Lorena Sombra*
Yolanda Moliner-Martínez
Soledad Cárdenas
Miguel Valcárcel

Department of Analytical Chemistry,
University of Córdoba,
Córdoba, Spain

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Research Article

Carboxylic multi-walled carbon nanotubes as immobilized stationary phase in capillary electrochromatography

Carboxylic multi-walled carbon nanotubes (c-MWNT) have been immobilized into a fused-silica capillary for capillary electrochromatography. The c-MWNT were successfully incorporated after the silanization and coupling with glutaraldehyde on the inner surface of the capillary. The electrochromatographic features of the c-MWNT immobilized stationary phase have been evaluated for the analysis of different compounds of pharmaceutical interest. The results indicated high electrochromatographic resolution, good capillary efficiency and retention factors. In addition, highly reproducible results between runs, days and capillaries were obtained.

Keywords:
Capillary electrochromatography / Carbon nanotubes / Pharmaceutical analysis
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1 Introduction

In the recent years, the development of novel stationary phases to improve the performance of the separation techniques is a target research topic as it provides an elegant alternative to enhance the resolution power of these techniques. In addition, carbon nanotubes (CNT) have been also subjected to an intense research owing to their properties. The use of CNT as carbon-based sorbents is one of the most exploited approaches. Concretely, a review on the main uses of CNT as sorbents has been recently published [1]. The combination of these two interesting subjects has lead to the development of new CNT-based stationary phases for liquid chromatography (LC), gas chromatography (GC) or CE. This combination provides benefits and enhances the separation characteristic and the chromatographic or electrophoretic features of each separation technique. Basically, the modification of the capillaries to obtain stationary phases has been carried out through non-covalent and covalent methods. In general, non-covalent methods are simpler [2] while covalent methods provide stronger and more stable immobilizations [3].

Correspondence: Professor Miguel Valcárcel, Department of Analytical Chemistry, University of Córdoba, Campus de Rabanales, Marie Curie Building Annex, Córdoba, Spain
E-mail: qa1meobj@uco.es
Fax: +34-957-218-616

Abbreviations: APTS, 3-aminopropyl triethoxysilane**; CNT,** carbon nanotubes**; c-CNT,** carboxylic carbon nanotubes**; c-MWNT,** carboxylic multi-walled carbon nanotubes**; c-SWNT,** carboxylic single-walled carbon nanotubes**; SWNT,** single-walled carbon nanotubes**; MWNT,** multi-walled carbon nanotubes

Non-covalent methods to yield CNT-based stationary phases are grounded on the physical adsorption of CNT in a precoated capillary. Polymers such as poly(diallyldimethylammonium) chloride, vinylbenzyl chloride combined with ethylene dimethacrylate or proteins such as albumin have been used for the precoating step [2, 4, 5]. Single-walled carbon nanotubes (SWNT) as well as carboxylic single-walled carbon nanotubes (c-SWNT) have been used as coating for capillaries in capillary zone electrophoresis [2], microchip electrophoresis [4] and electrokinetic chromatography [5]. Additionally, the incorporation of CNT through non-covalent methods has also been described for chromatographic techniques. vinylbenzyl chloride and ethylene dimethacrylate combined with SWNT have been employed in μ-HPLC as stationary phase [5]. GC columns have been modified *via* adsorption of the CNT. Yuan *et al.* [6] described the immobilization of CNT using ionic liquids and SWNT to enhance the chromatographic separation of aliphatic and aromatic compounds.

Covalent modification of capillaries has been described for GC and LC leading to the development of new columns with classical chromatographic behaviour and improved chromatographic characteristics. Li and Yuan [7] proposed a gas chromatographic column with multi-walled carbon nanotubes (MWNT) as an alternative to charcoal or Carbopack B. Saridara and Mitra [8] also employed MWNT to obtain open tubular GC stationary phases with high-resolution separation for different compounds. SWNT have also been described as stationary phases. High-resolution separations of aliphatic and aromatic hydrocarbons have

* Permanent address: Lorena Sombra, Area of Analytical Chemistry, National University of San Luis, Chacabuco y Pedernera, San Luis CP 5700 CONICET, Argentina

also been described with SWNT film self-assembled by catalytic chemical vapour deposition inside silica-lined steel capillary columns [9]. Micro GC columns have been also developed with SWNT for well-resolved ultra fast separations [10]. The combination of CNT and silica microspheres has been also proposed as stationary phase for LC by Menna *et al.* [11]. However and to the best of our knowledge, the covalent modification of capillaries for its application in capillary electrochromatography has not been described.

Thus, the aim of the present paper is to explore the performance of carboxylic multi-walled carbon nanotubes (c-MWNT) immobilized fused-silica capillary through covalent modification of bare capillaries for the electrophoretic separation of different pharmaceutical compounds. In addition, we compared the results with c-SWNT immobilized fused-silica capillary following the same procedure. We also examine different analytical parameters, and especially reproducibility and repeatability of the electrophoretic system.

2 Materials and methods

2.1 Chemicals

MWNT with diameters between 6 and 20 nm and length in the range of 1–5 μm were obtained from Mer Corporation (Tucson, AZ, USA). SWNT with diameters between 0.7 and 1.2 nm and lengths of 2–20 μm, 1,3-dicyclohexylcarbodiimide, 3-aminopropyl triethoxysilane (APTS), β-lactams antibiotics (amoxicillin, ampicillin, cloxacillin, piperazillin and penicillin G), non-steroidal anti-inflammatory drugs (ketoprofen and flurbiprofen), chloramphenicol and sodium dodecyl sulphate were purchased from Sigma-Aldrich (Madrid, Spain). Anhydrous acetone, glutaraldehyde, sulphuric acid (98%), nitric acid (60%), boric acid and dimethylformamide were supplied by Panreac (Barcelona, Spain). The pH of the electrophoretic buffer was adjusted with 1 M NaOH. Stock standard solutions of the individual analytes were prepared at a concentration of 100 mg/L by dissolving the appropriate amount in Milli-Q water. Working standard solutions were prepared on a daily basis by rigorous dilution of the stocks in Milli-Q water.

2.2 Apparatus

A Beckman Coulter (Palo Alto, CA, USA) P/ACE 5500 CE system equipped with a diode array detector was used to separate and quantify the analytes. The background electrophoretic buffer used was 40 mM boric acid adjusted at pH 9 with 1 M NaOH. Samples were injected hydrodynamically at 0.5 psi for 10 s. In all cases, the temperature of the capillary was set at 20°C and the applied voltage for the electrophoretic separation was 15 kV. The wavelength was fixed at 214 nm. Initially, the carboxylic carbon nanotubes (c-CNT) immobilized capillary was sequentially conditioned by flushing Milli-Q water for 5 min, and then with running buffer for 15 min. Between runs, the capillary was flushed sequentially at 20 psi with Milli-Q water (2 min) and the electrophoretic buffer (2 min). The functionalized CNT were characterized by a Bruker Tensor37 FT-IR spectrometer, equipped with a diamond ATR cell with a circular surface of 3 mm diameter and three internal reflections. A liquid nitrogen-cooled mercury-cadmium-telluride detector was used for spectra acquisition. Spectra were collected between 4000 and 700 cm^{-1} at a 4-cm^{-1} resolution with 128 co-added scans each. The SEM images were obtained with a Jeol JSM-6300 Scanning Microscopy. For this aim, different circular sections of the bare capillary and the immobilized capillary were cut and the images were taken along the inner surface of the capillaries. Figure 1 shows the SEM micrographs for a given section of the c-MWNT immobilized fused-silica capillary at different magnifications. As can be seen in the micrographs, the treatment of the capillary with c-MWNT resulted in the presence of a network of c-MWNT through the entire capillary.

2.3 Preparation of c-CNT

c-MWNT were prepared by adding 20 mg of MWNT to 80 mL of H_2SO_4:HNO_3 (3:1). This mixture was ultrasonicated (50 W, 60 Hz) for 5 h, diluted with water (1.5 L) and filtered through a 0.45-μm cellulose acetate filter. Finally, c-MWNT were washed with distilled water and left to dry at room temperature [12]. c-SWNT were prepared following the procedure described by Suárez *et al.* [13].

2.4 Immobilization of c-MWNT

Fused-silica capillaries (75 μm id) with an effective length between inlet and detector of 50 cm (total length of 57 cm) obtained from Analysis Vinicos (Ciudad Real, Spain) were used. c-MWNT were immobilized by the following procedure: First, the capillary was rinsed with 1 M of NaOH for 30 min, followed by Milli-Q water (5 min). The second step was the introduction of an amino group by using a solution of 2% v/v APTS prepared in anhydrous acetone (15 min), followed by flushing with water (5 min) and methanol (5 min) to eliminate the excess of APTS. In the next step, a 10% v/v glutaraldehyde dissolved in 50 mM borate buffer at pH 9.0 was applied to the capillary for 1 h. Finally, a c-MWNT solution (5 mg/mL) dissolved in 4.5 mL of dimethylformamide containing 0.5 mg of 1,3-dicyclohexylcarbodiimide was passed through the capillary for 1 h. Finally, the capillary was rinsed with water to remove the unimmobilized c-MWNT.

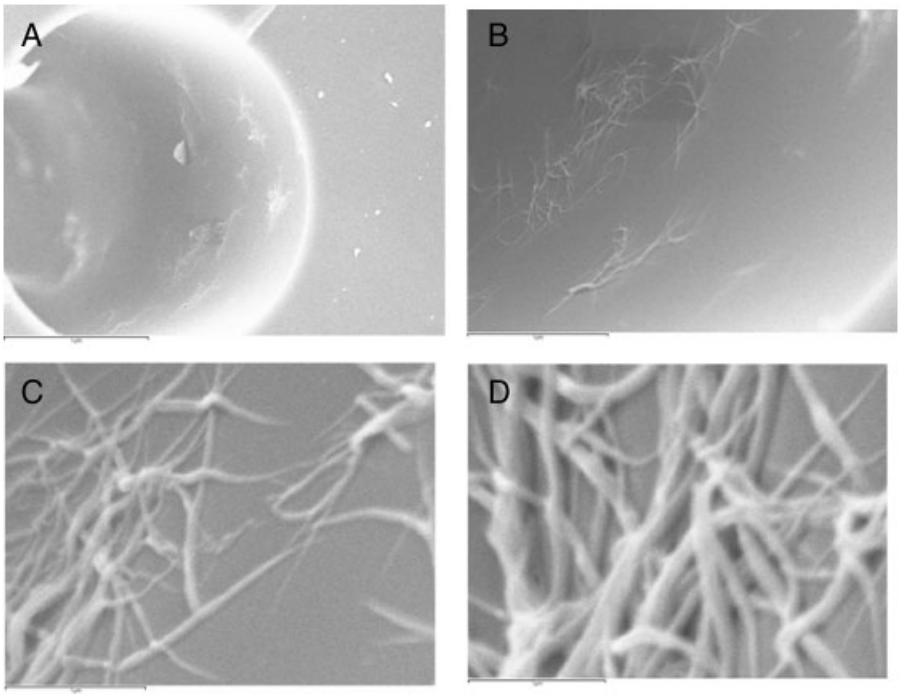

Figure 1. SEM micrographs obtained for the inner surface of the c-MWNT immobilized fused-silica capillary at different magnifications: (A) 1200, (B) 3500, (C) 20 000 and (D) 33 000. The voltage used was 20 kV.

2.5 Sample preparation

Three pharmaceutical formulations containing 750 mg of amoxicillin (tablets), 50 mg of ketoprofen (capsules) and 5 mg/mL of chloramphenicol (eyedrops solution) were obtained from a local drugstore.

For the analysis of samples, five tablets or the content of 15 capsules were weighted and ground in a mortar. An amount of solid equivalent to 600 mg of the pure compound was placed in a glass vessel mixed with 200 mL, dissolved by sonication for 20 min and filtered through a filter paper. The filtrate was diluted with methanol to a final volume of 250 mL (final concentration 2.4 g/L). For CE analysis, the sample standard solutions were diluted with Milli-Q water to obtain a final concentration of 10 mg/L. The eyedrops solution was directly diluted in Milli-Q water to the same final concentration.

3 Results and discussion

The procedure followed to immobilize c-CNT in the inner surface of the capillary comprised two steps: (i) activation of the capillary by means of the addition of glutaraldehyde to a previously silanized bare fused-silica capillary [14]; and (ii) immobilization of the CNT, which requires the presence of a carboxylic group in the CNT in order to obtain a moiety that can react with the functional groups previously added [13].

The structure of c-MWNT was confirmed by ATR FT-IR [15]. Figure 2 shows the IR spectra obtained for c-MWNT. Besides the CH_2 band at 1336 cm^{-1}, the adsorption bands at 1725 cm^{-1} and 1245 cm^{-1} are in correspondence with C═O and C–O stretchings, respectively, which corroborates the existence of carboxyl groups in the functionalized MWNT.

3.1 Preparation of the c-MWNT immobilized capillary

The challenge of this work was to obtain a c-MWNT immobilized capillary as the sorbent properties of the nanostructures made them especially attractive for this aim. The immobilized capillary was prepared taking advantage of a previously described procedure in which c-CNT were immobilized on controlled-pore glass for its application in solid-phase extraction [13].

The electroosmotic mobility (μ_{eof}) of the immobilized capillary was $(38 \pm 1) \times 10^{-5}\,cm^{-2}\,V^{-1}\,s^{-1}$. This result indicates that the immobilized capillary was negatively charged because of the carboxylic groups of the c-MWNT. The comparison of this value with that obtained for a bare fused-silica capillary, $(67 \pm 1) \times 10^{-5}\,cm^{-2}\,V^{-1}\,s^{-1}$, pointed out that the net negative charge in the inner surface of the bare capillary should be higher than that of the immobilized one. Probably, this is due to the presence of residual unreacted amino groups. It is important to remark that higher concentrations of c-MWNT in the immobilization step or an increase in the immobilization time had a negligible effect on the electroosmotic flow. The electrophoretic behaviour was evaluated as a function of the pH within the interval 7–10. As can be seen in Fig. 3, the electroosomotic flow increased with increasing pH values as the likely result of the higher concentration of charged carboxylic groups of the

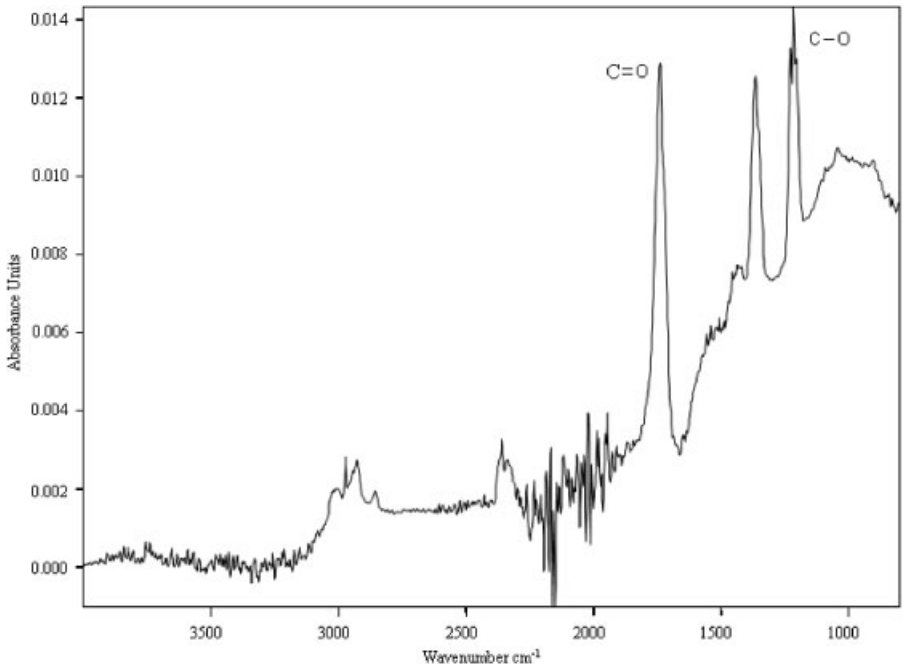

Figure 2. IR spectra obtained for the c-MWNT used in the functionalization of the inner surface of the capillary.

c-MWNT on the inner surface of the capillary. That increase was lower than that typically observed for a bare fused-silica capillary, which corroborates the differences observed in the $\grave{\imath}_{eof}$ for both capillaries. It was expected that the interactions between the analytes and the surface of the capillary were of electrostatic nature by means of hydrogen bond interactions and interactions between the analytes and the surface of the c-MWNT. The predominance of one or another will depend on the nature of the analytes.

The c-MWNT immobilized fused-silica capillary and the capillary treated with the above-mentioned procedure without the addition of c-MWNT in the last step were compared. Probably, in absence of c-MWNT, the inner surface of the capillary should be neutral. On one hand, 1,3-dicyclohexylcarbodiimide cannot activate the aldehyde groups present in the capillary introduced by the addition of glutaraldehyde. On the other hand, 1,3-dicyclohexylcarbodiimide could react with unreacted amino groups in the inner surface of the capillary. Probably, the heterogeneity of the capillary coating resulted in the instability of the baseline and current losses. Thus, the resolution of the mixture of analytes was ascribed to the c-MWNT coating of the capillary and not to any other compound used in the pretreatment of the capillary.

3.2 Electrophoretic separation

The performance of the c-MWNT immobilized fused-silica capillary was evaluated using a mixture of non-steroidal anti-inflammatory drugs, β-lactams antibiotics and chloramphenicol. Those compounds were selected considering their widespread use.

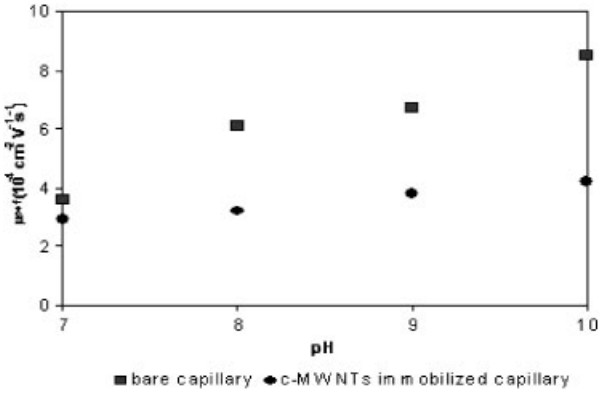

Figure 3. Influence of the pH on the electrophoretic mobility of the electroosmotic flow with the c-MWNT immobilized fused-silica capillary.

Table 1 presents the electrophoretic characteristics of the c-MWNT coated fused-silica capillary. As can be seen, good separation efficiencies were obtained for all the analytes. The retention factors obtained for the analytes were also higher than those of the bare fused-silica capillary (between 0.24 and 0.65) with satisfactory resolution factor values. Electrophoretic mobilities are also given in Table 1. Such results reflect that the incorporation of c-MWNT in the fused-silica capillary resulted in an enhancement of its electrochromatographic characteristics. Taking into account the nature of the target analytes, the electrophoretic conditions and the results obtained, we concluded that the interactions that took place inside the immobilized capillary were between the hydrophobic moiety of the analytes and

Table 1. Comparison of number of theoretical plates, *N*; retention factor, *k'*; resolution, *R*; and electrophoretic mobilities of the c-MWNT immobilized fused-silica capillary

	Number of theoretical plates, *N* (plates/m)	Retention factor, *k'*	Resolution, *R*	Electrophoretic mobility ($\times 10^5$ cm^2 s^{-1} v^{-1})
Chloramphenicol	5087	0.46		11.9 ± 0.6
$R_{clor--pip}$			7.40	
Piperacillin	25 830	0.73		16.0 ± 0.5
$R_{pip--clox}$			7.55	
Cloxacillin	36 692	0.92		18.0 ± 0.4
$R_{clox--amp}$			3.52	
Ampicillin	46 719	0.99		19.0 ± 0.5
$R_{amp--pen}$			2.24	
Penicillin G	41 847	1.04		19.5 ± 0.3
$R_{pen--amox}$			4.35	
Amoxicillin	77 140	1.13		20.1 ± 0.3
$R_{amox--ket}$			7.45	
Ketoprofen	61 175	1.28		21.2 ± 0.3
$R_{ket--flur}$			5.04	
Flurbiprofen	56 815	1.39		22.0 ± 0.1

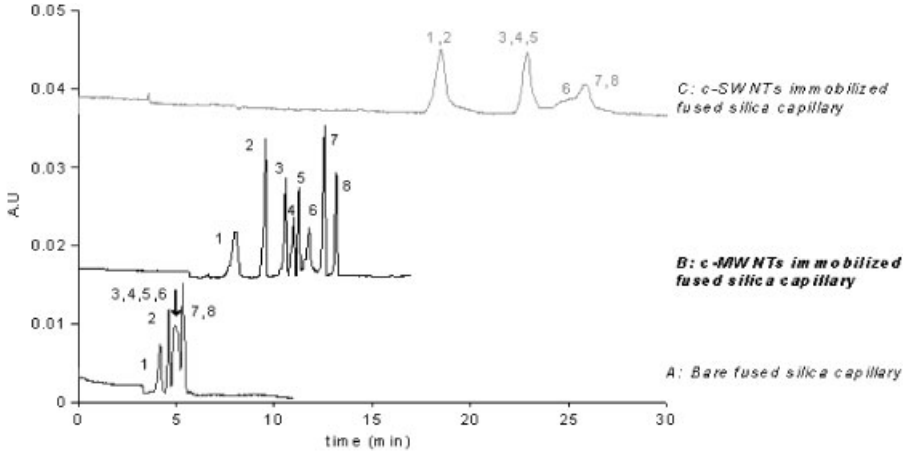

Figure 4. Comparison of the electrophoretic behaviour of a mixture of 1: chloramphenicol, 2: piperacillin, 3: cloxacillin, 4: ampicillin, 5: penicillin G, 6: amoxicillin, 7: ketoprofen and 8: flurbiprofen (10 mg/L each except flurbiprofen, which is 5 mg/ L) using a bare fused-silica capillary (A) and (B) with the c-MWNT immobilized fused-silica capillary. AU: arbitrary units.

the surface of the CNT. Despite the lower intensity of these interactions, compared with electrostatic interactions or hydrogen bonds, in this case, they were selective enough for the separation of the target analytes.

Figure 4 compares the electropherograms obtained for a mixture of the target analytes with a bare fused-silica capillary (Fig. 4A) and with the c-MWNT coated fused-silica capillary (Fig. 4B) under the same conditions (40 mM borate buffer at pH 9.0 and 15 kV). As can be seen, the coating of the capillary allowed the separation of the analytes with high resolution without band-broadening and without distortion of the baseline. The interactions between the analytes and the c-MWNT resulted in an increase of the migration time and probably this is the reason for the front tailing effect observed in Fig. 4. As it was expected, a worse separation was achieved with the unmodified capillary (see Fig. 4A).

In an attempt to a better understanding of the electrophoretic system, the effect of pH and BGE composition were also studied. Figure 5 shows the dependence of the resolution for β-lactams antibiotics as a function of the concentration of boric acid in the BGE and the pH. The dotted line indicates the threshold resolution value at which analytes are separated. The resolution of β-lactams antibiotics strongly depends on the pH (Fig. 5A) as their migration times were very similar. As can be seen, pH 9.0 was the optimum value to achieve the complete resolution. The variation of the resolution factor with the concentration of boric acid is depicted in Fig. 5B. Separation was achieved at concentrations higher than 30 mM (pH 9.0), because at this value penicillin G and amoxicillin were only partially resolved. Thus, with 40 mM of boric acid a complete baseline separation could be obtained. The effect of voltage was also studied, and the results showed that 15 kV was the optimum value.

The analytical parameters for the target analytes with the c-MWNT immobilized fused-silica capillary were

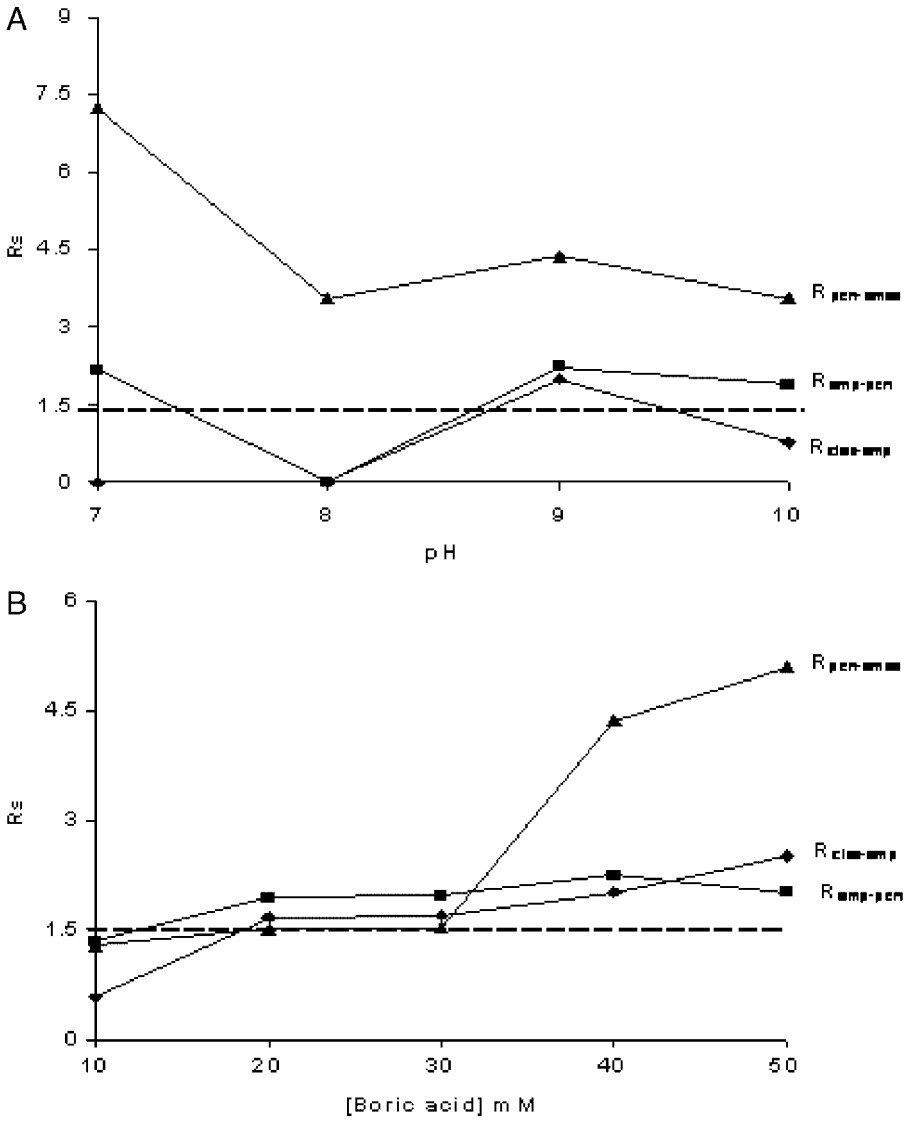

Figure 5. Resolution values (R_s) obtained for cloxacillin and ampicillin ($R_{clox--amp}$), ampicillin and penicillin G ($R_{amp--pen}$) and penicillin G and amoxicillin ($R_{pen--amox}$) as function of the pH and boric acid concentration in the BGE. The concentration of the β-lactams antibiotics was 10 mg/L. The dotted line indicated the threshold value for the baseline separation.

calculated and are listed in Table 2. The presence of c-MWNT in the capillary resulted in a decrease in the limits of detection (LODs) with respect to those obtained with optimized methods described in the literature. By way of example, detection limits published are 0.39 mg/L (chloramphenicol), 1.43 mg/L (piperacillin), 0.36 mg/L (cloxacillin), 0.93 mg/L (ampicillin), 0.91 mg/L (penicillin G), 0.82 mg/L (amoxicillin), 0.34 mg/L (ketoprofen), 0.62 mg/L (flurbiprofen) [16, 17]. Probably, the improvement in the LODs can be attributed to an improvement on the peak shape as narrower electrophoretic peaks were obtained using c-MWNT immobilized fused-silica capillary.

Besides, a comparison of the performance of c-SWNT as stationary phase was also carried out. The electropherogram obtained for a mixture of all the analytes is shown in Fig. 4C. As can be seen, an excessive increase in the migration time was obtained, which indicated higher interactions between the analytes and the c-SWNT coated capillary with a great worsening on the resolution. Thus, c-MWNT provided better results than c-SWNT under the conditions studied.

3.3 Reproducibility and stability

The reproducibility and stability of the electrophoretic system were evaluated. Firstly, the reproducibility between runs and days was tested for all the analytes (10 mg/L). Figure 6A and B shows the run-to-run ($n = 5$) and day-to-day ($n = 10$) RSD values obtained for the migration times and peak areas. Concerning the migration times, the precision was acceptable as it was close to 1% in both conditions. In the case of the peak areas, the values were also satisfactory and no differences were found between these values and the RSD values reported by other CE modalities.

Table 2. Analytical parameters obtained with the c-MWNT immobilized fused-silica capillary

	$a \pm s_a$	$b \pm s_b$ (mg/L)	R^2	$S_{x/y}/b$	LOD (mg/L)	LOQ (mg/L)
Chloramphenicol	0.01 ± 0.07	0.381 ± 0.002	0.999	0.2004	0.12	0.60
Piperacillin	0.02 ± 0.01	0.346 ± 0.004	0.998	0.3646	0.24	0.60
Cloxacillin	0.05 ± 0.02	0.379 ± 0.008	0.992	0.7490	0.13	0.60
Ampicillin	0.04 ± 0.01	0.270 ± 0.005	0.995	0.4317	0.16	1.00
Penicillin G	0.04 ± 0.05	0.243 ± 0.002	0.999	0.1593	0.30	1.00
Amoxicillin	0.02 ± 0.06	0.217 ± 0.002	0.998	0.1893	0.27	1.50
Ketoprofen	0.02 ± 0.03	0.427 ± 0.001	0.993	0.4767	0.09	0.50
Flurbiprofen	0.05 ± 0.02	1.100 ± 0.010	0.998	0.6526	0.05	0.20

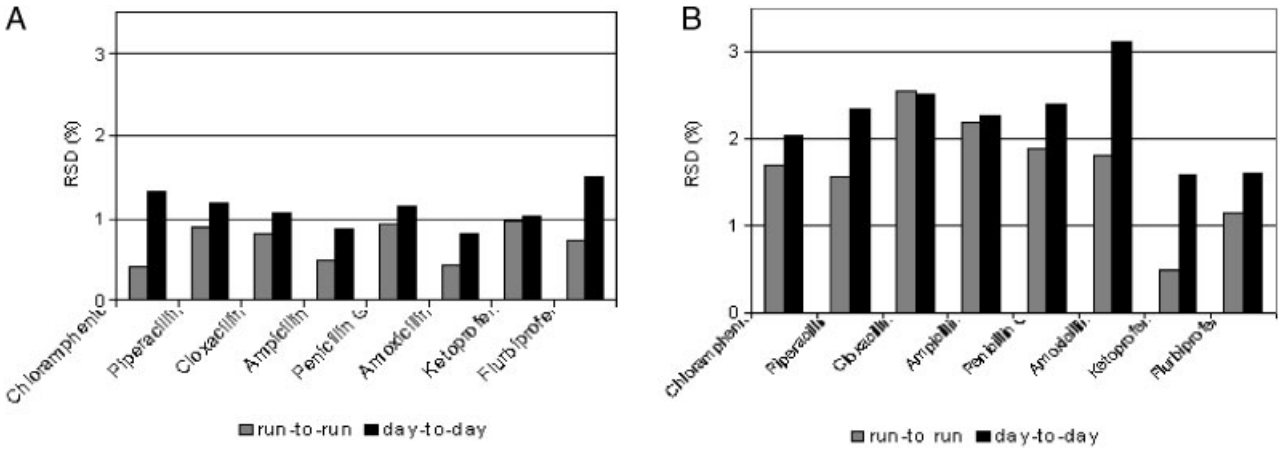

Figure 6. Reproducibility data, RSD (%); for the c-MWNT immobilized fused-silica capillary (A) run-to-run and (B) day-to-day for a mixture of all the analytes (10 mg/L).

After the injection of ca. 60 standards, it was observed that the electrophoretic mobility of the EOF increased and the resolution decreased. In order to check this behaviour, three different c-MWNT immobilized capillaries were prepared. The results showed that they were stable for 60 ± 8 injections with negligible variation in the quantitative/qualitative parameters studied. It can be ascribed to the fact that the binding between the c-MWNT and the activated inner surface of the capillary was negatively affected by the consecutive application of the electric field. Thus, in order to extent the lifetime of the c-MWNT immobilized fused-silica capillary, the possibility of including a regeneration step was investigated. It was demonstrated that the capillary was completely regenerated by passing through it a fresh solution of c-MWNT during 30 min. The RSD values for the migration times and peak areas after three regenerations obtained for a mixture of the analytes (10 mg/L) were between 0.70 and 1.24 and 1.00 and 3.64 ($n = 15$), respectively. Moreover, we studied the variations on the resolution of amoxicillin, ampicillin, penicillin G and amoxicillin as their separation was more critical than for the other analytes. The RSD values for resolution were 7, 5 and 5% ($n = 15$) for $R_{\text{clox}--\text{amp}}$, $R_{\text{amp}--\text{pen}}$ and $R_{\text{pen}--\text{amox}}$, respectively. In addition, these analytes were completely separated in all cases. The capillary can be used for at least 6 months including the regeneration step every 60 injections.

Finally, the capillary-to-capillary repeatability was also evaluated. The RSD obtained for the migration times of all the analytes (10 mg/L) were between 1.85 and 3.00%. Although these values are higher than those accepted for the migration time (1%), it cannot be considered a limitation of the c-MWNT immobilized capillaries, as the separation of the mixture was always complete. The relative standard deviations of the resolution of a mixture of β-lactams antibiotics (10 mg/L each) measured in three different capillaries ($n = 30$) were 10, 14 and 6% for $R_{\text{clox}--\text{amp}}$, $R_{\text{amp}--\text{pen}}$ and $R_{\text{pen}--\text{amox}}$, respectively. Therefore, this fact suggested that although variation in the migration times can be produced, the resolution capability of the c-MWNT immobilized in the inner capillary surface remained inalterable.

3.4 c-MWNT immobilized stationary phase: a practical approach

To demonstrate the applicability of the c-MWNT immobilized fused-silica capillary, three pharmaceutical preparations containing amoxicillin, ketoprofen and chloramphenicol and commercialized under different presentations were analysed. The content of each pharmaceutical was determined by three independent determinations.

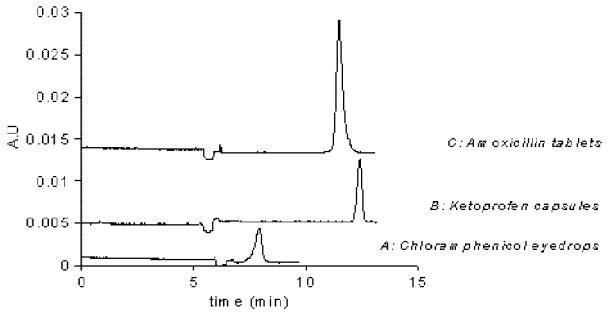

Figure 7. Electropherograms obtained for the pharmaceutical formulations analysed: (A) 5 mg/mL of Chloramphenicol (eyedrops solution), (B) 50 mg of ketoprofen (capsules) and (C) 750 mg of amoxicillin (tablets). AU: arbitrary units.

Table 3. Results obtained for the pharmaceutical preparations

Labelled	Found	Recovery (%)	RSD (%)
Amoxicillin (750 mg)	743 ± 9 mg	96 ± 2	1.2
Ketoprofen (50 mg)	47 ± 1 mg	94 ± 3	2.1
Chloramphenicol (5000 mg/L)	4663 ± 181 mg/L	93 ± 3	3.9

Figure 7A–C shows the electropherograms for 5 mg/mL of chloramphenicol (eyedrops solution), 50 mg of ketoprofen (capsules) and 750 mg of amoxicillin (tablets), respectively. Table 3 presents the results obtained for each sample using the immobilized capillary with c-MWNT and the comparison with the content specified by the manufacturer. The concentration found for each compound using the proposed methodology was satisfactory and in accordance with the labelled content. The recovery values were between 93 and 96% ($n = 3$) and are in good agreement with the tolerances allowed in pharmaceutical analysis. The RSD values are also given in Table 3 being acceptable in all instances.

4 Conclusions and future trends

The recently published papers using CNT as analytical tools in the different modalities of CE show the potential of those carbon nanostructures to enhance the features of this technique. This is the aim of the present paper, in which we have developed a promising c-MWNT immobilization procedure on fused-silica capillaries in a rapid and simple way.

We have investigated the electrophoretic features of the novel c-MWNT immobilized fused-silica capillary by covalent modification of the inner surface of the capillary.

Good run-to-run, day-to-day and capillary-to-capillary reproducibility have been obtained. In addition, we have demonstrated that the regeneration of the functionalized capillary allows its reusability for at least 6 months. Finally, its applicability for quality control in pharmaceutical analysis has been demonstrated.

It contributes to open new doors to the development of novel stationary phases for the achievement of better analytical performance in capillary electrochromatography. By way of example, other carbon nanostructures can confer to capillaries' new and different interactions that could also improve electrophoretic separations. Anyway, further investigations must be done to a better knowledge of these new stationary phases.

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The authors have declared no conflict of interest.

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