J Appl Electrochem (2014) 44:1393–1399
DOI 10.1007/s10800-014-0764-1

RESEARCH ARTICLE

A comparative study of different microchips for capillary electrophoresis with electrochemical detection

Eustaquio M. Erro · Patricia I. Ortiz

Received: 1 August 2014 / Accepted: 26 September 2014 / Published online: 1 October 2014

Abstract This work describes a comparison of the performance of different microchip configuration for microchip capillary electrophoresis with electrochemical detection. Two electrodes gold and multistrand carbon fibers and two microchip construction materials polydimethylsiloxane/polydimethylsiloxane (PDMS/PDMS) and polydimethylsiloxane/glass hybrid (PDMS/glass) were analyzed. The electrode is integrated into the microchip for in-channel triple pulse amperometric detection. Two different mixtures were analyzed (i.e., paracetamol (PA)-4-aminophenol (4-AP) and Dopamine (DO)-Dopac) to demonstrate the electrode and microchips performance. Other variables, such as injection and separation potentials, buffer pH, surfactants addition and injection time, were also analyzed. Hydrodynamic voltammograms were used to select working potential values, and +0.9 V for PA and 4-AP and +0.8 V for DO and dopac were chosen. The migration potential was modified in the 1,500–2,500 V range, and the employed value depends on the microchip materials. The separation process was tested by analyzing the current and migration time variation coefficients. The experimental results demonstrated that the hybrid PDMS/glass microchip with a carbon fiber electrode exhibited a better performance for both samples analyzed.

Keywords Microchip capillary electrophoresis · Gold and carbon fiber electrode · PDMS/PDMS and PDMS/glass microchip · Triple pulse amperometric detection

E. M. Erro · P. I. Ortiz (✉)
INFIQC-CONICET, Departamento de Fisicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, X5000HUA Córdoba, Argentina
e-mail: portiz@fcq.unc.edu.ar

1 Introduction

The technology of microfluidics has experienced explosive growth after its debut in the 1990s. Currently, microfluidics are being employed in chemical, biological, and medical research areas and exhibit great potential in miniaturized, portable, and low-cost commercial devices [1–3]. A significant feature of microfluidics is that the material of the device dominates its functions. Therefore, to achieve certain functions, special attention should be paid to choosing the right material for the device because it endows the inherent property of the device and determines the applicable microfabrication approaches. In the past two decades, various materials have been introduced in microfluidics, and there are some excellent reviews on specific technologies with certain materials [4–6].

Electrochemical detection is becoming one of the most popular detection methods for microchip analyses due to its high sensitivity, ease of miniaturization and integration [7, 8]. Electrochemical detection was first integrated with electrophoresis microchips, and microelectrodes were fabricated on glass substrates using standard photolithographic techniques [9]. While glass is still commonly used as a substrate material for microelectrodes, polymers have received much attention because they are biocompatible, inexpensive and suitable for making disposable microchips. Microchips capillary electrophoresis CE devices have been constructed with different materials, such as glass, quartz [10, 11] and polymers, such as PDMS (polydimethylsiloxane) [12, 13] and PMMA (polymethylmethacrylate) [14–16]. PDMS-fabricated devices for microchannel separations are widely used due to their ease of preparation, and the resulting chip is pliable, extremely durable and can be reversibly or irreversibly sealed to a variety of other materials [17]. In addition, several different

electrodes materials have been proposed, such as carbon materials [18–32] including carbon fiber or nanotubes by themselves [21, 22] or in a modified form [23] as well as different versions of grapheme composites [18–21], platinum disk [24–26], gold [27–30], copper [31], and even three-material electrodes (i.e., Au-Ag-Pt or C-Ag-Pt) [32].

Although many articles on microchip capillary electrophoresis with electrochemical detection have been published, very few compare the performance with different materials and electrodes. In this study, a comparison between two homemade microchip capillary electrophoresis systems that consist of a high voltage supplier [12] with a gold or multistrand carbon fiber electrodes, which were placed in an end-channel arrangement in either PDMS/PDMS or hybrid PDMS/glass microchip, is reported. The system was tested for the separation of two mixtures (i.e., paracetamol-4-aminophenol and dopamine-dopac). Several experimental variables were analyzed and optimized. We demonstrated that capillary electrophoresis with a hybrid microchip PDMS/glass and carbon fiber electrode using triple pulse amperometric detection exhibits good performance and can be easily miniaturized.

2 Experimental

2.1 Instrumentation

A 3-channel programmable high-voltage power supply (supplied voltages ranging from 0 to +4,000 V, Department of Chemistry, Colorado State University, Fort Collins, USA) was employed to perform sample injection and separation [33]. A CHI 660 electrochemical analyzer (CHI Instruments Austin, USA) was used for pulsed amperometric detection. A personal computer was employed to control the electrochemical analyzer and collect data.

2.2 Reagents and solutions

All the solutions were prepared from analytical grade reagents and purified water (18 MΩ resistance, MilliQ, Millipore System). *N*-(4-Hydroxyphenyl)ethanamide or paracetamol (PA), 4-(2-aminoethyl)benzene-1,2-diol or dopamine (DO) and 2-(3,4-dihydroxyphenyl)acetic acid or dopac were obtained from Sigma, and 4-aminophenol (4-AP) was obtained from Riedel de Haën. Monobasic and dibasic potassium phosphate, sodium borate, sodium acetate and sodium dodecyl sulfate (SDS) were obtained from J.T.Baker. Working standard solutions of PA, 4-AP, DO and dopac were prepared daily by dissolving the reagents in the appropriate buffer solution, and these solutions were also used as running buffers. Sodium hydroxide and hydrochloric acid were obtained from J. T. Baker.

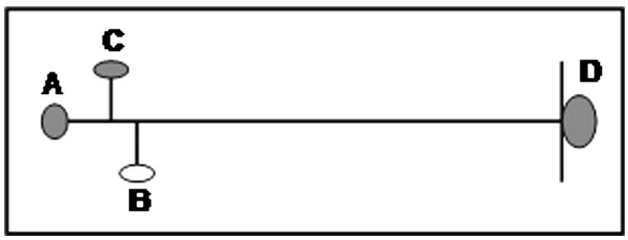

Fig. 1 Schematic representation of the microchip channel microarray. *a, c* buffer reservoirs; *b* sample reservoir; *d* waste reservoir and electrochemical detection cell

2.3 Microchip fabrication

A molding master wafer (Department of Chemistry, Colorado State University Fort Collins, USA) [33] with a double T injection area (1.4 nL injected volume) and a 50 μm × 50 μm × 55 mm separation channel design was employed to fabricate a PDMS layer with a microchannel pattern on the surface. A degassed mixture of Sylgard 184 silicone elastomer (Dow Corning, Midland, USA) and a curing agent (10:1) was poured over the wafer. Then, the wafer was cured for at least 12 h at 80 °C. The cured PDMS was separated from the mold, and sample, buffer and waste reservoirs were made at the end of each channel using a 6 mm circular punch. Either a 25 μm gold wire or multistrand carbon fibers were aligned using an optical microscope at the end of the separation channel in the perpendicular channel designed for this purpose (Fig. 1). The multistrand carbon fibers consisted of a 6–8 μm diameter carbon fiber bundle that was put together in a hundred member group. It is important to note that although the carbon fiber bundle size was wider than the microchip channel, it is not detrimental for microchip sealing or performance. A 10 cm × 5 cm PDMS piece or glass was used to complete the microchip assembly. The glass was cleaned using a 3 mol L^{-1} KOH/ethanol solution followed by an ultrasonic treatment for at least 15 min and rinsed with deionized water. Both the PDMS/PDMS and PDMS/glass layers were placed in an air plasma cleaner (Plasma Cleaner/Sterilizer PDC-32G, Harrick Plasma, Ithaca, USA), oxidized for 15 min and immediately brought into contact to achieve an irreversible seal. Finally, electrical connections were made using copper wire and silver paint. The constructed microchannel pattern is shown in Fig. 1 [13].

2.4 Electrophoresis separation

Prior to the experiments, the microchannels were conditioned with 0.3 mol L^{-1} NaOH for 15 min followed by a buffer solution for 10 min. Different buffer solutions in the

Table 1 Potential settings and solutions used on microchips reservoirs during microchip functioning

Reservoir	Containing	Injection/V	Separation/V
A	Buffer	−160	+1,000 to +2,500
B	Sample	+410	+410
C	Buffer	−160	+410
D	Waste	Ground	Ground

Table 2 Triple pulsed amperometric detection parameters

	Potential/V	Time/s
Cleaning	+1.5	0.05
Reactivation	−0.5	0.05
Detection	+0.7–0.9	0.15

20–50 mmol L^{-1} concentration range at different pH values were used as running solutions. In some experiments, a 10 mmol L^{-1} SDS aliquot was added to improve the electropherogram resolution. Platinum wires were used for the electrical connections between the microfluidic and the power supply. Double-T injection was used to load the sample prior to running the electrophoretic separation, and the potential settings for each step are listed in Table 1.

2.5 Electrochemical detection

Electrochemical detection was performed using triple pulse amperometry with a three electrode array placed in the waste reservoir (D). The reference electrode was Ag/AgCl/3 M NaCl (CHI Instruments Austin, USA), and a 1 mm O.D. platinum wire was used as an auxiliary electrode. Triple pulse amperometry was selected for use as the detection technique. To avoid working electrode fouling, a high positive first potential pulse was applied, and the second pulse was negative and produced superficial regeneration. The third potential step was employed to perform the detection. The sequence of steps and potential settings are listed in Table 2, and they are repeated continuously during the experiment. However, only the current corresponding to the last segment of the third step is recorded.

As previously mentioned, two working electrodes (i.e., either gold or carbon fibers) were used for electrochemical detection, and these electrodes were conditioned at the beginning of the day or with each new microchip, as described below.

Gold wire electrode: First, a 10 V versus Ag/AgCl/3 M NaCl potential pulse was applied for 30 s in 0.1 mol L^{-1} H_2SO_4 (gold oxide layer is formed and a red color appeared). Second, the solution is changed to 1 mol L^{-1} HCl and left for 3 min (gold oxide layer dissolves and red color disappear). Third, an additional solution change to a 70:30 mixture of H_2SO_4/H_2O_2 and left for 5 min. Finally, the detection reservoir was thoroughly washed with deionized water and cyclic voltammetry in 0.1 mol L^{-1} H_2SO_4 was performed to check the surface state.

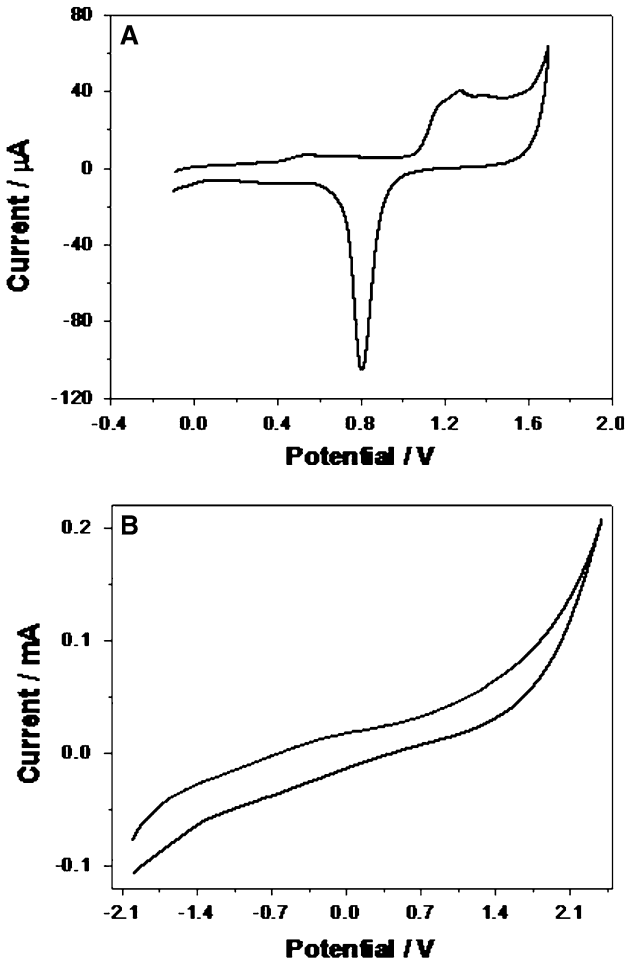

Fig. 2 Cyclic voltammogram at 0.1 V s^{-1} **a** gold electrode in a PDMS/PDMS microchip in 0.1 mol L^{-1} H_2SO_4. **b** Carbon fiber electrode in a PDMS/glass microchip in a 50 mmol L^{-1} borate buffer solution (pH 9.4)

Carbon fiber electrode Cyclic voltammetry in 1 mol L^{-1} NaOH in the −0.4–1.2 V potential range at 0.1 Vs^{-1} was performed until a stable voltamperometric profile was obtained. Superficial electrochemical activation occurs, and the fibers became more reactive and ready for use.

The conditioning of both electrodes produced surfaces that are more efficient for charge transfer reactions. Therefore, higher current values were obtained. Next, either cyclic or hydrodynamic voltammograms were obtained with both electrodes for each compound.

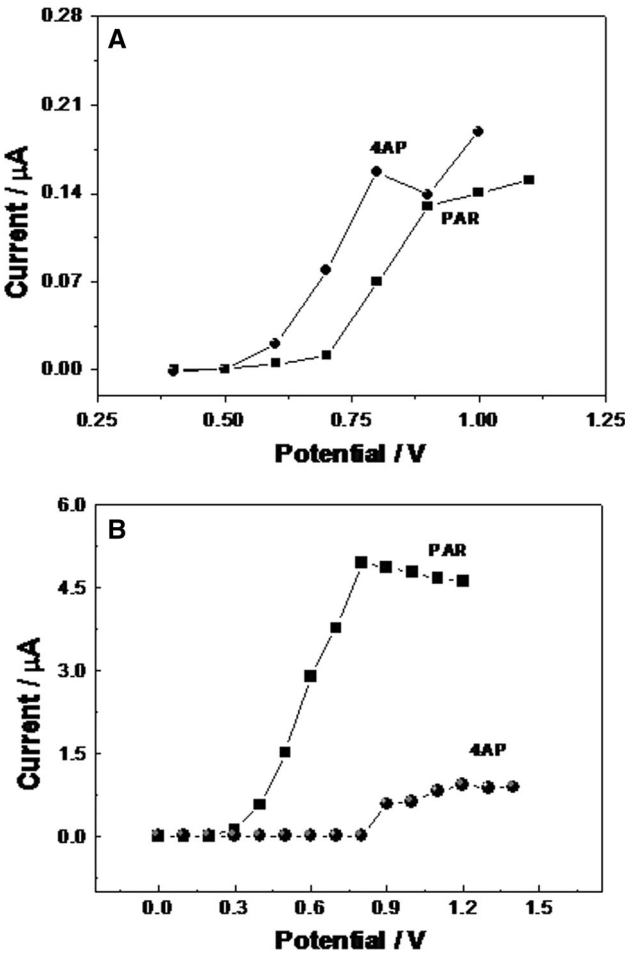

Fig. 3 Hydrodynamic voltammograms for 1×10^{-3} mmol L^{-1} PA and 4-AP in **a** the PDMS/PDMS microchip with a gold electrode detector in a 50 mmol L^{-1} borate buffer solution (pH 9.4) and **b** the PDMS/glass microchip with a multistrand carbon fiber electrode in a 20 mmol L^{-1} phosphate buffer solution at pH 12.0. Einj: 500 V; tinj: 5 s; Emig: 1,000 V

3 Results and discussion

The general microchip fabrication procedure has been described in the experimental section. After microchip and electrode conditioning, cyclic voltammograms were obtained to confirm that the device was working properly. Figure 2 shows the cyclic voltammograms at 0.1 V s^{-1} for both electrodes in the microchip devices. Figure 2a shows the cyclic voltammogram of the gold electrode in a PDMS/PDMS microchip in 0.1 mol L^{-1} H_2SO_4, and Fig. 2b shows the cyclic voltammogram of the carbon fiber electrode in a PDMS/glass microchip in a 50 mmol L^{-1} borate buffer solution (pH 9.4).

Both electrodes exhibit good signals that are similar to those obtained with standard electrochemical cells [34], indicating that the electrode surfaces possess good responses.

However, as previously mentioned in the experimental section, the electrochemical detection was performed amperometrically with a triple pulse. Therefore, to determine the working potential, hydrodynamic voltammograms were obtained for both electrodes and each compound by sequential injections of different aliquot using the same microchip and setting the detector at increasing potential values. Figure 3 shows the hydrodynamic voltammograms for 1×10^{-4} mol L^{-1}or 1×10^{-3} mol L^{-1} PA and 1×10^{-3} mol L^{-1}4-AP with two different microchips and electrodes. The results in Fig. 3a were obtained with a gold electrode in a PDMS/PDMS microchip in a 50 mmol L^{-1} borate buffer at pH 9.40, and the results in Fig. 3b correspond to the carbon fiber electrode with a PDMS/glass microchip in a 20 mmol L^{-1} phosphate buffer solution at pH 12.0. For both experiments, the injection conditions were 500 V (E_{inj}) and 5 s (t_{inj}), and the migration potential (E_{mig}) was 1,000 V. For all of the cases, the typical S shaped current/potential curves were obtained for both electrodes and compounds with a current plateau starting at potential values ranging between 0.8 and 0.9 V. However, the multistrand carbon fiber electrode presented higher current signals than those obtained with the gold wire electrode (Fig. 3a, b). In addition, the electrochemical activity for PA was higher than for 4-AP with the carbon fiber electrodes (Fig. 3a, b). The selected working potential for both electrodes was +0.9 V, as at this potential value, a good electrochemical signal for both PA and 4-AP was obtained. However, it is important to note that PA at the carbon fiber electrode exhibited a current plateau at lower potential values (0.7 V) (Fig. 3b), which allows for determination at this potential value and avoids possible interferents. Similar results were obtained with the DO/dopac mixture (results not shown). However, in this case, the selected potential was 0.8 V, and both hydrodynamic voltammograms have a similar shape and current plateau values.

The microchip performance was optimized by analyzing all of the variables that affect the separation process, such as the running buffer (composition and pH), applied migration potential and addition of surfactants. Therefore, a mixture of PA (pKa = 9.4) and 4-AP (pKa = 9.5) was used to test the microchip performance. Two buffer solutions (i.e., borate and phosphate) were analyzed at pH values higher than both pKa values to ensure that the analytes were charged. No significant changes are observed at pH values between 9.5 and 11.5. However, for pH values higher than 11.5 an elution time increase is observed probably due to phenol adsorption on the capillary wall. Therefore, the best results were obtained for phosphate buffer solution at pH 11.0. Furthermore, because the PA and 4-AP pKa values were similar, a good resolution was not achieved. Therefore, SDS was added to improve the

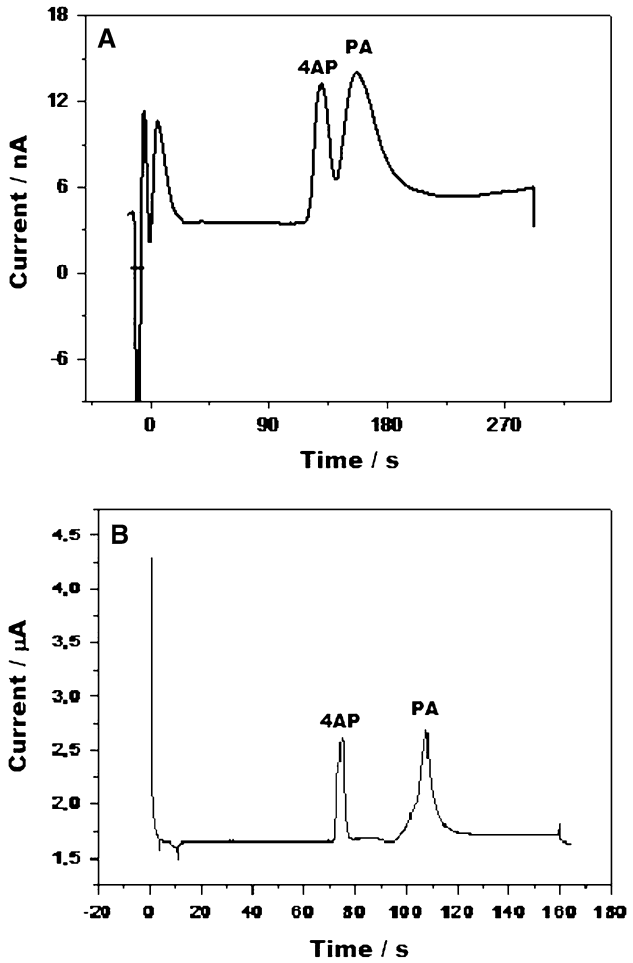

Fig. 4 Electropherograms with a hybrid PDMS/glass microchip for a mixture of 1×10^{-3} mol L^{-1} PA and 4-AP with different electrodes and buffers. **a** Gold electrode in a 50 mmol L^{-1} borate buffer (pH 9.5), Einj: 500 V; tinj: 5 s; Emig: 1,000 V; ATP Edet: 0.9 V. **b** Carbon fiber electrode in a 20 mmol L^{-1} phosphate buffer solution (pH 11.0) + 10 mmol L^{-1} SDS, Einj: 500 V; tinj: 5 s; Emig: 2,500 V, ATP Edet: 0.9 V

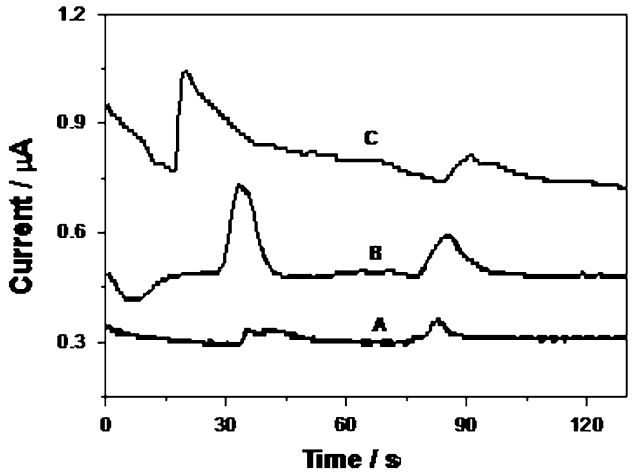

Fig. 5 Electropherograms with a hybrid microchip PDMS/glass and a carbon fiber electrode for a mixture of 1×10^{-3} M dopamine and dopac in a 20 mmol L^{-1} phosphate buffer solution at different pH values: *a* 2.5; *b* 6.6 and *c* 12.2. Einj: 500 V; tinj: 5 s; ATP; Edet: 0.8 V; Emig: 1,500 V

separation process. The improvement in the resolution results from minimizing the interactions between molecules and the capillary walls due to the presence of the surfactant. To analyses SDS response several blanks were run, in all the cases no electrochemical response was observed. With the PDMS/PDMS microchips, the highest migration potential that can be used is 1,000 V because at higher potential values, Joule heating is obtained which results in solution darkening. However, with the PDMS/glass hybrid microchip, migration potential values as high as 2,500 V can be used. This behavior demonstrates that the use of glass improves the microchip performance. The electropherograms obtained with a hybrid PDMS/glass microchip for a mixture of 1.0×10^{-3} mol L^{-1} PA and 4-AP with different conditions are shown in Fig. 4. Figure 4a shows the results for the gold electrode in a 50 mmol L^{-1} borate buffer at pH 9.5 with $E_{mig} = 1{,}000$ V. The peaks resolution was not sufficient, and the whole migration time was approximately 180 s. Figure 4b shows the electropherograms for a 20 mmol L^{-1} phosphate buffer at pH 11.0 plus 10 mmol L^{-1} SDS with $E_{mig} = 2{,}500$ V. In this case, a very good resolution was obtained, and the separation process requires less than 120 s.

A similar analysis was performed with a mixture of dopamine (pKa = 8.9) and dopac (pKa = 4.4). In this case, the pKa values were quite different. Therefore, there should not be problem to solve the mixture. Nevertheless, an appropriate pH value must be employed to obtain both peaks at reasonable migration times. Different buffer solutions in the 4–12 pH range were tested. However, if sodium acetate was used as a running buffer, dopac adsorption was observed. Figure 5 shows the electropherograms for a 1×10^{-3}mol L^{-1} dopamine/dopac mixture at different phosphate buffer pH values. The mixture was resolved at all of the tested pH values because peaks separation is sufficiently wide. However, the best peak shape was obtained at a pH of 6.6 (Fig. 5b), and at the other pH values (Fig. 5a, c), the peak broadening indicated that the diffusion process inside the capillary might be important.

Finally, a stability analysis of the electropherograms indicated that with the PDMS/PDMS microchips and a gold electrode, the coefficients of variation (CV) for the current values are in the 10–20 % range, and the migration time CV was 1–2 %. The results obtained with the hybrid microchip PDMS/glass and carbon fiber electrode exhibited a better current CV of approximately 4–5 %, and the migration time had a CV of 0.6–0.8 %, which indicated

that the electrophoretic separation has a better reproducibility in this assembly. These CV values for the hybrid microchip are compatible with those obtained by other techniques for these compounds [35–38].

4 Conclusions

Two electrodes (i.e., gold and carbon fibers) and two microchip materials (i.e., PDMS/PDMS and PDMS/glass) were analyzed for capillary electrophoresis separation with electrochemical detection using two mixtures to determine the best system. The comparison was carried out by analyzing all of the parameters of the separation and detection processes, such as pH, composition and concentration of the running buffer, migration potential and detection potential. Better responses were obtained with the hybrid microchips (PDMS/glass) and carbon fiber electrode. The device was useful for the separation and detection of two different mixtures (i.e., paracetamol/4-aminophenol and dopamine/dopac) resulting in an excellent choice for application as a portable analysis tool. Electrochemical detection allows for the simultaneous determination of several analytes.

References

1. Reyes DR, Iossifidis D, Auroux PA, Manz A (2002) Micro total analysis systems. 1. Introduction, theory, and technology. Anal Chem 74:2623–2636
2. Squires TM, Quake SR (2005) Microfluidics-Fluid Physics at the Nanoliter Scale. Rev Mod Phys 77:977–1026
3. Whitesides GM (2006) The Origins and the Future of Microfluidics. Nature 442:368–373
4. Sollier E, Murray C, Maoddi P, Di Carlo D (2011) Rapid prototyping polymers for microfluidic devices and high pressure injections. Lab Chip 11:3752–3765
5. Berthier E, Young EWK, Beebe D (2012) Engineers are from PDMS-Land, biologists are from polystyrenia. Lab Chip 12:1224–1237
6. Timerbaev AR (2013) Element speciation analysis using capillary electrophoresis: twenty years of development and applications. Chem Rev 113:778–812
7. Huang XJ, O'Mahony AM, Compton RG (2009) Microelectrode arrays for electrochemistry: approaches to fabrication. Small 5:776–788
8. Vázquez M, Frankenfeld C, Coltro WKT, Carrilho E, Diamond D, Lunte SM (2010) Dual contactless conductivity and amperometric detection on hybrid PDMS/glass electrophoresis microchips. Analyst 135:96–103
9. Woolley AT, Lao K, Glazer AN, Mathies RA (1998) Capillary electrophoresis chips with integrated electrochemical detection. Anal Chem 70:684–688
10. Arora A, Simone G, Salieb-Beugelaar GB, Kim JT, Manz A (2010) Latest developments in micro total analysis systems. Anal Chem 82:4830–4847
11. Breadmore MC (2012) Capillary and microchip electrophoresis: challenging the common conceptions. J Chromatogr A 1221:42–55
12. Lin K, Huang Y, Su H, Hsieh Y (2008) In-channel simplified decoupler with renewable electrochemical detection for microchip capillary electrophoresis. Anal Chim Acta 619:115–121
13. García CD, Henry CS (2003) Direct determination of carbohydrates, amino acids, and antibiotics by microchip electrophoresis with pulsed amperometric detection. Anal Chem 75:4778–4783
14. Pfleging W, Kholer R, Schierjott P, Hoffman W (2009) Laser patterning and packaging of CCD-CE-Chips made of PMMA. Sens Actuators B 138:336–343
15. Ruecha N, Siangproh W, Chailapakul O (2011) A fast and highly sensitive detection of cholesterol using polymer microfluidic devices and amperometric system. Talanta 84:1323
16. Castaño-Álvares M, Fernandez-Abedul M, Costa-García A (2006) Amperometric detector designs for capillary electrophoresis microchips. J Chromatogr A 1109:291–299
17. Ghanim MH, Abdullah MZ (2011) Integrating amperometric detection with electrophoresis microchip devices for biochemical assays: recent developments. Talanta 85:28–34
18. Sheng S, Liu S, Zhang L, Chen G (2013) Graphene/poly(ethylene-co-vinyl acetate) composite electrode fabricated by melt compounding for capillary electrophoretic determination of flavones in *Cacumenplatycladi*. J Sep Sci 36:721–728
19. Xu J, Zhang L, Chen G (2013) Fabrication of Graphene/poly(-ethyl 2-cyanoacrylate) composite electrode for amperometric detection in capillary electrophoresis. Sens Actuators B 182:689–695
20. Sheng S, Zhang L, Chen G (2012) Low-cost fabrication of graphene ball electrodes for the amperometric detection of capillary electrophoresis. Electrochem Commun 24:13–16
21. Zestos AG, Nguyen MD, Poe BL, Jacobs CB, Venton BJ (2013) Epoxy insulated carbon fiber and carbon nanotube fiber microelectrodes. Sens Actuators B 182:652–658
22. Vilela D, Garoz J, Colina A, González MC, Escarpa A (2012) Carbon nanotubes press-transferred on PMMA substrates as exclusive transducers for electrochemical microfluidic sensing. Anal Chem 84:10838–10844
23. Li X, Chena Z, Zhongb Y, Yang F, Pan J, Liang Y (2012) Cobalt hexacyanoferrate modified multi-walled carbon nanotubes/graphite composite electrode as electrochemical sensor on microfluidic chip. Anal Chim Acta 710:118–124
24. Li X, Chen Z, Yang F, Pan J, Li J (2013) Development of a microchip-pulsed electrochemical method for rapid determination of L-DOPA and tyrosine in *MucunaPruriens*. J Sep Sci 36:1590–1596
25. Sheng J, Zhang L, Lei J, Ju H (2012) Fabrication of tunable microreactor with enzyme modified magnetic nanoparticles for microfluidic electrochemical detection of glucose. Anal Chim Acta 709:41–46
26. Li Y, Wang G, Jin J, Wang X (2013) Using active carbon as counter electrodes: a two electrode configuration for pulse amperometric detection. J Electroanal Chem 705:13–18
27. Chen A, Tsao M-J, Chuanga J-F, Lin C-H (2013) Electrochemical determination of verapamil with a microchip embedded with gold nanoelectrode ensemble electrodes. Electrochim Acta 89:700–707
28. Islam K, Jha SK, Chand R, Han D, Kim Y-S (2012) Fast detection of triazine herbicides on a microfluidic chip using capillary electrophoresis pulse amperometric detection. Microelectron Eng 97:391–395
29. Power A, White B, Morrin A (2013) Microfluidic thin-layer flow cell for conducting polymer growth and electroanalysis. Electrochim Acta 104:236–241
30. Álvarez-Martos I, Fernández-Abedul MT, Anillo A, Fierro JLG, García Alonso FJ, Costa-García A (2012) Poly (Acrylic Acid) microchannel modification for the enhanced resolution of catecholamines microchip electrophoresis with electrochemical detection. Anal Chim Acta 724:136–143

31. Li P, Zhao W, Wang X, Shi G, Zhou T (2013) Stacking and simultaneous determination of estrogens in water samples by ce with electrochemical detection. J Sep Sci 36:334–340
32. Liu J, Qin J, Li J, Li D, Xu Z, Zhang X, Du L, Liu C (2013) Monolithic integration of three-material microelectrodes for electrochemical detection on PMMA substrates. Electrochem Commun 31:20–23
33. García C, Liu Y, Anderson P, Henry C (2003) Versatile 3 channel high voltage power supply for microchip capillary electrophoresis. Lab Chip 3:324–328
34. Zachek MK, Hermans A, Wightman RM, McCarty GS (2008) Electrochemical dopamine detection: comparing gold and carbon fiber microelectrodes using background subtracted fast scan cyclic voltammetry. J Electroanal Chem 614:113–120
35. Lourencão BC, Medeiros RA, Rocha-Filho RC, Mazo LH, Fatibello-Filho O (2009) Simultaneous voltammetric determination of paracetamol and caffeine in pharmaceutical formulations using a boron-doped diamond electrode. Talanta 78:748–752
36. Kang X, Wang J, Wu H, Liu J, Aksay IA, Lin Y (2010) A graphene-based electrochemical sensor for sensitive detection of paracetamol. Talanta 81:754–759
37. Li J, Liu J, Tan G, Jiang J, Peng S, Deng M, Qian D, Feng Y, Liu Y (2014) High-sensitivity paracetamol sensor based on Pd/graphene oxide nanocomposite as an enhanced electrochemical sensing platform. Biosens Bioelectron 54:468–475
38. Kutluay A, Aslanoglu M (2014) An electrochemical sensor prepared by sonochemical one-pot synthesis of multi-walled carbon nanotube-supported cobalt nanoparticles for the simultaneous determination of paracetamol and dopamine. Anal Chim Acta 839:59–66