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

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ABSTRACT

Sulfonylureas (SUs) are one of the most widely used herbicides to control weeds in crops. Herein, capillary electrophoresis (CE) was used to determine four sulfonylureas in natural waters, namely chlorsulfuron (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 tetrafluoroborate (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 sulfonylureas 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

Sulfonylureas (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, sulfonylureas 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 ≥ 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 (∼4.10^5–5.10^5), sodium dodecyl sulfate (SDS), sodium tetra-borate ($Na_2B_4O_7 \cdot 10H_2O$, purity ≥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 MΩ cm) was produced from an Elgastat apparatus (Elga, Villeurbanne, France). Syringes and polyvinylidenedifluoride (PVDF) Millex-HV Syringe Filters, pore size 0.45 μm, 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 μm 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