted by the separation buffer (90% ACN in 20 mM ammonium acetate) with 3.5 kV applied from reservoir B to SL and detected by MS.

All MS experiments were conducted on an LTQ linear ion-trap mass spectrometer (Finnigan MAT, San Jose, CA), and data were acquired in a full scan mode (m/z 100–400). The microinjector short column device was mounted on the nanoelectrospray source (Finnigan MAT, San Jose, CA). The position of the interface was adjusted via the micrometer screws of a XYZ stage. A nebulizing gas was not necessary, and the heated capillary was kept at a temperature of 250°C.

3 Results and discussion

3.1 PDMS-based microinjector

A chip-based microinjector was used to provide automatic sample injection and to facilitate the setup a flat CEC-MS

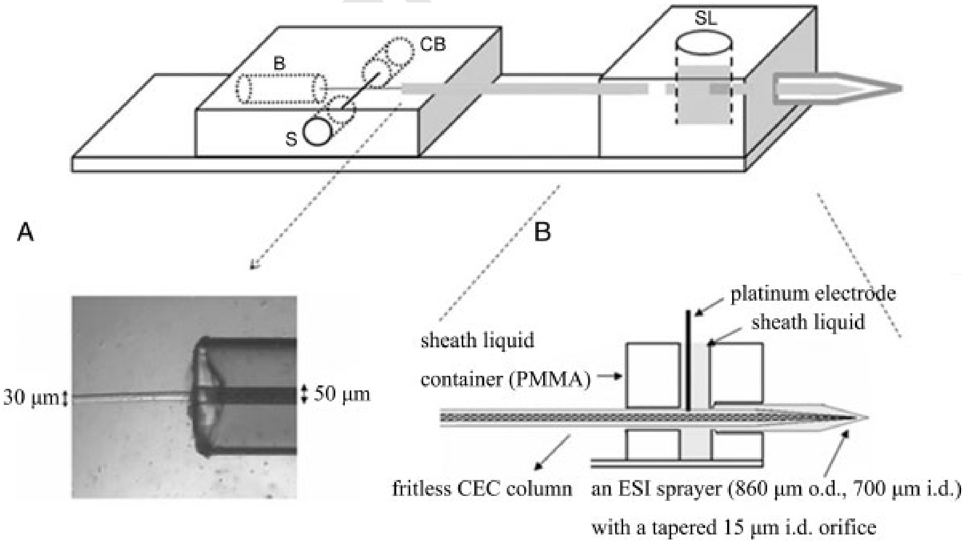

Figure 2. Schematic diagram of the chip-based short column CEC-MS interface. (A) The connection between the PDMS microinjector and the packed column. (B) The flat low-sheath-flow interface. Reservoirs: S, sample; B, separation buffer; CB, condition buffer; SL, sheath liquid.

device where no bending is needed for inserting the column inlet end into the sample vial, thus shortening the minimum column length for fast CEC-MS operation.

The major reason of choosing PDMS instead of other polymeric materials to fabricate the microinjector was the elastic property of PDMS. Because of the elastic property of PDMS, a column can be sealed to the microinjector by inserting the column into a hole, which is slightly smaller than the od of the column. Therefore, the diameter of channel e (Fig. 1) was set to 365 μm to seal a 375 μm od CEC column. Because no sealant was required, column blocking during the application of sealant was eliminated.

To fabricate a PDMS microinjector, a PMMA mold was constructed (Fig. 1) as described in Section 2. The use of PDMS for microinjector fabrication provides two other benefits. First, because the cross section made by the two contacted tungsten wires was surrounded by PDMS prepolymer before polymerization, bonding and alignment of a top plate with a bottom plate as in PMMA chips were not necessary. Second, because no master was used, a clean room and fabrication facilities were not needed, making the method more broadly accessible.

One problem of packed CEC is the difficulty of making a frit in the column end to retain the stationary phase. To avoid this problem, a fritless single-tapered CEC column was used in this study. As a result, the manufacturing of the packed column is simple and there is no concern for bubble formation from the frit. In order to reduce the possibility that the negatively charged particles might flow out of the column under the electric field [29], channels b and d were both set to 30 μm diameter which was smaller than the id of the packed column (50 μm). CEC-MS analysis was performed continuously for 2 h and no particles were observed inside the microinjector, suggesting that the particles were successfully retained in the fritless single-tapered CEC column.

3.2 CEC-MS interface

For a tapered CEC column, a sheathless approach would be a convenient choice because the tapered tip could act both as a restrictor during column packing and as a sprayer during CEC-MS analysis. However, sheathless approaches have the problem of requiring a solution that is optimized both for sample elution and electrospray ionization. In addition, unlike the sheathless CE-MS, it is much more difficult to repair a sheathless CEC-MS sprayer once the conductive coating peels off from the tip. Consequently, once the conductive coating peels off from the tip, it is difficult to recoat the tip of a packed CEC column. To alleviate these problems, a low-sheath-flow instead of a sheathless interface was adopted in this microinjector packed CEC device. The dead volume was minimized because it is possible to insert the tapered column into the very end of the sprayer (Fig. 2B).

3.3 Online pre-concentration and CEC analysis of triazines

In comparison with CE, one advantage of CEC is the ease of online pre-concentration before CEC analysis because the stationary phase can also act as a solid-phase extractor. The effectiveness of on-column pre-concentration in regular packed CEC-UV has been reported [30, 31]. The sample was bound to ODS stationary phase with the non-eluting solvent, and then eluted with a mobile phase of high eluting strength. To evaluate the utility of the microinjector short column CEC-MS, feasibility for the analysis of low concentration triazines was investigated.

In CEC-MS analysis without pre-concentration step, triazines (10 ppm) were injected into the packed column by EOF ($\sim 4.6\times10^{-5}\,cm^2\,V^{-1}\,s^{-1}$ measured by current monitoring method [32]) for 5 s. The separation was conducted by applying a mobile phase (90% acetonitrile in acetate buffer). As shown in Fig. 3, the six-triazine mixture was partially separated within 4 min and had peak widths at half-height

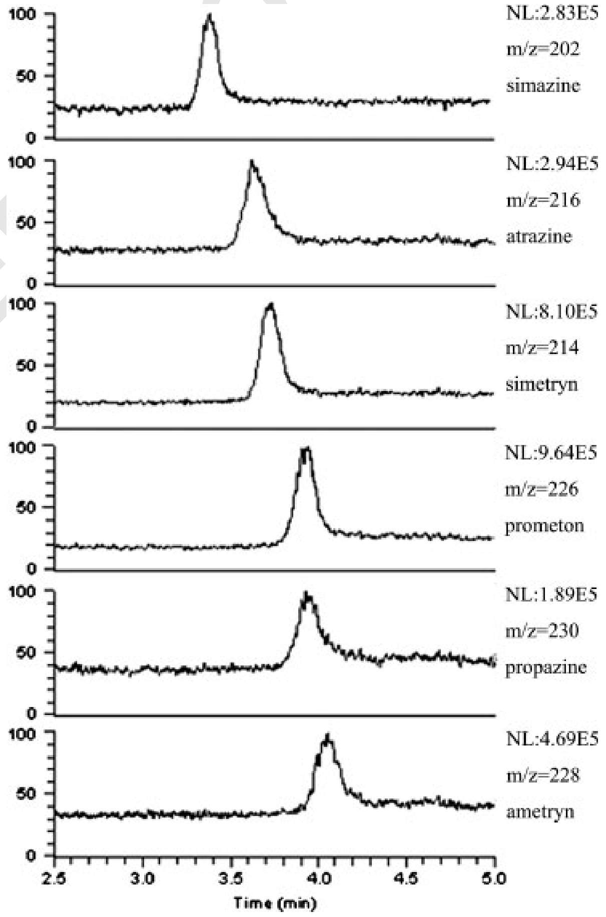

Figure 3. Mass electrochromatograms of a 10-ppm six-triazine mixture for CEC-MS experiment (5 s injection). Sample buffer: 20 mM ammonium acetate in ACN/H_2O (30:70 v/v), pH 7.0. Separation buffer: 20 mM ammonium acetate in ACN/H_2O (90:10 v/v), pH 7.0. Sheath liquid: methanol/water/formic acid (50:50:1 v/v/v).

($W_{1/2}$) ranging from 6 to 10 s. The theoretical plates of the six peaks ranged from 88 000 to 93 000 plates/m. The run-to-run RSDs ($n = 3$) and the column-to-column RSDs ($n = 3$) of the retention times for a triazine mixture were found in the range of 5–6 and 9–12%, respectively. The run-to-run RSDs ($n = 3$) and the column-to-column RSDs ($n = 3$) of the peak areas were found in the range of 8–11 and 13–23%, respectively.

In CEC-MS with pre-concentration, 50 ppb triazines was injected for 180 s with the non-eluting solvent under the EOF of ~$4.0 \times 10^{-5}\,cm^2\,V^{-1}\,s^{-1}$. The pH during loading step was adjusted to 7.0 and makes triazines neutral [33]. Under this condition, only the hydrophobic interaction could contribute to the pre-concentration process. After the washing step, the sample was eluted using eluting buffers. As shown in Fig. 4, five triazines could be detected, and no significant effect on $W_{1/2}$ was observed. The observed increases in migration times probably resulted from the evaporation of ACN over the course of the enrichment step [34]. The comparisons between pre-concentration and without pre-concentration were summarized in Table 1. The results illustrated that in comparison with the injection without pre-concentration, the analytes were effectively trapped onto the CEC column. The peak area ratios ranged from 0.1 to 0.5 and approached to the theoretical ratio of ~0.16. The theoretical ratio of sample amounts was calculated based on sample concentrations, EOFs, and injection times between the two conditions $((0.05 \times 4.0 \times 10^{-5} \times 180)/(10 \times 4.6 \times 10^{-5} \times 5))$. To further characterize the enrichment performance of the CEC-MS system, a signal enhancement factor (SEF) was calculated using the following equation:

$$\mathrm{SEF} = \frac{A/C}{A_0/C_0} \quad (1)$$

where A and A_0 are the peak areas of the sample under the pre-concentration and normal CEC conditions, respectively; C and C_0 are the concentrations of the sample solutions used in the pre-concentration and normal CEC experiments, respectively. Table 1 shows that the SEF values for each compound varied from 20 to 99 after the enrichment step. To evaluate the repeatability of the separation performance after the pre-concentration step, repeated analyses of the triazine

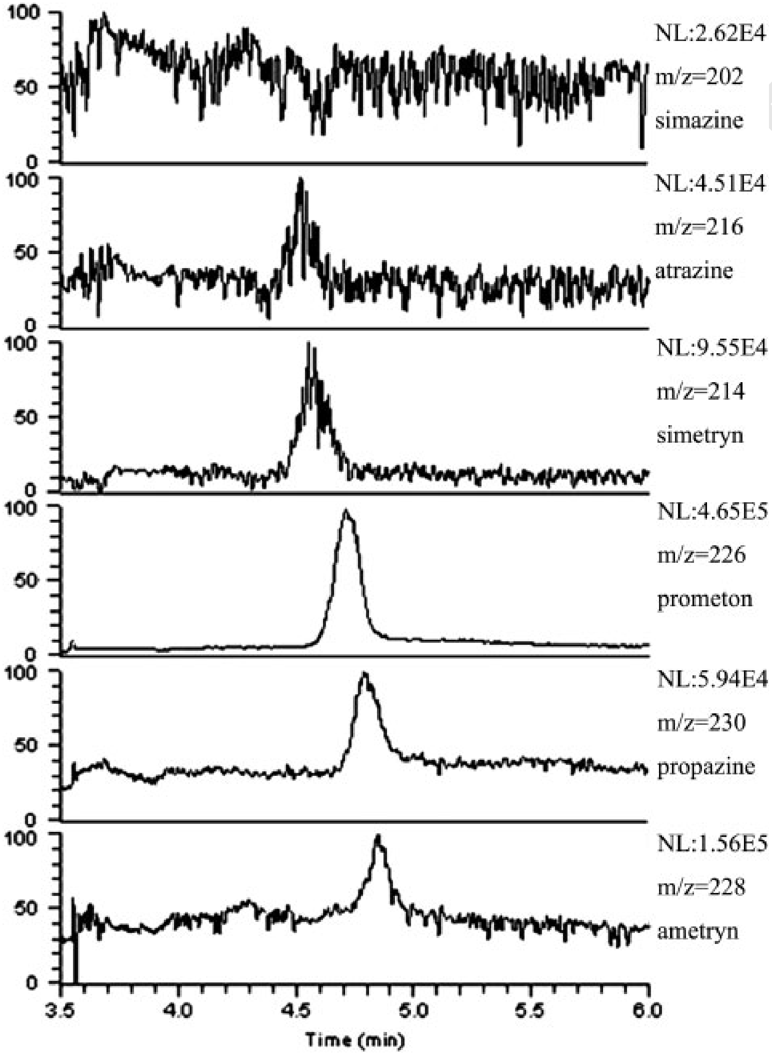

Figure 4. Mass electrochromatograms of a 50-ppb six-triazine mixture. Sample injection time: 180s. All conditions were the same as shown in Fig. 3.

Table 1. Peak areas and SEF values of triazines obtained from the CEC-MS analysis (10 ppm for 5 s) and the online preconcentration CEC-MS analysis (50 ppb for 180 s)

	Peak area		A/A_0	SEF
	10 ppm 5 s (A_0)	50 ppb 180 s (A)	0.16[b]	
Simazine	1 465 147	n.d.[a]	n/a	n/a
Atrazine	1 786 921	217 388	0.12	24
Simetryn	5 208 690	528 622	0.10	20
Prometon	6 048 317	3 006 933	0.50	99
Propazine	1 104 190	250 008	0.23	45
Ametryn	2 434 291	595 900	0.24	49

a) Not detected.
b) Theoretical ratios of sample loading amounts.

mixtures (500 ppb with the injection time of 90 s) were performed. The relative standard deviations of the migration times and the numbers of theoretical plates were in the range of 4–5 and 7–13% ($n = 3$), respectively.

4 Concluding remarks

A fast CEC-MS device based on a PDMS microinjector and a fritless short packed CEC column was developed. By using a PMMA mold and a short CEC column, a simple, inexpensive, and integrated chip-based CEC-MS device was easily fabricated. This approach provided an alternative to chip-CEC-MS analysis as good selectivity, good sensitivity, and a rapid analysis was achieved without complicated chip fabrication or operating procedures. The feasibility of online pre-concentration and separation was demonstrated by the analysis of low concentration trazines. The SEF was found to be 20–99 using a 180-s sample injection. The success of the fast CEC-MS platform suggests that the microinjector-based CEC-MS approach has the potential to be applied to other low-level compounds for pre-concentration and CEC-MS analysis.

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The authors have declared no conflict of interest.

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