



Nano-sized anion-exchangers as a stationary phase in capillary electrochromatography for separation and on-line concentration of carboxylic acids

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ABSTRACT

Nano-sized anion-exchangers (NSAE) are promising materials in electrophoretic separation methods due to their high ion-exchange capacity, large surface-to-volume ratios, high adhesion to the quartz surface and pH-independent positive charge. In current research we describe a simple approach for NSAE synthesis, which includes two-step grinding of macroanionite followed by centrifugation. The synthesized stable aqueous suspension of NSAE particles was applied as physically adsorbed modifier of fused-silica capillary walls for CEC separation of carboxylic acids. We proposed fast and simple approach to formation of NSAE-based stationary phase on the internal fused-silica surface, which included 15 min rinsing of the capillary with diluted water suspension of NSAE. Formed physically-adsorbed coating turned out to be extremely stable in a wide range of pH (from 2 to 10). NSAE modified capillaries provided high separation efficiency ($N = 148\text{--}732 \cdot 10^3$ t.p./m) and selectivity ($R_s = 1.2\text{--}5.7$) of carboxylic acids. Simultaneous application of NSAE-modified capillaries with various on-line concentration techniques (such as field amplified sample stacking and field amplified sample injection) provided both low detection limits (up to 1–3 ng/mL) and high separation selectivity of carboxylic acids. It was useful for their quantitative determination in wines samples. Physically-adsorbed coatings based on NSAE exhibit higher selectivity and lower detection limits compared to commonly used dynamic modifier of fused-silica capillary walls - cetyltrimethylammonium bromide. NSAE-based coatings do not require equilibrium sustaining to maintain the surface coverage. It makes them appropriate for CE-MS application.

1. Introduction

Nanomaterials possess large surface-to-volume ratios and a wide variety of chemistry options, which conjecture their wide application in capillary electrophoresis (CE) [1]. NPs could improve thermal conductivity and mass transfer during the separation process, which may cause higher separation efficiency [2,3]. For example, metallic NPs, polymeric and carbon nanomaterials [6] could be used as pseudostationary phases in the CE [4–6]. However the most promising application of NPs is stationary phases in open-tubular [7] or monolith [8] capillary electrochromatography (CEC). Extraordinary high specific surface area opened for the interaction is responsible for improving separation selectivity and the CEC-column efficiency.

During the last decade the various possibilities of NPs in terms of their application as a stationary phases for CEC were reviewed [9,10]. According to Gottlicher and Bachmann [11] nanoparticles should meet

the following criteria for their successive application in electrokinetic and chromatographic separations: 1. provide analytes separation selectivity, 2. form a stable suspension, 3. to be charged in order to avoid co-elution with electroosmotic flow, 4. do not interfere the detection process, 5. provide low mass transfer resistance, 6. possess equal mobility for minimizing of overall band broadening, and 7. to be small and porous with a large surface area. The type of functional groups on the surface of NPs is responsible for the type of analytes for separation, e.g. cationic and anionic groups could provide a selective separation of anions and cations, correspondently, with predomination of ion-exchange mechanism.

The method of stationary phase preparation is of great importance in CEC and has a substantial effect on separation performance. Nowadays there are two main approaches to nanoparticles immobilization on the internal surface of the fused-silica capillary: physical adsorption and covalent bonding based on the mode of attachment

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of the coating material [12]. The most commonly used modification of the capillary wall is covalent bonding, which provides good stability, high reproducibility and moderate lifetime. But the shortcoming of covalent coatings is time-consuming implementation [13]. On the contrary, physical adsorption is a very simple procedure, but it obtains a short life-time. Thus, the development of a simple method for obtaining stable stationary phases for the CEC, which will be able to provide high efficiency and selectivity remains still an actual challenge. NPs in this regard are extremely promising.

For instance, Hutchinson et al. in [14] proposed silica monoliths coated with latex nanoparticles functionalized with quaternary ammonium groups for separation of inorganic anions in monolith IC-CEC mode. Washing the column with aqueous suspension of nanoparticles led to the pores filling and electroosmotic flow reversing. Variation of nature (phosphate or perchlorate) and concentration of the counterions allowed to control the ion-exchange interactions between the stationary phase and the analytes, which in turn allowed to regulate selectivity separation. However, such columns have significant drawbacks. In particular, silica backbone imposed for low electrolytes and its fragile nature can lead to blockages and reduced lifetime of the column. In [15] polychloromethylstyrene nanoparticles functionalized with trimethylamine were used to solve the similar problems. Bromate ions were determined in tap water on polychloromethylstyrene nanoparticles-modified capillary in combination with on-line preconcentration. The proposed method reduced the detection limits of bromate anion from 80 to 8 ng/mL.

In the current manuscript we describe the application of basic nano-sized anion-exchanger (NSAE) based on the anionite of the AB-17 type as a stationary phase in capillary electrochromatography aiming to achieve high separation efficiency and selectivity of carboxylic acids. NSAE was obtained previously by the method described in [16]. It has been already applied for creation of highly efficient columns for ion chromatography [17] and sensitive determination of heavy metals by the photoluminescence method [16]. NSAE has a high ion-exchange capacity and adhesion to the quartz surface, which makes it a perspective stationary phase for the separation of ionic analytes by CEC. The major drawback of the NSAE is their UV-adsorption in the range of analytes detection which could significantly decrease the limits of detection (LODs). To solve this problem we suggest to apply the various on-line preconcentration techniques which may provide detection of extremely low concentrations of analytes, about ppm, as in [15]. For instance, in the previous research [18], we proved that application of field-amplified sample injection on the NSAE-modified capillaries resulted in sufficient LODs decrease (up to 1–3 pg/mL) of inorganic anions.

Thus, the goal of current investigation is the application of polystyrene-divinylbenzene NPs functionalized with quaternary ammonium groups [16] as the stationary phases in CEC together with on-line preconcentration for separation of carboxylic acids. The quantitation of the later is of great importance for establishing of beverages authenticity and quality.

2. Experimental part

2.1. Reagents and solutions

Cetyltrimethylammonium bromide (CTAB) and ammonium acetate were purchased from Sigma-Aldrich (analytical grade, USA). Carboxylic acids: acetic, formic, lactic, oxalic, succinic, citric, malic and tartaric were purchased from "Reakhim" (analytical grade, Saint-Petersburg, Russia). Dimethylformamide (DMF) and diethanolamine (DEA) were purchased from "Grand" (Russia) and "Biochem chemopharma" (France), respectively. Suspension of nano-sized anion-exchanger AB-17x8 type in OH-form (NSAE) in water was prepared by [16]. The NSAE particle size was 50–250 nm, functional groups concentration was 43 mM, solid phase concentration – 18 g/L.

The stock solutions of carboxylic acids (1 mg/mL) were prepared with deionized water and were diluted before use to final concentration of 25 µg/mL.

The stock solutions of 100 mM acetate buffer pH 2, 3 and 5 were prepared by dissolving of 0.770 g of ammonium acetate in 90 mL of deionized water, adjusting the pH with acetic acid and making up the volume to 100 mL. The background electrolyte consisting of benzoic acid and DEA was prepared by mixing of 25 mL 20 mM stock solution of benzoic acid (0.244 g in 100 mL of deionized water) and 5, 10, 15 and 20 mL 100 mM DEA (2.1 g in 100 mL of deionized water) and making up the volume to 50 mL. BGEs containing 10, 20, 30 and 40 mM DEA had pH 7, 8, 9 and 10, respectively.

2.2. Instrumentation

Electrophoretic separations of carboxylic acids were performed using a CE system "Capel-105M" (Lumex, St. Petersburg, Russia) equipped with UV detector 190–380 nm (spectral bandwidth 10 nm) and external water-bath temperature control. Both electrokinetic and hydrodynamic injections were available. Experiments were performed in fused-silica capillaries with external polyimide coating (Lumex, St. Petersburg, Russia), id 50 µm, od 360 µm, effective length 50 cm, total length 60 cm. The CE data were processed using Elforun software (Lumex). Laboratory pH meter (Seven Easy, METTLER TOLEDO) and analytical balance (OHAUS Pioneer, PA214C, e = 1 mg, d = 0.1 mg) were also used.

Microimages of the capillary surface were obtained using scanning electron microscope Zeiss Merlin.

2.3. Coating development

Before the preparation of NSAE-coating, the capillary was rinsed for 30 min with 0.5 M HCl, deionized water for 10 min followed by 2 h with 2 M NaOH for pre-activation of the fused-silica surface of the capillary walls. Pressure during conditioning was 1000 mbar.

Various concentrations of NSAE suspensions were tested for coating development. In this regard, the capillary was flushed with aqueous suspensions of NSAE with 0.005; 0.01; 0.05; 0.1 mM concentrations of functional groups for 5, 10, 15, 30 and 45 min. The EOF mobility was used to evaluate the modification of capillary surface and to assess the stability of the developed coatings. DMF dissolved in water was used as an EOF marker.

To evaluate the stability of NSAE coating in acid and basic conditions the modified capillary was flushed with 0.1 mM NaOH and 0.1 mM HCl. The stability of coating was also evaluated by sequential cycles of EOF measuring in BGE the pH of which was increased from 2 to 10 and turned back. The acetate buffer solution and benzoic acid with DEA additives were used as BGE to create pH 2, 3, 5 and pH 7, 8, 9, 10, respectively.

2.4. Electrophoretic conditions of carboxylic acids separation

The conditions of electrophoretic analyses were as follows: water-bath temperature control of the capillary was set at 20 °C, hydrodynamic sample injection at 30 mbar*2s; UV indirect detection at 224 nm; voltage at –20 kV. Before each injection, the capillary was flushed with BGE for 3 min. In order to ensure accuracy, the buffer solution was changed every 7–8 runs.

The separations of carboxylic acids were carried out using the BGE consisted of 10 mM benzoic acid and 9 mM DEA. As an additives to the BGE the NSAE suspensions were used (0.05; 0.025; 0.01; 0.005 mM). The following compositions of BGE were also tested during the optimization of carboxylic acids separation: 5, 10, 15 mM benzoic acid, 9, 15, 20 mM DEA.

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