Chun Wang[1,2]
Sergio de Rooy[1]
Cheng-Fei Lu[1]
Vivian Fernand[3]
Leonard Moore Jr.[1]
Paula Berton[1,4]
Isiah M. Warner[1]

[1]Department of Chemistry, Louisiana State University, Baton Rouge, LA, USA
[2]College of Science, Agricultural University of Hebei, Baoding, Hebei, P.R. China
[3]Department of Chemistry and Physics, LeTourneau University, Longview, TX, USA
[4]Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Mendoza, Argentina

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Research Article

An immobilized graphene oxide stationary phase for open-tubular capillary electrochromatography

The research literature currently abounds with studies of graphene-related materials as a result of the extraordinary properties of such materials. On the basis of these citations, it is clear that the range of applications for such materials is substantial. In this manuscript, we report the immobilization of graphene oxide (GO) onto a fused-silica capillary to form a potential stationary phase for use in open-tubular CEC. We successfully incorporated GO through an in situ condensation reaction with (3-aminopropyl)triethoxysilane after silanization with (3-aminopropyl)triethoxysilane on the inner surface of the capillary. This GO-incorporated capillary was then characterized by use of SEM, infrared spectroscopy, and measurements of EOF. The electrochromatographic features of this stationary phase have also been investigated. Evaluation of acquired data indicates high electrochromatographic resolution and good capillary efficiency. Highly reproducible results between runs, days, and capillaries were also obtained.

Keywords:
Capillary electrochromatography / Coating / Graphene oxide / Open-tubular
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1 Introduction

Graphene (G)-based carbon materials are novel and interesting chemical species which have engendered tremendous attention in recent years as a result of their exceptional electronic, thermal, optical, adsorptive, and mechanical properties as well as very high specific surface [1–3]. It is well established that G, a 2D single-layer sheet of sp^2-bonded carbon, is the "mother of all graphitic forms" of nanocarbon, including 0D buckyballs, 1D carbon nanotube, and 3D graphite. Other forms of G-based materials, including graphene oxide (GO), reduced GO, and exfoliated graphite, have also been reliably produced in bulk [4]. The chemical versatility and tunability combined with solution processibility make graphene-based materials attractive for a wide range of applications, such as electronic and photonic devices, energy, targeted drug delivery, bioimaging, catalysis, adsorption, and sensors [4–6].

Since the large delocalized π-electron system of graphene-related materials can form strong hydrophobic and π-stacking interactions with organic molecules [7, 8], this property suggests a promising candidate for an adsorbent and stationary phase. In this regard, graphene and its composite materials have been used as adsorbent in solid-phase microextraction [9–13], solid-phase extraction [14–16], and magnetic solid-phase extraction [17–25].

CEC is a hybrid electroseparation technique that couples the selectivity of HPLC and the separation efficiency of CE. Therefore, CEC provides high resolution, short analysis time, reduced sample and buffer consumption, and efficiencies of 5–10 times higher than those of HPLC. The separation in CEC is based upon the electrophoretic mobility of the solutes and their partitioning between the stationary and mobile phase. In the development of CEC, packed, monolithic, and open-tubular column configurations have been reported. In recent years, the developments in monolithic columns and open-tubular CEC (OT-CEC) have gained increasing attention in the chromatographic sciences. A major advantage of these systems is the elimination of problems associated with frits and silica particles in packed-CEC. Recently, Yan et al. reported the fabrication of GO nanosheets incorporated into a monolithic column via a one-step room temperature polymerization for CEC. The results indicated that incorporation of GO into monolithic columns greatly increased interactions between the tested neutral analytes (alkyl benzenes and polycyclic aromatics) and the stationary phase which produced significant improvement in CEC separation of these molecules [26].

In the OT-CEC design, a stable coating is added onto the inner walls of the capillary and acts as the stationary phase. The separation process is thus a consequence not only of the electrophoretic mobility differences of the analytes, but also

Correspondence: Professor Isiah M. Warner, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA
E-mail: iwarner@lsu.edu
Fax: +1-225-578-3971

Abbreviations: **APTES**, (3-aminopropyl)triethoxysilane; **G**, graphene; **GO**, graphene oxide; **NSAID**, nonsteroidal anti-inflammatory drug; **OT-CEC**, open-tubular CEC; **OT-CLC**, open-tubular capillary liquid chromagraphy

of their interactions with the stationary phase. Hence, better peak resolution and more reproducible EOF are typically obtained. The most commonly used approaches to wall coatings for modifying the capillary include (i) dynamic coating performed by adding the cationic or neutral modifier to the electrolytes, (ii) adsorbed cationic modifier on the capillary wall by physical adsorption, and (iii) fixation of the hydrophilic layer by covalent bonding or cross-linking [27]. However, dynamic coating is known to cause problems when CE is coupled to MS. In addition, the presence of a nonvolatile buffer may deteriorate the ionization of the analytes. Although physical adsorption has a simple and rapid coating procedure as well as good reproducibility, it has been shown to have a short lifetime and limited pH range. In many cases, physically adsorbed coatings show poor stability, which limits their routine applications. In contrast, some of the covalent bonded or cross-linked materials have a long lifetime, but require a more complicated coating procedure. Obviously, an ideal coating procedure would be one that is both simple and stable.

In this study, with the aim of obtaining a simple, stable, and reproducible coating, GO was immobilized onto a fused-silica capillary as a potential stationary phase in OT-CEC. The study complements and in certain areas extends independent work recently reported by Qu and co-workers, where GO and graphene were used as stationary phases in OT-CEC and open-tubular capillary liquid chromagraphy (OT-CLC) for the separation of various polyaromatic hydrocarbons (PAHs) and proteins [28]. The coating process was performed according to a simple procedure, that is, continuous dynamic rinsing of the reagents through the capillary. We note that GO not only possesses a large delocalized π-electron system and oxygen functional groups, but also provides ionized oxygen-containing functional groups which could possibly modify the EOF in OT-CEC and affect the separation through π–π interactions, hydrogen bonding, and hydrophobic interactions with the target analytes. The performance and stability of this GO-modified capillary as a novel separation medium is evaluated and reported.

2 Materials and methods

2.1 Reagents and chemicals

Natural graphite powder (320 mesh), (3-aminopropyl) triethoxysilane (APTES), fenoprofen, ketoprofen, suprofen, indoprofen, flurbiprofen, and naproxen were obtained from Sigma Chemical Co. (St. Louis, MO, USA). The profens were all of analytical grade (99%). DMSO, isopropanol, sodium tetraborate, potassium hydroxide, sodium hydroxide (NaOH), methanol, hydrochloric acid, and phosphoric acid were all obtained from Fisher Scientific (Fair Lawn, NJ, USA). All materials were used as received without further treatment or purification. A 5.0 g/L aqueous dispersion of GO was obtained from Graphene Laboratories (Calverton, NY, USA).

A stock solution containing a mixture of the six nonsteroidal anti-inflammatory drugs (NSAIDs) at 1.0 mg/mL was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with methanol-water (1:1, v/v) in a 10 mL volumetric flask. All the standard solutions were stored at 4°C in the dark. A stock buffer electrolyte of 0.5 mol/L borate solution was prepared using deionized water as a solvent and then diluted to different concentrations with an appropriate amount of deionized water to attain the mobile phase. The pH of the BGE, 50 mmol/L borate solution, was adjusted with 1.0 mol/L NaOH or 1.0 mol/L HCl. All solutions were filtered using a 0.45 μm polypropylene filter (Nalgene, Rochester, NY, USA) and sonicated for 15 min prior to use. Purified water (18 MΩ cm) from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for preparation of aqueous solutions.

2.2 Apparatus

All CE experiments were performed on a Beckman P/ACE MDQ Capillary Electrophoresis System (Beckman Coulter, Fullerton, CA, USA), equipped with an autosampler and a DAD. The temperature of the capillary was controlled using a liquid coolant in the capillary cartridge.

A fused-silica capillary, with internal diameter of 50 μm, was purchased from Polymicro Technologies (Phoenix, AZ, USA). The total length of the capillaries used in this study was 50 cm (40 cm effective length). The applied voltage ranged from 15 to 30 kV. Analytes were detected at 214 nm using a 800 μm × 100 μm aperture to maximize sensitivity. All operations were computer-controlled using Beckman P/ACE MDQ software.

FTIR spectroscopy analysis was performed using a Bruker Tensor 27 FTIR spectrometer. Samples were analyzed in pure form by use of a DuraSamp IR apparatus. All spectra were obtained by collecting 32 scans for both sample and background, with a resolution of 4 cm^{-1}. The morphology of the inner surface of the capillary was observed by use of SEM using an SM-6610, JSM-6610LV electron microscope operated at 10 kV.

2.3 Procedure for GO coating

During coating, the temperature of the capillary was maintained at 40°C. First, the capillary was conditioned before coating using a 5-min rinse of water to remove contaminants originated from the capillary manufacturing process. The column was then conditioned by rinsing with 1 mol/L NaOH for 60 min. Deionized water was flushed through the capillary for an additional 15 min. The second step involved introduction of functional amino groups by use of 1% v/v APTES solution prepared in isopropanol (60 min), followed by a water (10 min) and methanol (5 min) rinse, respectively, to eliminate excess APTES. A 5.0 mL aqueous GO solution (1 mg/mL) containing 10.0 mg of potassium hydroxide was subsequently passed through the capillary for 1 h. Finally,

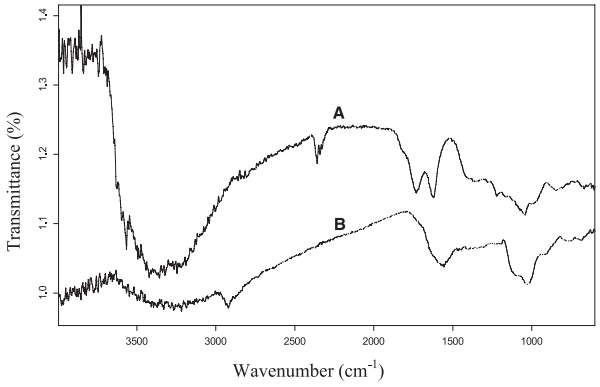

Figure 1. FTIR spectra of GO (A) and APTES-GO (B) samples.

the capillary was rinsed with water for 10 min to remove non-immobilized GO, and rinsed with buffer until a stable current was achieved. All processes were performed via continuous dynamic rinsing of the reagents through the capillary at 138 kPa.

To confirm a condensation reaction between silanized capillary and GO, APTES-GO was prepared according to a previously reported method. In brief, 30 mL of aqueous solution containing GO (1.0 mg/mL) and APTES (10.0 μL/mL) was maintained at 40°C for 1 h. The prepared APTES-GO was ultimately washed with water for three times and dried at room temperature.

2.4 General electrophoresis procedure

To ensure reproducibility, the capillary was flushed for 5 min with triply distilled water between consecutive analyses, followed by a BGE rinse for 5 min. The BGE buffer borate concentration was 50 mmol/L (pH 10.0). The sample solution was introduced into the capillary by use of hydrodynamic injection at 3.45 kPa (vacuum) for 5 s. Electrophoresis was performed at a constant voltage of +25 kV at 25°C, with diode array detection at 214 nm.

3 Results and discussion

3.1 Preparation of the GO-immobilized capillary

The procedure followed for immobilization of GO onto the inner surface of the capillary comprised two steps: (i) the fused-silica capillary was first hydroxylated by NaOH solution. The Si–OH groups were then transformed to $-NH_2$ groups by reacting with APTES solution; followed by (ii) immobilization of the GO, which contains plentiful and reactive epoxy groups [29]. The GO sheets are mainly grafted onto the inner wall of the capillary according to an S_N2 nucleophilic displacement reaction between epoxy groups of GO and amino moieties of APTES. Alternatively, GO can also self-assemble onto the wall of the capillary through van der Waals interactions. The reaction between GO and APTES was confirmed by subjecting the prepared APTES-GO powders to IR analysis. The IR spectra of samples of both GO and APTES-GO are shown in Fig. 1.

GO is a layered material with a wide range of oxygenated functional groups including hydroxyl, epoxy, and carboxyl groups located on the basal planes and the sheet edges. Figure 1A provides the FTIR spectrum for GO, which reveals the characteristic O–H stretching band at 3367 cm^{-1} (C–OH). The carboxyl group in GO appears at ca. 1724 cm^{-1} (C=O stretching) and the C–O vibrations of the epoxy groups appear at ca. 1055 and 870 cm^{-1}. The FTIR spectrum of APTES-GO is shown in Fig. 1B. It can be seen that the signals of Si–O–Si appeared at ca. 1015 and 918 cm^{-1}, which are ascribed to the hydroxylation of APTES molecules in aqueous solution. As expected, the characteristic epoxy vibrational bands at ca. 1055 cm^{-1} and 870 cm^{-1} disappeared. The signal at 1190 cm^{-1} corresponds to the C–N of the alkyl chains of the APTES moieties in APTES-GO. Moreover, the disappearance of C=O (1724 cm^{-1}) in the carboxyl group and the newly emerged bands at 1566 cm^{-1} suggest a partial reduction of GO during the heating process. Hence, the chemical bonding reactions between the silanized fiber and GO are verified. Figure 2 shows the SEM images of the inner surface of the bare capillary (A) and the GO-immobilized capillary (B). A clear GO coating appears to completely cover the inner wall of the capillary, which suggests successful fabrication of the GO-coated capillary column.

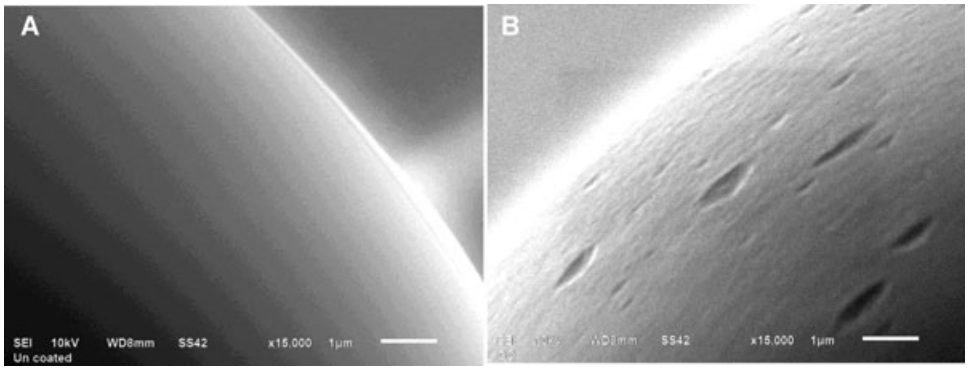

Figure 2. SEM images of the inner surface of the bare fused-silica capillary (A) and the GO-immobilized capillary (B).

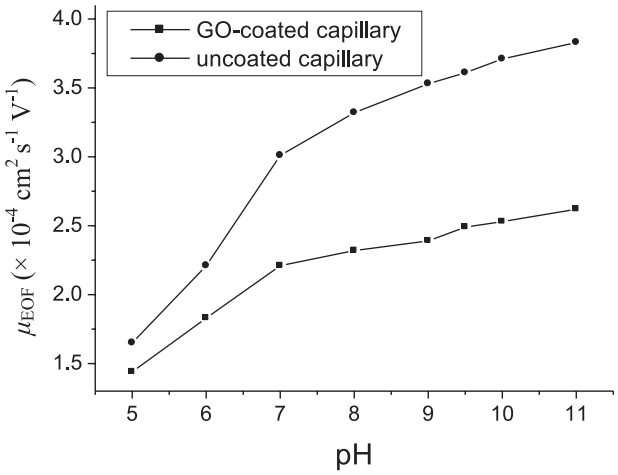

Figure 3. Effects of pH on EOF mobility in the bare fused-silica capillary (A) and the GO-coated capillary (B). Conditions: buffer electrolyte: 50 mmol/L borate; applied voltage: 25 kV; temperature: 25 °C; capillary: 50 cm (total length), 40 cm (effective length), 50 μm id; injection: 3.45 kPa for 5 s; detection: 214 nm.

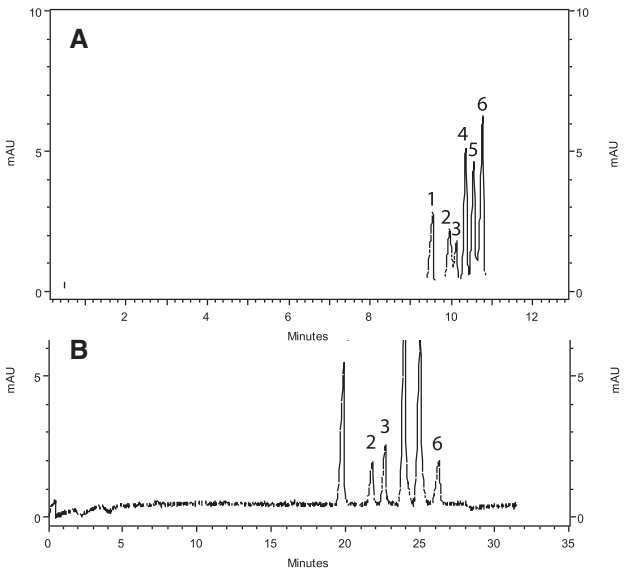

Figure 4. Electrochromatograms for separation of model NSAIDs using a bare fused-silica capillary (A) and the GO-immobilized fused-silica capillary (B). Conditions: buffer electrolyte: 50 mmol/L borate at pH 10.0; applied voltage: 25 kV; temperature: 25°C; capillary: 50 cm (total length), 40 cm (effective length), 50 μm id; injection: 3.45 kPa for 5 s; detection: 214 nm, concentration of the analytes: 50.0 μg/mL. Peak identity: 1, indoprofen; 2, ketoprofen; 3, suprofen; 4, fenoprofen; 5, flurbiprofen; 6, naproxen.

In CEC, the transport of mobile phase through the capillary is achieved by the EOF, which is established as a result of the charge on the capillary wall, the applied electric field, and the attraction of ions in the BGE to the capillary surface charge. The magnitude, direction, and reproducibility of the EOF reveal the property of the capillary inner surface and the effect of the coating. The curves shown in Fig. 3 illustrate the dependence of EOF mobilities on the pH levels of the borate buffer for the bare fused-silica capillary and the GO-coated capillary. From the graphs, we observe that the EOF in a bare capillary shows strong pH dependence, that is, the EOF increases markedly as the pH increases from 5.0 to 7.0 due to increased ionization of the silanol groups. The GO-coated capillary has a similar response as the bare capillary but with a decreased EOF value, indicating that the GO-coating could suppress the EOF. Coated capillaries exhibit a cathodic EOF, which indicates that the immobilized capillary was negatively charged.

3.2 Electophoretic separation

To demonstrate the effectiveness of the prepared GO-coating, the separation performance of the GO-coated capillary was compared with that of the bare capillary. Figure 4 compares the electropherograms obtained for the model analytes, six NSAIDs, with a bare fused-silica capillary (Fig. 4A) and with the GO-coated fused-silica capillary (Fig. 4B) under the same conditions. The NSAIDs contain an arylpropionate moiety and similar p*K*a values, so the electrophoretic mobilities of them are not remarkably different. As can be seen in Fig. 4, the NSAIDs could not be separated completely by a bare fused-silica capillary, and the resolutions of the test analytes were much improved by using the GO-coated capillary.

Table 1 reports the electrophoretic characteristics of the GO-coated and bare fused-silica capillary including retention time (t_R), resolution (*R*s), number of theoretical plates (*N*), and retention factor (*k*). As seen, good separation efficiencies were obtained for the model analytes by use of the GO-coated capillary. A remarkable improvement in resolution was achieved when the analytes were separated with GO-coated capillary in comparison with the bare capillary. This is attributed to the intrinsic properties of GO, properties such as a large delocalized π-electron system and oxygen functional groups, which might enhance the separation in OT-CEC through π–π interaction with the phenyl groups in the analytes, hydrogen bonding, and hydrophobic interaction with the analytes. Such results reveal that incorporation of GO into the capillary resulted in enhanced electrochromatographic characteristics. However, a slight decrease on the efficiency of the capillary (represented as the number of theoretical plates) was observed due to the increase of the retention times and of the broadening of the peaks. A previous study of Qu and co-workers focused on GO and graphene as stationary phase in OT-CEC and OT-CLC for various PAHs, amines, and proteins, obtaining poor separation in comparison with GO-coating [28].

In an attempt to better understand the proposed electrophoretic system, the effect of pH and BGE composition was also investigated. The p*K*a values of the NSAIDs are all ~4. The effects of borate buffer at six different pH values (8.0, 8.5, 9.0, 9.5, 10.0, and 10.5) on the separation selectivity were investigated. It was found that when increasing the pH, the

Table 1. Comparison of the performance of a GO-coated capillary and the bare capillary

Analytes	GO-coated capillary					Bare capillary				
	t_R (min)	RSD (%)	R_s a)	k b)	N c) ($\times 10^4$ m^{-1})	t_R (min)	RSD (%)	R_s a)	k b)	N c) ($\times 10^4$ m^{-1})
Indoprofen	19.84	1.15		1.84	7.7	9.48	0.71		0.82	9.3
Ketoprofen	21.76	1.16	5.25	2.12	5.2	9.95	0.72	1.90	0.91	7.5
Suprofen	22.63	1.18	2.43	2.24	12.8	10.12	0.76	0.65	0.95	13.7
Fenoprofen	23.92	1.20	3.15	2.43	9.8	10.31	0.82	1.10	0.98	14.3
Flurbiprofen	24.97	1.20	2.23	2.58	10.1	10.51	0.87	1.06	1.02	13.6
Naproxen	26.23	1.21	2.72	2.76	10.3	10.68		1.31	1.05	13.7

Conditions: buffer electrolyte: 50 mmol/L borate at pH 10.0; applied voltage: 25 kV; temperature: 25°C; capillary: 50 cm (total length), 40 cm (effective length), 50 μm id; injection: 3.45 kPa for 5 s; detection: 214 nm.
a) Resolution, $R = 2\ (t_{R2} - t_{R1})\ /\ (W_1 + W_2)$.
b) Retention factor, $k = (t_R - t_0)\ /\ t_0$.
c) Number of theoretical plate, $N = 5.54\ (t_R/W_{1/2})^2$.

separation improved, but no significant difference was observed between 10.0 and 10.5. Consequently, a borate buffer of pH 10.0 was chosen as the optimal. Buffer concentration has a significant effect on the separation performance because it can influence Joule heating, the EOF, ionic strength, and the current produced in the capillary. To obtain the best separation of the six NSAIDs, the effect of the borate buffer concentration on the separation was interrogated by changing its concentration to 30.0, 40.0, 50.0, 60.0, and 75.0 mmol/L, respectively. The results demonstrated that with increased concentration of borate, longer migration times and better resolution were observed. However, increasing the buffer concentration also resulted in an increase in initial current and baseline noise, as well as Joule heating which led to peak broadening. In order to avoid problems due to Joule heating, 50.0 mmol/L borate was selected for subsequent investigations. The effect of voltage on the separation efficiency was also studied, and the results indicated that 25 kV was the optimum value.

3.3 Reproducibility and stability

It is well known that excellent reproducibility for run-to-run, day-to-day, and capillary-to-capillary is necessary for obtaining reliable analytical results. Therefore, reproducibility and stability of the proposed electrophoretic system were investigated. The reproducibility of the EOF was evaluated by monitoring the average retention time of the EOF marker (DMSO) and % RSD. Each capillary was prepared according to the coating procedure previously described for the optimized separation. The run-to-run reproducibility for the EOF was calculated based on 30 consecutive runs using the same capillary. The day-to-day reproducibility for the EOF was evaluated based on the use of one capillary for five days with replicate analyses. Finally, the capillary-to-capillary reproducibility was evaluated based on three different capillaries with three consecutive runs for each. The results of this study are summarized in Table 2. Evaluation of the results indicates that all measured RSD were below 2.86%. In addition, good reproducibility of the migration times for the six NSAIDs was obtained, which confirms the high stability of the coating.

Table 2. Reproducibility studies of the GO coating

	Average EOF migration time (min)	% RSD of EOF
Run to run ($n = 30$ runs)	6.98	1.28
Day to day ($n = 5$ days)	7.10	1.82
Capillary to capillary ($n = 3$ capillaries)	7.18	2.86

Conditions: buffer electrolyte: 50 mmol/L borate at pH 10.0; applied voltage: 25 kV; temperature: 25°C; capillary: 50 cm (total length), 40 cm (effective length), 50 μm id; EOF marker: DMSO; injection: 3.45 kPa for 5 s; detection: 214 nm.

3.4 Linearity, LODs, and precision

A series of standard solutions containing each of the NSAIDs at eight different concentration levels of 1.0, 5.0, 10.0, 20.0, 50.0, 100.0, 200.0, and 500.0 μg/mL were prepared to establish a calibration curve. Good linearity was achieved over the concentration range of 5.0–500.0 μg/mL with correlation coefficients (r) ranging from 0.9985 to 0.9992. The LODs at a S/N ratio of 3 (S/N = 3) varied between 1.0 to 1.8 μg/mL. To assess the precision of this method, six parallel experiments were performed at concentrations of 10.0 μg/mL and 50.0 μg/mL for each of the NSAIDs. The RSDs varied from 3.0 to 4.6%. The characteristic calibration data obtained are summarized in Table 3. These results demonstrated high sensitivity and precision for the method.

4 Concluding remarks

In this study, GO was immobilized onto a fused-silica capillary as a stationary phase for OT-CEC. The resolutions of the model analytes, that is, the six NSAIDs, were significantly improved by use of this GO-coated capillary as compared to

Table 3. Analytical performance data for the NSAIDs by the GO-coated capillary

Analytes	LR (μg/mL)	*r*	RSD (%) ($n = 5$)	LOD (μg/mL)
Indoprofen	5.0–500.0	0.9992	3.6	1.0
Ketoprofen	10.0–500.0	0.9985	3.0	1.7
Suprofen	10.0–500.0	0.9987	3.8	1.5
Fenoprofen	5.0–500.0	0.9993	4.6	1.2
Flurbiprofen	5.0–500.0	0.9992	3.7	1.5
Naproxen	10.0–500.0	0.9987	4.2	1.8

LR, linear range.

the bare capillary. This approach demonstrated that highly efficient and reproducibility peaks could be obtained using the stationary phase prepared with the facile procedure outlined in this manuscript. The GO-coated capillary exhibited good stability. The findings in this study corroborate recently published work by Qu and co-workers who independently developed a method based on immobilizing graphene and GO onto a silica stationary phase in OT-CEC and CLC for the separation of PAHs and proteins [28]. In the current study, an improvement on the resolution was obtained for a series of NSAIDs. As a result of these findings, GO can be considered a unique coating for OT-CEC with promising potential applications.

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