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Carbon nanotubes paste electrodes as new detectors for capillary electrophoresis

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Abstract

Carbon nanotubes paste electrodes (CNTPE) prepared with short (1–5 μm length) and long carbon nanotubes (5–20 μm length) of 20–50 nm diameter have demonstrated to be highly useful as detectors in flow injection analysis and capillary electrophoresis. Compared to the classical graphite paste electrode, CNTPE improved the detection limits of dopac, ascorbic acid, dopamine, norepinephrine and epinephrine. The content of agglutinant has shown to be an important variable in the preparation of these carbon nanotubes composites. Even when no substantial differences were observed between the electrodes, those prepared with long carbon nanotubes (55.0%, w/w) and mineral oil (45.0%, w/w) have allowed us to obtain less noisy and more reproducible signals. In this article we also report the successful use of a new electrochemical cell for the detection in capillary electrophoresis that allows an easier handling and more reproducible responses. Therefore, the combination of the carbon nanotubes electrocatalytic activity with the known advantages of composite materials, the efficiency of the new electrochemical cell and the excellent separative properties of capillary electrophoresis represents a very important alternative for new electroanalytical challenges.

Keywords: Carbon nanotubes paste electrodes; Capillary electrophoresis; Nuerotransmitters; Electrochemical detection in capillary electrophoresis

1. Introduction

Carbon nanotubes (CNT) have received enormous attention in the last years due to their unique structural, mechanical, geometric and chemical properties [1]. Their closed topology and tubular structure have made them a very attractive material [2,3]. CNTs have demonstrated to be extremely useful for the development of new electrode materials. Their electrocatalytic properties have been widely demonstrated in connection with several compounds of clinical, biological and environmental interest [4].

Wang and Musameh [5] have reported on a composite electrode based on the dispersion of carbon nanotubes within a Teflon binder. An important electrocatalytic effect on the oxidation of NADH and on the oxidation and reduction of hydrogen peroxide was obtained with this electrode, that allowing the effective biosensing of glucose and ethanol in connection with the immobilization of glucose oxidase and alcohol dehydrogenase/NAD^+. The composite electrode has demonstrated to be adequate for flow injection analysis, where a stable, highly sensitive and reproducible response was obtained.

We reported for the first time the excellent properties of a composite electrode obtained by dispersion of multiple wall carbon nanotubes within mineral oil [6]. The electrode was used for the immobilization of different biomolecules such as nucleic acids [7], glucose oxidase [6], lactate oxidase,

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polyphenol oxidase and alcohol dehydrogenase [8]. The important decrease in the overvoltages for the oxidation of NADH, the reduction of hydrogen peroxide and the reduction of quinones has allowed the highly sensitive and selective determination of glucose [6], ethanol, phenols, catechols and lactate [8].

Palleschi and co-workers [9] have also reported on the electrochemical behavior of carbon nanotubes paste electrodes prepared by mixing single wall carbon nanotubes with mineral oil. They reported a noticeable improvement in the electrochemical behavior of ferricyanide, sodium hexachloroiridate(III) hydrate, catechol, dopamine, serotonin, 5-hydroxytryptamine, caffeic acid and hydrogen peroxide.

Britto et al. [10] have made a comparison of the electroreduction of oxygen at graphite and carbon nanotubes paste electrodes and found that the current densities are at least five times higher for the pastes with nanotubes and that at the graphite paste electrode these peaks are not well defined and shifted towards more negative potentials.

Wang and co-workers [11] have reported on the use of a carbon nanotube paste electrode for the determination of homocystein. A decrease of 120 mV in the overpotential for the oxidation of this compound and other thiolated species like cysteine, glutathione and *n*-acetylcysteine, as well as a noticeable improvement in the signal-to-noise ratio was obtained in comparison with the classical graphite paste electrode. Wang et al. [12] have also reported on the advantages of using carbon nanotubes paste electrode modified with copper for the amperometric detection of carbohydrates after capillary electrophoresis microchip separations. The electrode demonstrated to be highly suitable for the low potential detection of carbohydrates in microfluidic chip devices.

Hu and co-workers [13] have reported on the use of glassy carbon electrode modified with a carbon nanotubes film prepared by casting the electrode with 5 μL of the suspension of carbon nanotubes in dihexadecyl hydrogen phosphate and distilled water followed by the evaporation at room temperature. The resulting electrode was used for the quantification of dopamine and 5-hydroxytryptamine with detection limits of 1.1×10^{-8} and 5×10^{-9} M for dopamine and 5-hydroxytryptamine, respectively. An excess of 200-fold concentration of AA showed only a minimal influence on the oxidation signals of dopamine and 5-hydroxytryptamine.

Luo and co-workers [14] have proposed an electrode prepared by intercalating carbon nanotubes activated in a strongly acidic solution on a graphite surface for the simultaneous determination of dopamine and serotonin.

This article reports on the successful use of carbon nanotubes paste electrodes (CNTPE) as detectors in flow systems such as flow injection analysis (FIA) and capillary electrophoresis (CE, with a new electrochemical cell adapted to a commercial instrument). The influence of the nature of carbon nanotubes and paste composition on the electrochemical response of dopamine and related compounds as well as the analytical performance of the resulting electrodes in FIA and CE are discussed in the following sections.

2. Experimental

2.1. Reagents

3,4-Dihydroxyphenyl acetic acid (dopac), 3-hydroxytyramine (dopamine), artenerol ([±]-norepinephrine) hydrochloride, (±)epinephrine (4-[1-hydroxy-2-(methyl-amino)-ethyl]1,2 benzenediol) hydrochloride and L-(+)-ascorbic acid were purchased from SIGMA. Uric acid was purchased from Merck. All stock solutions were prepared before starting each set of experiments and stored under refrigeration in dark. Diluted solutions were prepared just before use from the stock solutions. Other chemicals were of analytical-reagent grade. All solutions were prepared with water from a Milli-Ro Milli-Q system (Millipore). For capillary electrophoresis the buffers and samples were sonicated 5 min and microfiltered through a 0.45 μm MFS-13 filters (Advantec MFS, Inc., USA).

2.2. Apparatus

Cyclic voltammetry experiments were performed with an EPSILON potentiostat (BAS). The electrodes were inserted into the cell (BAS, Model MF–1084) through holes in its Teflon cover. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, Model RE–5B) were used as counter and reference electrodes, respectively. All potentials are referred to the latter. A magnetic stirrer provided the convective transport during the amperometric measurements.

Carbon nanotubes paste electrodes (CNTPE) were prepared by mixing in an agata mortar multiwalled carbon nanotubes powder (NanoLab, USA, 95% purity) of 20–50 nm diameter and 1–5 μm (short carbon nanotubes) or 5–20 μm (long carbon nanotubes) length and mineral oil (Aldrich) in a given ratio. The classical carbon (graphite) paste electrode (CPE) was prepared in a similar way by mixing graphite powder (Fisher grade # 38) with mineral oil. A portion of the resulting paste was packed firmly into the cavity (3.0 mm diameter) of a Teflon tube. The electric contact was established via a stainless steel screw. A new surface was obtained by smoothing the electrode onto a weighing paper.

Flow injection (FIA) experiments were performed with an amperometric detector LC–4C (BAS, West Lafayette, USA) connected to a Perkin-Elmer 56 recorder. The electrodes were inserted into a wall-jet cell EA–1096 (Metrohm) containing a gold wire and Ag/AgCI, 3 M NaCl (Metrohm) as counter and reference electrodes, respectively. A peristaltic pump ISM 834 (ISMATEC) was used to provide the flow during the experiments. The valve was a Rheodyne type 50, four-way loop pressure valve (Altech, USA) (100 μL sample loop). The connections were made with an interconnecting PTFE tubing (0.8 mm i.d.).

Capillary electrophoresis experiments were carried out with a Spectra PHORESIS 100 (Thermo Quest Corporation, Spain). Data acquisition and processing were accomplished using a 486/PC equipped with two channels and a

Chrom-Card software package (Thermo Quest Corporation, Spain). Amperometric detection was performed with an amperometric detector LC-4C (BAS, West Lafayette, USA) connected to the second channel of the Chrom-Card software package. No variations were introduced in the original commercial set up. A 50 cm fused silica column with a 2 cm Nafion decoupler was used for electrophoretic separations with electrochemical detection. Inner and outer diameters of the column were 75 and 365 μm, respectively (Supelco, cat. No 77500, Bellefonte, USA). At the beginning of each day, the capilar was conditioned by successive flushing with 1.0 M NaOH, 0.10 M NaOH, purified water and separation buffer (5 min each). Between runs, the capillary was rinsed consecutively with water and separation buffer for 3 min. The time for every run was 12 min. Samples were introduced by hydrodynamic mode for 0.5 s (the injected volume being 20 nL).

The cell can be mounted in a short period of time (approximately 2 min) by assembling three pieces (Fig. 1A): two Plexiglas blocks (1 and 2) and a PTFE gasket (3) placed between them. Platinum (4) and silver (5) wires, which actuate as counter and pseudo-reference electrodes, respectively, were fixed to the body cell (2) with non-conductive cyanoacrilate glue (Loctite, Spain). All potentials given in this work are referred to this reference electrode. Working electrodes were fixed to the body cell through nuts (6) and they can be easily replaced if necessary. The separation capillary column was inserted into the cell through an inlet thread (7). The geometrical disposition of the electrodes inside the cell, in an inverse wall-jet arrangement, has allowed us to reduce the distance between them and the capillary outlet. The electrolyte solutions can be easily changed or renewed with the help of a syringe connected to the drain outlet (8). The cell is joined to the capillary electrophoresis equipment through a Plexiglas vial (9), in the way previously described [15]. This vial holds the decoupler and can be easily filled and drained with the help of a syringe (10). The PTFE tube (11) has allowed us the coupling of the vacuum tube (12) to the vacuum system. Fig. 1B shows the final position of the cell into the capillary electrophoresis equipment.

Working electrodes holders were constructed by fixing the 20 mm PTFE tubes (0.5 mm i.d. and 1.6 mm o.d.) with non-conductive cyanoacrilate glue to conventional FIA nuts. CNTPE and CPE were prepared by filling one side of the tube with the paste and packing them from the other side with a 0.5 mm diameter cooper wire, which also serves as electrical contact.

Scanning electronic microscopy (SEM) pictures were obtained with a Hitachi S3000N Microscope.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 2 displays cyclic voltammograms obtained at 0.100 V/s for 1.0×10^{-3} M dopamine (A), ascorbic acid (B), dopac (C) and uric acid (D) at CNTPEs prepared with carbon

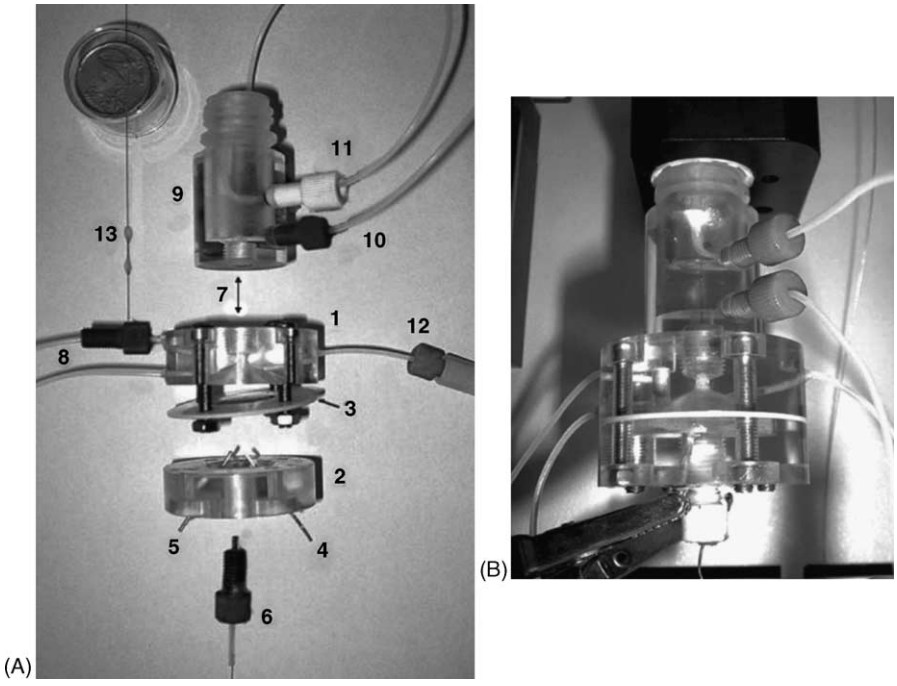

Fig. 1. Schematic representation of the electrochemical cell (A) and picture of the same cell once incorporated into the capillary electrophoresis equipment (B). (A): (1) Upper block of the cell, (2) lower block of the cell, (3) PTFE gasket, (4) auxiliary Pt electrode, (5) reference silver electrode, (6) working electrode, (7) connection between body cell and plexiglass vial, (8) drain outlet of the cell, (9) plexiglass vial for connecting the cell to the capillary electrophoresis equipment, (10) drain outlet of vial, (11) vacuum connection between capillary electrophoresis equipment and cell, (12) vacuum connection of the cell, (13) capillary column showing the nafion decoupler.

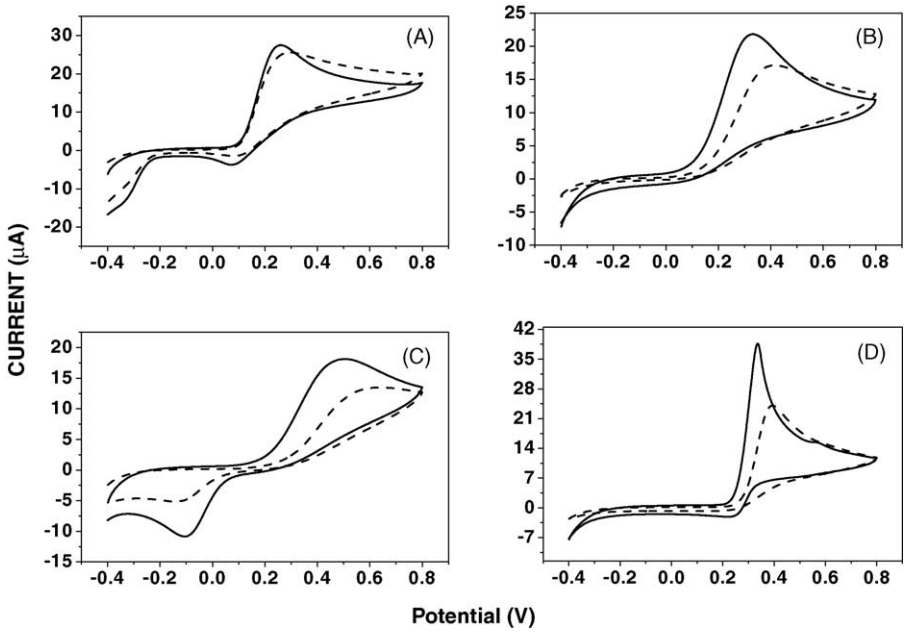

Fig. 2. Cyclic voltammograms obtained for 1.0×10^{-3} M dopamine (A), ascorbic acid (B), dopac (C) and uric acid (D) at carbon nanotubes paste electrodes (CNTPEs) prepared with short (—) and long (- - -) carbon nanotubes. Composition: 55.0% (w/w) carbon nanotubes and 45.0% (w/w) mineral oil. Scan rate: 0.100 V/s.

nanotubes of 1–5 μm (short carbon nanotubes (CNTs), full line) and 5–20 μm (long CNTs, dotted line) length. In both cases the composition of the electrodes was 55.0% (w/w) CNTs and 45.0% (w/w) mineral oil. At CNTPE prepared with short CNTs there was an improvement in the reversibility of dopamine and dopac (Fig. 2A and C). In fact, the ΔE_P for dopamine and dopac decreased 54 and 150 mV, respectively, while the anodic-to-cathodic peak currents ratio decreased from 4.9 to 3.3 for dopamine and from 4.7 to 2.6 for dopac. Almost no increase in the oxidation current was observed for dopamine. Regarding the oxidation of ascorbic and uric acids, the oxidation peak potentials decreased 79 and 58 mV, while the currents increased 23 and 65%, respectively (Fig. 2B and D).

The effect of the amount of mineral oil in the composite matrix on the performance of the CNTPEs was also evaluated (not shown). In the case of CNTPEs prepared using short CNTs in a proportion 60.0% (w/w) of CNTs and 40.0% (w/w) oil, the electrochemical response for dopamine, dopac, ascorbic acid and uric acid was similar to that obtained using 55.0/45.0% (w/w) CNTs/oil. Using CNTPE prepared with 50.0% (w/w) short CNTs the oxidation of these compounds occurred at higher overvoltages, the paste was difficult to handle and the response was non-reproducible. In the case of CNTPEs prepared with long CNTs, due to the characteristics of the powder, larger amounts of oil demonstrated to be necessary to obtain an easy-to-handle paste. At variance with CNTPEs prepared with short CNTs, a paste containing 40.0% (w/w) was very difficult to handle. CNTPEs prepared with 55.0% (w/w) gave slightly smaller signals than that obtained for pastes prepared containing 55.0% (w/w) short CNTs. It is important to mention that the composite matrix containing 50.0% (w/w) mineral oil, at variance with that obtained with short CNTs, can still be handle without problems giving reproducible response.

Fig. 3 shows SEM pictures of CNTPEs prepared with short and long CNTs (55.0% (w/w) CNTs and 45.0% (w/w) mineral oil). The surface of CNTPE prepared with short CNTs (Fig. 3A) looks more homogeneous than that of CNTPE prepared with long CNTs (Fig. 3B). Another important aspect shown in Fig. 3B is that the contact between nanotubes is more effective in the case of a CNTPE prepared with short CNTs due to the inherent nature of the long CNTs powder that requires more oil to obtain a homogenous dispersion. Therefore, for the same content in oil, the short nanotubes are dispersed in a more ordered way than the long ones, facilitating in some extension, the electron transfer.

3.2. Flow injection analysis

The usefulness of CNTPEs in flow systems was evaluated by using flow injection analysis in connection with the amperometric response of 1.0×10^{-6} M dopamine at 0.400 V. Fig. 4 shows the influence of the flow rate (between 0.25 and 4.75 mL/min) on the oxidation of dopamine at CNTPEs prepared with short and long CNTs in different carbon/oil ratios. The signals increases with the flow rate due to the smaller contribution of the dispersion, while for flow rates higher than 3.0 mL/min they level off due to the shorter interaction time between analyte and electrode. Therefore, the selected flow rate was 4.0 mL/min. The profiles were similar almost independently of the length of the nanotube and the oil percentage in the paste, demonstrating that the excellent properties of carbon nanotubes paste electrode demonstrated

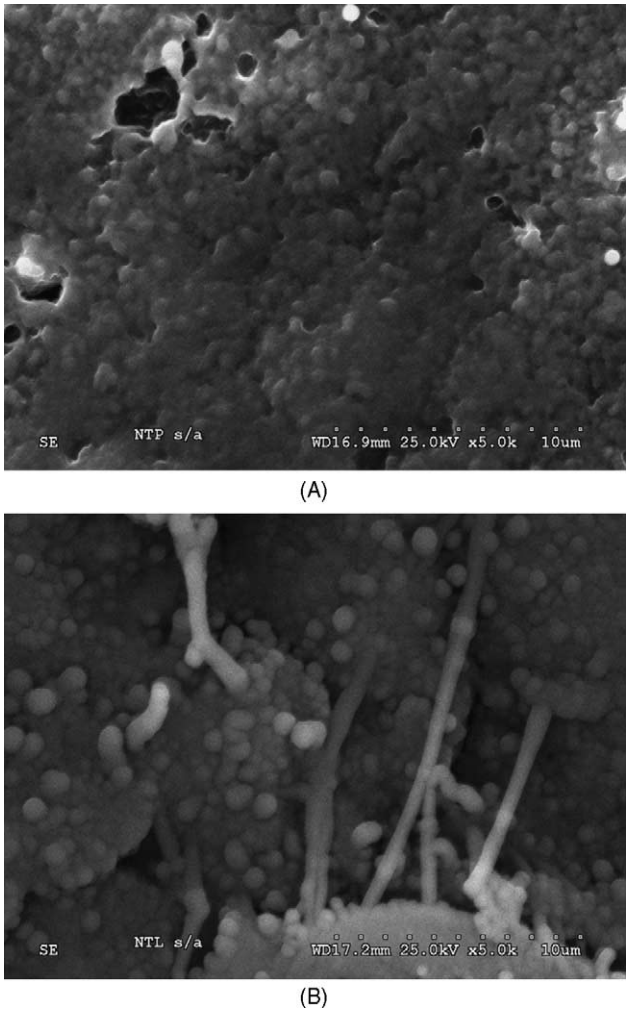

Fig. 3. SEM pictures of CNTPEs prepared with short (A) and long (B) carbon nanotubes. Composition: 55.0% (w/w) carbon nanotubes and 45.0% (w/w) mineral oil. Magnification: 5000×.

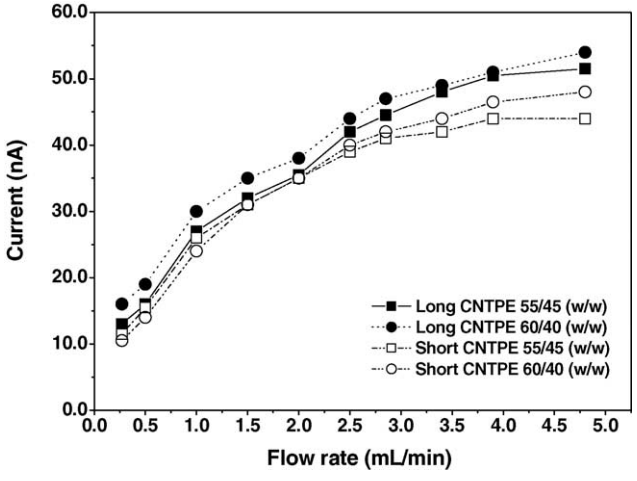

Fig. 4. Dopamine oxidation signal as a function of the flow rate for CNTPEs prepared with short and long carbon nanotubes and different amounts of mineral oil and carbon nanotubes. Detection potential: 400 mV. Dopamine concentration: 1.0×10^{-6} M.

in batch experiments, are also present in flow experiments, opening the doors to new capabilities.

Amperometric experiments were performed with the different electrodes at 0.400 V for successive additions of dopamine. Even when no significant differences were observed, CNTPEs prepared with long CNTs presented better short term stability, less noisy signal and faster stabilization of the base line current than those obtained when using CNTPEs prepared with short CNTs. Therefore, the selected electrode for flow experiments was CNTPE prepared with long CNT in a 55.0/45.0% (w/w) carbon/oil ratio.

Fig. 5 shows hydrodynamic voltammograms for 1.0×10^{-6} M dopamine (A), dopac (B), epinephrine (C) and norepinephrine (D) at the classical graphite paste electrode (a) and at CNTPE (b). In agreement with previous results, the oxidation of these compounds started at less positive potentials and the corresponding currents are higher than those obtained at CPE due to the electrocatalytic activity of carbon nanotubes. It is widely known that carbon nanotubes present a better performance as electrode material than other forms of carbon mainly due to the nanotubes dimensions, electronic structure and topological defects present on their surface [16]. As in the case of the composite with Teflon [5], it has been demonstrated that even in the presence of an organic phase like mineral oil, the nanotubes maintain their excellent electron transfer properties [6,8,9].

3.3. Capillary electrophoresis

The cell used in this work is a new design based on the one previously reported [15] (Fig. 1). It can be used in connection with a commercial capillary electrophoresis instrument without any modification. The improvements of this new version of the cell are the following: absence of liquid junctions by using a silver pseudo-reference electrode incorporated into the cell; decrease in the inner resistance of the cell due to the spatial configuration of the auxiliary and reference electrodes that makes it possible the setting of the working electrode close to the end of the capillary column; small size (small volume) and improvement in the efficiency of the vacuum.

The performance of CNTPE comparatively to that of classical graphite paste electrode (CPE) as electrochemical detectors for capillary electrophoresis is described in this section. The experiments were run in a 0.035 M boric acid adjusted at pH 9.7. As is widely known, the alignment and distance between working electrode and capillary outlet are two critical parameters when electrochemical detection is carried out in capillary electrophoresis. The electrochemical cell we are proposing here avoids the use of micropositioners and optical instruments that are usually incorporated to the detectors set up. The careful cell design and the use of working electrodes with surfaces relatively larger than the capillary bore size (0.5 mm against 75 μm) allow the automatic alignment when the detector is assembled. The gap distance between the working electrode and the capillary outlet was evaluated, 100 μm being the optimum. In this

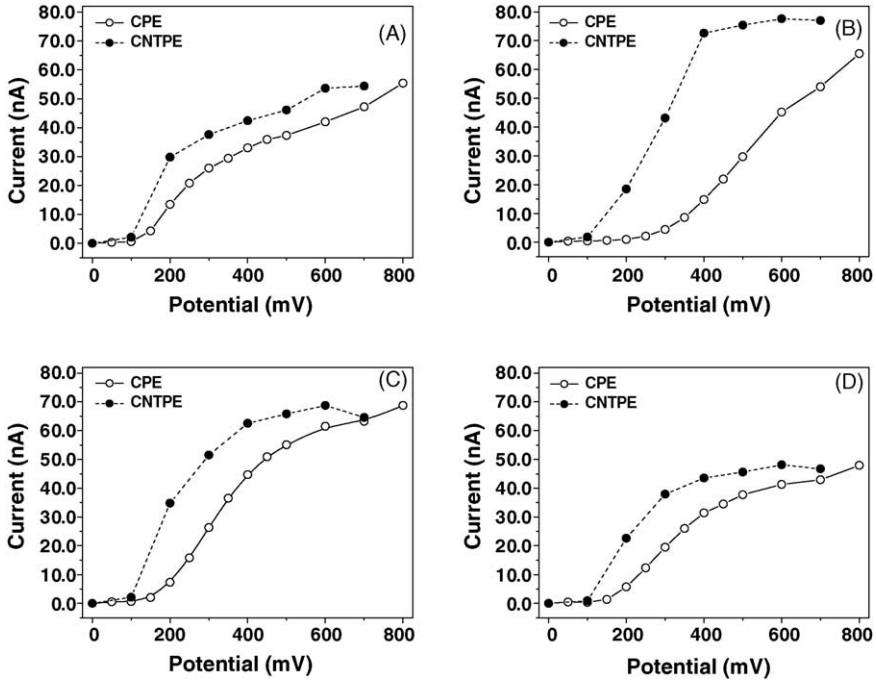

Fig. 5. Hydrodynamic voltammograms for 1.0×10^{-6} M dopamine (A), dopac (B), epinephrine (C) and norepinephrine (D) at graphite paste electrode (CPE) and carbon nanotube paste electrode (CNTPE) obtained by flow injection analysis. Flow rate: 4.0 mL/min. Carrier: 0.050 M phosphate buffer solution pH 7.40.

way it was possible to avoid back-pressures or even column clogging.

The effect of the applied voltage on the separation efficiency and sensitivity was studied between 5 and 25 kV. Although the resolution improved when increasing the voltage from 5 to 20 kV, the selected running voltage for subsequent studies was 17.5 kV (42 μA) to avoid Joule's heating effect and get analysis times sufficiently short (7 min). It is important to mention that no interference was observed in the detection cell when this voltage was applied.

Hydrodynamic voltammograms corresponding to the electrophoretic separation of different neurotransmitters and related compounds such as dopamine, epinephrine, norepinephrine, ascorbic acid and dopac, were obtained at CNTPE and CPE. As expected, according to the results obtained in FIA experiments, the oxidation currents at CNTPE are shifted towards lower potentials with an enhancement in the peak currents in all cases. These effects are specially pronounced for ascorbic acid and dopac. According to these results, it was possible to perform the electrochemical detection of the five compounds at 400 mV with good sensitivity.

Standard solutions of dopamine, epinephrine, norepinephrine, ascorbic acid and dopac ranging from 1.0×10^{-6} to 1.2×10^{-4} M for dopamine, epinephrine and norepinephrine and from 2.5×10^{-6} to 4.2×10^{-4} M for ascorbic acid and dopac, were determined by capillary electrophoresis using CNTPE and CPE. The experiments were performed at three different potentials. Typical electropherograms obtained at 0.400 V are shown in Fig. 6. Sensitivities, correlation coefficients and detection limits (according to the $3s_b/m$ criterion, where m is the slope of the calibration curve and s_b the standard deviation) are summarised in Table 1. The detection limits at 0.400 V using CNTPE were eight and five times lower than those at CPE for dopac and ascorbic acid, respectively; and two times lower for epinephrine and norepinephrine. At 720 mV the detection limit for dopac was even 11 times lower.

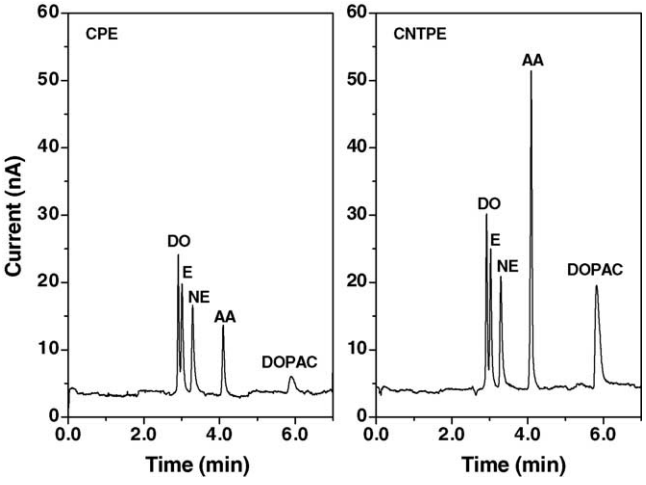

Fig. 6. Electropherograms for 1.2×10^{-4} M dopamine (Do), epinephrine (E) and norepinephrine (NE); 3.0×10^{-4} M ascorbic acid (AA) and 4.2×10^{-4} M dopac using CPE and CNTPE under optimal conditions. Electrode working potential: 400 mV. Fused silica column: 75 μm i.d. × 50 cm length, running buffer: 0.035 M boric acid adjusted to pH 9.70. Separation voltage: 17.5 kV. Hydrodynamic injection: 0.5 s.

Table 1
Analytical parameters obtained under optimal capillary zone electrophoresis conditions using different electrode working potentials at CPE and CNTPE

Compound	Working potential	CPE			CNTPE		
		Sensitivity (nA/μM)	Correlation coefficient ($n = 6$)	Detection limit (μM)	Sensitivity (nA/μM)	Correlation coefficient ($n = 6$)	Detection limit (μM)
Dopamine	400	0.16	0.9992	3.3	0.22	0.998	1.8
	600	0.41	0.9995	1.3	0.43	0.9997	0.9
	720	0.56	0.998	0.9	0.53	0.9997	0.7
Epinephrine	400	0.12	0.998	4.4	0.19	0.994	2.1
	600	0.30	0.9997	1.8	0.42	0.9996	0.9
	720	0.43	0.998	1.2	0.53	0.997	0.7
Norepinephrine	400	0.10	0.9990	5.3	0.14	0.994	2.8
	600	0.26	0.9997	2.0	0.32	0.9990	1.2
	720	0.41	0.998	1.3	0.57	0.997	0.7
Ascorbic acid	400	0.03	0.9990	17.7	0.12	0.9993	3.3
	600	0.05	0.99991	10.6	0.16	0.998	2.5
	720	0.07	0.994	7.1	0.16	0.997	2.5
Dopac	400	0.005	0.992	106	0.03	0.996	13.3
	600	0.014	0.996	38	0.11	0.997	3.6
	720	0.022	0.9990	24	0.19	0.998	2.1

Capillary zone electrophoresis conditions as in Fig. 6.

The excellent electrochemical properties of CNTPE are clearly demonstrated not only from sensitivities enhancements but also from the lowering in the noise associated with the base line current (0.18 nA for CPE versus 0.13 nA for CNTPE).

The reproducibility of the signals obtained at CNTPE was evaluated from series of 10 consecutive analysis (with a total of 120 min). In all cases the R.S.D.s were lower than 5%. On the other hand, the reproducibility of the signals after five processes of disassembling, renewing the electrode surface and re-assembling, was lower than 8.5% indicating that the electrochemical device provides a very effective and reproducible alignment operation. These results point out the high reproducibility and stability of CNTPE signals and their suitability for electrochemical detection in capillary electrophoresis.

4. Conclusions

CNTPEs either based on short or long carbon nanotubes have demonstrated to be highly efficient as flow detectors. The content of agglutinant is an important variable in the preparation of these composites and the optimum percentage depends on the nature of CNTs. CNTPE allows a more sensitive detection of neurotransmitters in FIA and CE, improving the detection limits of the determination of dopac, ascorbic acid, dopamine, norepinephrine and epinephrine. The new electrochemical cell for CE presented in this work is more specific for capillary electrophoresis performance, is easier to handle, possesses an improved vacuum system and reduced size compared to the previous cell. The combination of the advantages of the electrocatalytic activity of CNTs with the composite nature of the resulting CNTPEs, and the excellent separative properties of capillary electrophoresis opens the doors to new analytical challenges.

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