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Coated capillaries with highly charged polyelectrolytes and carbon nanotubes co-aggregated with sodium dodecyl sulphate for the analysis of sulfonyleureas by capillary electrophoresis

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Sulfonyleureas (SUs) are one of the most widely used herbicides to control weeds in crops. Herein, capillary electrophoresis (CE) was used to determine four sulfonyleureas in natural waters, namely chlor-sulfuron (CS), iodosulfuron methyl (IM), metsulfuron methyl (MSM) and mesosulfuron methyl (MSS). First of all, a bare silica capillary was chosen with 10 mM of 1-butyl-3-methylimidazolium tetrafluoro-borate (bminBF₄) as electrophoretic buffer (pH 9.6) containing 2 mg L⁻¹ of surfactant-coated single-wall carbon nanotubes (SC-SWCNTs). A dramatic deviation in migration times was observed. Therefore, a poly(diallyldimethylammonium) chloride (PDADMAC) statically coated cationic capillary was used to improve repeatability and to alter the selectivity of the separation. The electroosmotic flow (EOF) measurement revealed that the SC-SWCNTs were strongly adsorbed at the surface of the PDADMAC coating even in the absence of the surfactant-coated nanotubes in the electrolyte buffer. Consequently, a stable strong cathodic EOF and excellent repeatabilities were obtained with relative standard deviations (RSDs) on migration times and on corrected peak areas below 0.9 and 1.5%, respectively. The separation of the SUs was conducted in only 6 min. No regeneration of the coating between analyses was necessary, and high peak efficiencies up to 173,000 theoretical plates were obtained. The bi-layer coating was subsequently used to analyze sulfonyleureas in tap water, in several mineral waters as well as in underground waters spiked with SUs and directly injected into the CE capillary.

1. Introduction

Sulfonyleureas (SUs) are a family of environmentally compatible herbicides that were discovered by crop protection in 1975. They are one of the most important classes of pesticides which have been used worldwide for the control of many grasses [1–4]. Their use developed rapidly because of their low application rates, low toxicity to mammals and herbicidal activity. Nevertheless, the intensive application of these SUs has resulted in the contamination of the environment (water, soil, agricultural products, etc.) [5,6]. Various analytical techniques have been used for the determination of SUs in these different matrices [7]. Due to their polar characteristics, low volatility and thermal instability, SUs cannot

be directly analyzed by gas chromatography (GC) [8]. As a result, high performance liquid chromatography (HPLC) has been widely used for the determination of SUs [9–11]. Capillary electrophoresis (CE) showed several advantages for studying SUs such as faster separation, better resolution, lower detection limits and lower solvent consumption. Usually, sulfonyleureas are separated with background electrolytes (BGE) at a pH of 4.8 (acetate buffer) or 8 (borate buffer) [12–16]. Sometimes it is necessary to add chemical compounds (organic solvents, dispersed nanoparticles or ionic liquids) to the separation buffer to improve the electrophoretic resolution [17,18]. Moreover, ionic liquids (ILs) have been recognized as appropriate BGE in CE. Stalcup and co-workers [19] first reported using 1-ethyl-3-methylimidazolium (EMIM) ILs for the analysis of polyphenols. They considered that the separation mechanism involved interactions between the imidazolium cations of the IL and the polyphenols. Using 1-butyl-3-methylimidazolium-based ILs in the BGE has also been proved to be very efficient for the analysis of hydrophobic dyes [20] or bioactive herbs [21]. Since 2003, the number of research papers on the use of carbon

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nanotubes in CE has steadily risen [22,23]. A single-wall carbon nanotube (SWCNT) can be described as a sheet of graphene rolled into a hollow cylinder of carbon atoms. CNTs are characterized by remarkable physicochemical properties including an excellent structural rigidity, a large surface area, a high thermal conductivity and usually chemical inertness. Carbon nanotubes noticeably tend to aggregate and are intrinsically hydrophobic, which hinders their straightforward use as buffer additive in CE. Several methodologies may be used for nanotube dispersion [24]. The oxidation of carbon nanotubes in concentrated acids can lead to surface functionalization with carboxyl, carbonyl, or hydroxyl moieties. However, this treatment results in cutting the carbon cylinders into shorter pieces named carboxylic or carboxylated nanotubes. A straightforward alternative is to non-covalently adsorb onto the nanotubes various compounds including cationic polymers such as poly(diallyldimethylammonium chloride) or PDADMAC, anionic polymers such as poly (sodium 4-styrenesulfonate) or PSS [25,26], carbohydrates [27] and particularly surfactants such as sodium dodecyl sulphate (SDS) [28–30]. In this case, mild ultrasonic agitation is necessary to achieve the wrapping and separation of each individual nanotube. These non-covalent methods are preferred for most applications since they preserve the intrinsic structure and properties of the nanotube.

Upon addition of dispersed carbon nanotubes to the BGE, novel interaction sites for the analytes may be created and the selectivity may be altered [17,22,31]. The interaction mechanism is not completely understood. It certainly depends on the nature and the concentration of the functionalized nanotubes [22,32], the BGE properties (e.g. pH, presence of polymers or surfactants or organic solvents [23,33]) and the analyte structure [34]. Moreover, the compatibility with the detection system, particularly UV and fluorescence, limits the maximum amount of nanotubes that can be added to the BGE. For example, the maximum concentration for SDS-coated SWCNTs and Multi-wall carbon nanotubes (MWCNTs) [30] is 3.2 mg L^{-1} while it is 20 mg L^{-1} for carboxylated Multi-WNTs [35].

The use of charged polyelectrolytes for capillary coating has become popular in CE to prevent analyte adsorption and to control the electroosmotic flow (EOF) [36–38]. The polyelectrolytes may be adsorbed onto the capillary *via* electrostatic, hydrogen and hydrophobic interactions [39–41] resulting in a high charge on the capillary wall. Since the silanol groups are anionic, cationic polyelectrolytes such as PDADMAC may be used. This engenders reversion of the EOF. Physical adsorption of these cationic polymers can be obtained by a static or a dynamic approach. With the static approach, the coating of the capillary is performed before the analysis by simply rinsing with the coating solution. This approach is generally preferred to the dynamic approach where the coating agent is added to the separation electrolyte since this may alter the selectivity. Katayama et al. [41,42] introduced in 1998 successive multiple ionic polymer layer (SMIL) coating in CE, in which “a cationic polymer is sandwiched between an anionic polymer and the uncoated negative fused-silica capillary by noncovalent bonding”. This approach is simple and versatile since a wide variety of cationic and anionic compounds may be used.

Luong et al. [43] used for the first time silica capillaries non-covalently coated with a PDADMAC/carboxylated-SWCNT double layer to improve the selectivity of the analysis, allowing a baseline separation of a mixture of aniline derivatives. To our knowledge, there is only one publication that employs Surfactant-Coated-SWCNTs for the determination of SUs [44]. In this recent study, Lista et al. [44] used SWCNTs as an additive in the BGE to improve the resolution of the SUs in bare silica capillaries. Herein, a new approach is proposed for the separation of the four SUs, namely chlorsulfuron (CS), iodosulfuron methyl (IM), metsulfuron methyl (MSM) and mesosulfuron methyl (MSS). The interest of using coated capillaries to determine these compounds was evaluated. The

stability, the homogeneity and the efficiency of using carbon nanotubes for coating silica capillaries in CE were evaluated by monitoring EOF magnitude and direction, peak efficiency and asymmetry as well as analysis repeatability.

2. Materials and methods

2.1. Chemicals and materials

Acetonitrile (ACN), dimethyl sulfoxide (DMSO), orthophosphoric acid (purity 85% (w/w) in water), sodium hydroxide (purity $\geq 98\%$) and methanol (MeOH) were purchased from Fluka (St.-Quentin-Fallavier, France). 2-butanol, 1-butyl-3-methylimidazolium tetrafluoroborate, chlorsulfuron (CS), iodosulfuron methyl (IM), metsulfuron methyl (MSM), mesosulfuron methyl (MSS), anhydrous magnesium chloride (MgCl_2), poly(diallyldimethylammonium chloride) (PDADMAC, 20% (w/w) in water, high molecular weight ($\sim 4.10^5$ – 5.10^5), sodium dodecyl sulfate (SDS), sodium tetra-borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, purity $\geq 99.5\%$), single-walled carbon nanotubes (SWCNTs) with an average diameter of 0.6–1.1 nm (purity $> 95\%$) and α, α, α -Tris-(hydroxymethyl)-methylamine (TRIS) were purchased from Sigma–Aldrich (Lyon, France). The mineral waters were purchased from a local supermarket. The underground waters were from Guyana and were provided by BRGM (Bureau de Recherches Géologiques et Minières).

All reagents were of analytical grade and were used as received. Ultra-pure water ($18 \text{ M}\Omega \text{ cm}$) was produced from an Elgastat apparatus (Elga, Villeurbanne, France). Syringes and polyvinylidenedifluoride (PVDF) Millex-HV Syringe Filters, pore size $0.45 \mu\text{m}$, were purchased from Millipore (Molsheim, France).

2.2. Solutions

Carbon nanotube dispersion was performed according to the literature [45] to obtain surfactant-coated-SWCNTs (SC-SWCNTs). For this, 1 mg of SWCNTs was dispersed in a 100 mL of SDS at 17.5 mM containing 10% v/v of 2-butanol by using an ultrasonic bath (20 min). The background electrolyte solution was initially composed of 10 mM 1-butyl-3-methylimidazolium tetrafluoroborate and 2 mM borate. The effect of introducing 3.5 mM SDS or 2 mg L^{-1} SC-SWCNTs in the separation buffer was also evaluated. Unless otherwise stated, the pH of the BGE was 9.6. These solutions were stable for a week.

Individual stock solutions of sulfonylureas (SUs) were prepared in methanol at a concentration of 1000 mg L^{-1} . Individual and mixed test solutions for analysis were obtained by appropriate dilution of the stock solutions in water.

The PDADMAC coating solution was prepared by dissolving the cationic polyelectrolyte at a concentration of 0.2% (w/v) in a 20 mM TRIS aqueous solution adjusted to pH ~ 8.3 with orthophosphoric acid. The ionic strength (I) was set to 1.5 M by MgCl_2 addition. Coating solutions were used within one week and stored at 4°C when not in use. The EOF marker solution was a 0.05% (v/v) DMSO solution in water.

2.3. Instrumentation and operating conditions

CE analyses were performed using a P/ACE™ MDQ Capillary Electrophoresis System (Beckman Coulter, San Jose, CA, USA) equipped with a photodiode array detection system. MDQ software provided by Beckman (GOLD, v 2.3) was used to pilot the CE, for signal acquisition and for data treatment. CE analyses were performed in a fused-silica capillary (60.2 cm total length, 50 cm effective length, $75 \mu\text{m}$ i.d.) purchased from Polymicro Technologies (Phoenix, AZ, USA). The capillary temperature was 25°C . All rinse cycles were carried out at 50 psi. Separation was realized at

+25 kV (normal polarity). The BGE solution in the separation vials was renewed every three runs. Hydrodynamic injections were performed at 1 psi during 5 s (~56 nL). The UV detection was performed at 240 nm (bandwidth 10 nm). The CPA represents the peak area of an analyte which has been divided by the corresponding migration time. The relative standard deviation (RSD) on corrected peak areas and on migration times was used to assess repeatability. "n" is the number of repeated injections.

New capillaries were conditioned by rinsing with NaOH 1 M (15 min) and water (5 min). For the capillaries statically modified by the highly cationic charged PDADMAC, a 10 min rinsing step with the coating solution was then conducted [46]. This layer of PDADMAC was strongly attached to the silanol groups with no need for regeneration. Subsequently, PDADMAC-coated capillaries were dynamically modified with the SC-SWCNTs contained in the corresponding separation buffer to obtain the bi-layer coated capillaries.

Between two runs, bare-silica capillaries were flushed with 1 M NaOH (4 min), water (1 min) and BGE (4 min) whereas coated capillaries were only rinsed with the BGE (4 min). At the end of each working day, uncoated capillaries were rinsed with NaOH (10 min) and water (10 min) to ensure good cleaning of the inner capillary surface while coated capillaries were only rinsed with water (10 min). Capillaries were stored overnight in water.

2.4. Calculations

The selectivity (S) of the separation and the resolution (R_s) were calculated by using Eqs. (1) and (2), respectively:

$$S = \frac{\Delta\mu_{\text{eff}}}{\bar{\mu} + \mu_{\text{eof}}} = \frac{\mu_A - \mu_B}{\bar{\mu} + \mu_{\text{eof}}} \quad (1)$$

where $\Delta\mu_{\text{eff}} = \mu_A - \mu_B$ is the difference in effective mobility of two SUs, $\bar{\mu} = 1/2(\mu_A + \mu_B)$ the average effective mobility of two SUs and μ_{eof} is the mobility of the EOF.

$$R_s = 2 \frac{(t_2 - t_1)}{(\omega_2 + \omega_1)} \quad (2)$$

where t_1 and t_2 are the migration times, and ω_1 and ω_2 the peak widths at baseline of the SUs.

3. Results and discussion

3.1. Development of the CE method in bare silica capillaries

Four sulfonylureas were analyzed during this study (Fig. 1). Their pK_a values are between 3 and 5 [47]. The BGE was composed

of the ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate (bminBF4) and borate at pH 9.6. It was chosen by taking into account the interesting recent study by Lista et al. [44]. In the present work, interactions between imidazolium of bminBF4 and the negatively charged analytes were expected to improve SU separation. However, the resolution of the four SUs could not be obtained in these conditions. Adding 3.5 mM SDS to the BGE engendered satisfactory peak resolution, ranging between 1.6 and 2.4 (at 0.5 mg L⁻¹ concentration). This is certainly due to an additional hydrophobic interaction between SDS and the analytes. The migration order was: MSS, MSM, CS and IM. The analysis time was only 6 min. The peaks were symmetrical (asymmetry ~0.91; $n=3$) and high efficiencies of about 150,000 theoretical plates were obtained. However, a significant drift of the baseline was observed as well as of the migration times by about 5.5% after only 6 analyses despite rinsing between analyses for 4 min with NaOH 1 M. Working at higher pH 11 did not improve migration time reproducibility.

Adding SDS-coated carbon nanotubes to the BGE may be very advantageous since new interaction sites for the SUs may be created, thus improving the robustness of the analytical system. Good solubility of the SC-SWCNTs can be expected in bminBF4 due to the interaction between imidazolium cations of the latter and the π -electron network of the nanotubes. Lista et al. [44] considered that a novel interaction between the SUs and the SC-SWCNTs was responsible for peak resolution. In this work, we found that peak resolution was mainly due to the presence of SDS, either free in the BGE or fixed to the SWCNTs. Indeed, low selectivity values, ranging from 0.014 to 0.025 were noticed in the presence of SC-SWCNTs. These selectivities as well as peak resolution were similar to those previously obtained with the BGE containing only SDS with no SWCNTs. The migration order of SUs was unaffected, as was the analysis time of 6 min. High efficiencies of 110,000 theoretical plates were obtained. The peaks obtained were symmetrical (asymmetry $\sim 0.97 \pm 0.05$; $n=10$). The repeatability of migration times and of corrected-peak areas was significantly improved ($RSD_{tm} \sim 1.5\%$ and $RSD_{CPA} \sim 3.6\%$; $n=10$). From these results one can conclude that the advantage of adding SDS-coated carbon nanotubes in the BGE is to improve the robustness of the separation method. However, the carbon nanotubes did not improve the selectivity in the present study.

An attempt to decrease rinse times between analyses (particularly with NaOH) and to further improve the robustness of SU analysis was made. For this, the inner capillary wall was statically coated with the cationic polymer PDADMAC to enhance the stability of the EOF. Moreover, since it is well established that adding carbon nanotubes to the BGE in CE is limited by

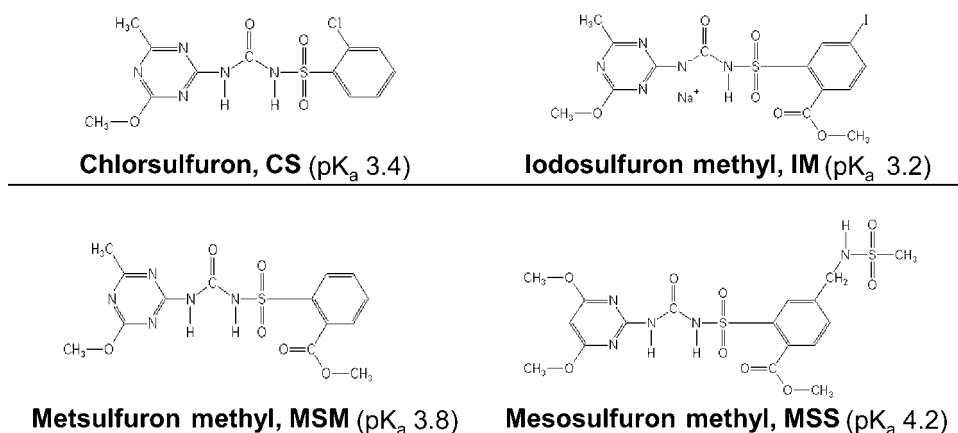


Fig. 1. Structures and pK_a values [47] of the studied sulfonylureas.

their solubility and by possible interferences with the detection system due to their black color, some alternative approaches were evaluated.

3.2. Sulfonylurea analysis in coated silica capillaries

As mentioned above, the use of PDADMAC coated capillaries is expected to improve the reproducibility of the analyses by controlling the EOF [46] without needing long rinses with NaOH 1 M between runs. The analysis time will also be probably reduced since the analytes have an anodic mobility (pH of the BGE higher than the pK_a of the SUs) in the same direction as the EOF.

The capillary was statically coated by rinsing with a 0.2% (w/v) aqueous solution of PDADMAC, containing 1.5 M $MgCl_2$. No PDADMAC was added to the BGE to avoid interactions with the anionic SUs and/or SDS. When using bminBF₄ and borate as BGE (pH 9.6), the PDADMAC layer was unstable due to the high pH of the BGE [48]. However, a rinse step between analyses of only 1 min with the coating solution was sufficient to obtain a stable strong anodic EOF: $\mu_{eof} = -5.10 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($RSD_{\mu_{eof}} = 1.2\%$; $n = 10$). The SUs were detected in this monolayer coated capillary by applying -25 kV (i.e. reverse polarity). The analytes migrate fast (analysis time of 3 min versus 6 min in uncoated capillary) and poor resolution was obtained. To improve resolution, SDS was added to the BGE at 3.5 mM. In these conditions, SUs were detected only by using normal polarity (+25 kV). In fact, EOF measurements revealed that the anionic SDS contained in the BGE was dynamically adsorbed to the cationic PDADMAC despite its low concentration. Consequently, the EOF was again cathodic. Its intensity was only $+2.34 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ showing that the cationic charges of the PDADMAC mono-layer ($\mu_{eof} = -5.10 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; see above) were not overcompensated as expected in the formation of successive multiple ionic-polymer layer (SMIL) coatings [49]. The repeatability, the peak shape as well as the resolution were not acceptable, showing that the coating PDADMAC/SDS was not robust and probably not homogeneous. Indeed, SDS molecules are only mono-charged which leads to weak electrostatic interactions with PDADMAC.

The SC-SWCNTs were then added to the BGE and the capillary was rinsed with this solution for 10 min. A very stable coating was dynamically obtained on the capillary surface that was already statically coated with PDADMAC. This can be attributed to electrostatic interactions between on the one hand the quaternary amine of the PDADMAC and on the other hand the anionic charge of the numerous SDS adsorbed onto the carbon nanotubes as well as the π -electron network of the nanotubes. It is known that carbon nanotubes adsorb several molecules of the anionic SDS to obtain a stable dispersion as multi-charged SC-SWCNTs [50]. Consequently, a strong repeatable cathodic EOF was measured: $\mu_{eof} = +5.30 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($RSD_{\mu_{eof}} = 0.4\%$, $n = 10$). Its intensity shows that surface charge overcompensation which is the basic principle behind the formation of SMIL coatings was respected. This was not the case when 'free' SDS was added to the BGE and used in the presence of the PDADMAC monolayer (see above). The capillary-to-capillary PDADMAC/SC-SWCNTs double layer reproducibility was excellent ($RSD_{\mu_{eof}} = 0.4\%$; $n = 4$) despite the fact that analyses were conducted in alkaline conditions (pH 9.6). When neither SC-SWCNTs nor SDS were present in the BGE, the EOF was again anodic ($\mu_{eof} = -3.60 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) showing that at least cationic PDADMAC was still adsorbed to the capillary wall. However, the intensity of the EOF measured in this case was almost 1.5 times lower than the one obtained when the capillary was properly coated with a mono-layer of PDADMAC. In order to understand this result, we tried to regenerate the double layer PDADMAC/SC-SWCNTs simply by rinsing (4 min) with the BGE containing SC-SWCNTs or with the BGE containing only

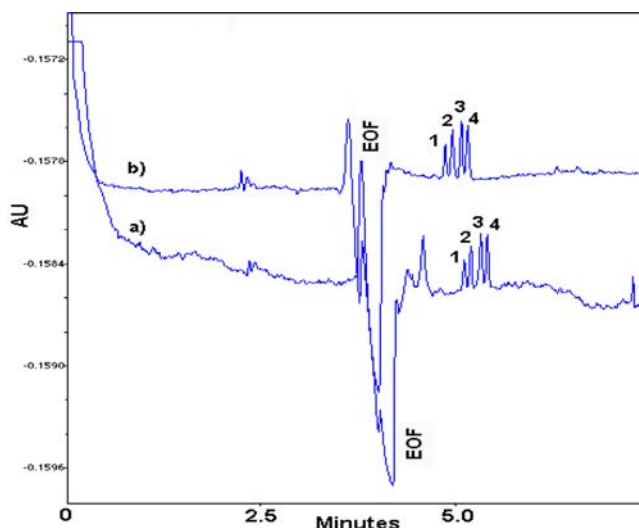


Fig. 2. Separation of standard solution of four sulfonylureas (0.5 mg L^{-1}) in PDADMAC/SC-SWCNT coated capillary. Analysis conditions: BGE (pH 9.6): 10 mM 1-butyl-3-methyl imidazolium tetrafluoroborate, 2 mM borate containing (a) 3.5 mM SDS and (b) 2 mg L^{-1} SC-SWCNTs. Injection: 1 psi \times 5 s ($\sim 56 \text{ nL}$). Separation voltage: +25 kV. Temp: 25 °C. Detection: 240 nm. Capillary: 60 cm \times 50 cm \times 75 μm i.d. Peak identification: 1, MSS; 2, MSM; 3, CS and 4, IM.

'free' SDS. Regeneration was achieved in both cases. This is very interesting since it proves for the first time that the carbon nanotubes remain strongly attached to the PDADMAC capillary coating whereas only the SDS is unattached. In other words, this study shows that the network of electrostatic interactions established between the cationic PDADMAC and the π -electrons of the SWCNTs is very strong. Indeed, several very interesting papers show that carbon nanotubes may be dispersed by PDADMAC in a stable manner [25,26].

The analysis of the SUs (Fig. 2) was conducted by using the bilayer coated capillary and a BGE containing either SC-SWCNTs or 'free' SDS. Table 1 shows that good results were obtained even in the absence of carbon nanotubes in the BGE which is very interesting to avoid potential solubility problems. When using the BGE containing SC-SWCNTs, the analysis time was short (about 6 min), the repeatability was very good ($RSD_{tm} \leq 0.9\%$ and $RSD_{CPA} \leq 1.5\%$; $n = 10$), the resolution was satisfactory (between 1.4 and 2.0, at 0.5 mg L^{-1} concentration), the peaks were symmetrical (asymmetry $\sim 0.97 \pm 0.05$; $n = 10$) and the efficiency was excellent (ranging from 140,000 to 173,000 theoretical plates). The linearity was proved for each SU ($r^2 \geq 0.992$) by plotting corrected peak areas versus SU

Table 1
Separation performance in PDADMAC/SC-SWCNTs coated capillaries.

Analyte	BGE containing SDS ($n = 10$)				
	t_m (min)	N	A_s	R_s	S
MSS	5.27 (1.1%)	121,341	0.87 ± 0.09	–	
MSM	5.37 (1.1%)	111,744	1.06 ± 0.04	1.5	0.018
CS	5.50 (1.0%)	112,230	1.02 ± 0.10	2.1	0.025
IM	5.59 (1.1%)	114,582	1.01 ± 0.03	1.4	0.017
Analyte	BGE containing SC-SWCNTs ($n = 10$)				
	t_m (min)	N	R_s	R_s	S
MSS	4.77 (0.9%)	173,033	0.97 ± 0.05	–	
MSM	4.85 (0.8%)	140,683	1.01 ± 0.05	1.5	0.015
CS	4.96 (0.9%)	147,188	0.92 ± 0.02	2.0	0.021
IM	5.04 (0.9%)	143,556	0.99 ± 0.08	1.4	0.014

N : efficiency; A_s : asymmetry; R_s : resolution; S : selectivity

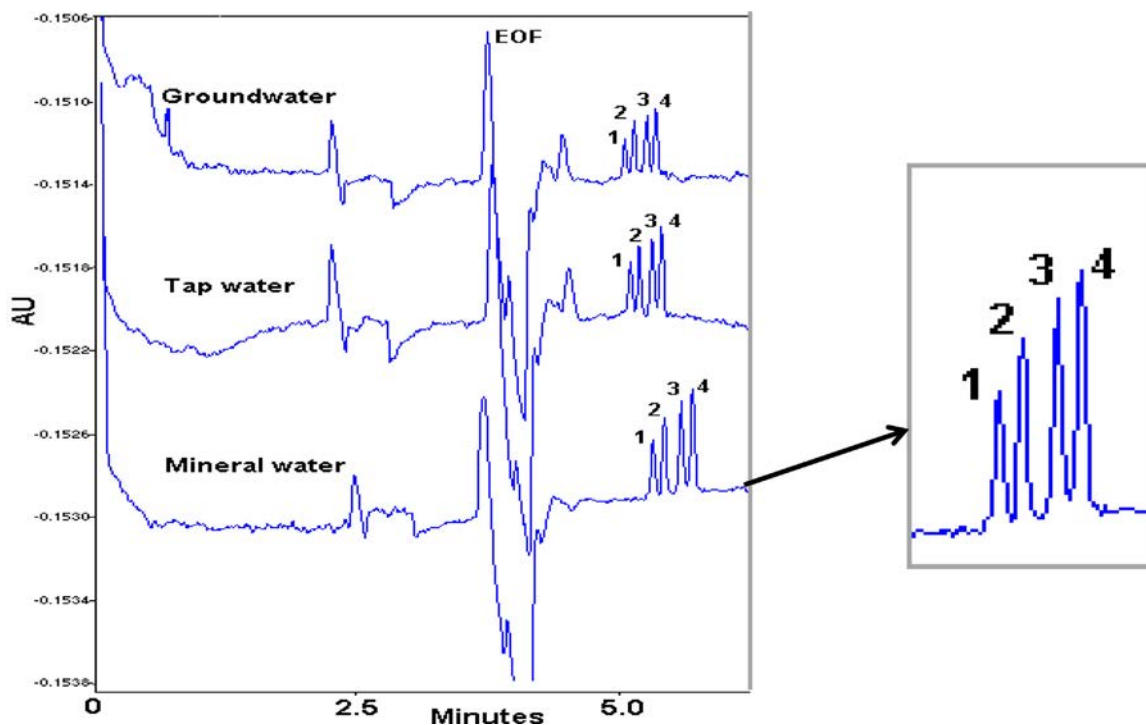


Fig. 3. Analysis of spiked natural waters in PDADMAC/SC-SWCNT coated capillary. Analysis conditions: BGE (pH 9.6): 10 mM 1-butyl-3-methyl imidazolium tetrafluoroborate, 2 mM borate containing 2 mg L⁻¹ SC-SWCNTs. SUs at 0.5 mg L⁻¹. Injection: 1 psi × 5 s (~56 nL). Separation voltage: +25 kV. T: 25 °C. Detection: 240 nm. Capillary: 60 cm × 50 cm × 75 μm i.d. Peak identification: 1, MSS; 2, MSM; 3, CS and 4, IM.

concentrations over the range 0.3–5 mg L⁻¹ at eight concentration levels. Low selectivities similar to those in uncoated capillaries were obtained, showing that no interaction occurred between the analytes and the capillary coating, particularly the adsorbed SDS. For comparison, the work by Luong et al. [43] described a non-covalent open-tubular capillary electrochromatography (CEC) with carbon nanotubes. Indeed, the presence of the carboxylated-carbon nanotubes (prepared at 50 mg L⁻¹) on the capillary wall was found to be essential for baseline resolution. In our study, SC-SWCNTs had no influence on resolution probably due to their relatively low concentration (2 mg L⁻¹) but were essential for the robustness of the developed method. Moreover, it is interesting to note that the double layer PDADMAC/SC-SWCNTs was stable in the presence of ACN as a sample solvent and even when the capillary was rinsed with ACN or MeOH for 30 min which is equivalent to about 350 times the capillary volume. EOF mobility ($\mu_{\text{eof}} = +5.10 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and peak efficiencies (ranging from 135,000 to 170,000 theoretical plates) were comparable to the values obtained before treating the capillary with these aggressive organic solvents. The presence of SC-SWCNTs in the BGE was found to be important for the robustness of the developed method since in this case inter-day deviation of SU migration times was only 1.6% (over 3 days). A higher inter-day deviation of about 4% on migration times ($n=3$) was observed when only SDS was present in the BGE. The presence of SC-SWCNTs in the BGE was therefore necessary for long-term coating stability and consequently for analysis reproducibility.

The capillary coated with the double layer PDADMAC/SC-SWCNTs was used to study natural waters spiked with SUs at 0.5 mg L⁻¹. Tap water as well as several mineral and underground waters with different contents of inorganic and small organic ions were examined. Examples of the obtained electropherograms are presented in Fig. 3. Good recovery percentages of $93 \pm 5\%$ ($n=3$) were obtained for the four SUs. A comparison with HPLC/UV analyses using a C18 or a C8 stationary phase and a mobile

phase containing ACN/H₂O (45/55 v/v) with 0.01% acetic acid was conducted. In this case, analytes were dissolved in the mobile phase. Results showed that when analyzing SUs in real samples, poor resolution and peak distortion were observed in HPLC [51] whereas only a minor influence of the matrix was observed in CE (peak efficiencies ranged from 75,000 to 97,000).

4. Conclusion

In this work, highly charged polyelectrolytes were successfully combined for the first time to carbon nanotubes, co-aggregated with SDS, to form stable homogeneous capillary coatings for CE with no need for covalent linkages with the silica wall. For this, statically PDADMAC coated capillaries were simply dynamically coated with SC-SWCNTs. The latter were found to be strongly adsorbed on the PDADMAC coating *via* electrostatic interactions.

Consequently, a new method was developed using CE to determine four sulfonylureas in natural waters, namely chlorsulfuron (CS), iodosulfuron methyl (IM), metsulfuron methyl (MSM) and mesosulfuron methyl (MSS). A very stable double layer PDADMAC/SC-SWCNTs was obtained in the presence of SDS or SC-SWCNTs in the BGE. In our study, the presence in the BGE of the SDS-SWCNTs had no influence on resolution due to their low concentration (2 mg L⁻¹) but was necessary for inter-day reproducibility. Excellent peak efficiencies greater than 110,000 theoretical plates were obtained. The CE method developed was successfully used to analyze sulfonylureas in mineral waters as well as in underground waters.

Moreover, the novel coating developed was found to be very stable at high pH (the pH of the BGE was 9.6). It also showed an excellent tolerance to aggressive organic solvents (ACN and MeOH), thus enabling its use for analyzing samples containing ACN. This shows the possibility of using these coatings in non-aqueous capillary electrophoresis.

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