Analytica Chimica Acta 761 (2013) 201–208

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Aligned electrospun nanofibers for ultra-thin layer chromatography

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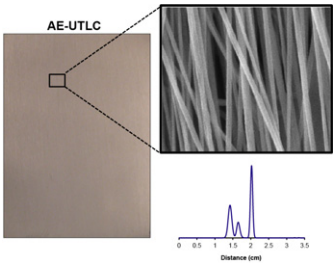
HIGHLIGHTS

- Aligned electrospun nanofibers are applied as a stationary phase in UTLC (AE-UTLC).
- AE-UTLC phases showed 2 times greater reproducibility than non-aligned phases.
- Aligning the nanofibers increased efficiency up to 100 times.
- AE-UTLC showed 2–2.5 times faster time of analysis relative to non-aligned E-UTLC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 July 2012
Received in revised form
12 November 2012
Accepted 18 November 2012
Available online 29 November 2012

Keywords:
Electrospinning
Nanofibers
Chromatography
Ultra-thin layer chromatography
Alignment
Drug analysis

ABSTRACT

The fabrication and implementation of aligned electrospun polyacrylonitrile (PAN) nanofibers as a stationary phase for ultra-thin layer chromatography (UTLC) is described. The aligned electrospun UTLC plates (AE-UTLC) were characterized to give an optimized electrospun mat consisting of high nanofiber alignment and a mat thickness of ~25 μm. The AE-UTLC devices were used to separate a mixture of β-blockers and steroidal compounds to illustrate the properties of AE-UTLC. The AE-UTLC plates provided shorter analysis time (~2–2.5 times faster) with improved reproducibility (as high as 2 times) as well as an improvement in efficiency (up to100 times greater) relative to non-aligned electrospun-UTLC (E-UTLC) devices.

1. Introduction

Originally developed in the 1950s, thin layer chromatography (TLC), also called planar chromatography, is widely used today in environmental analysis, food, clinical, and pharmaceutical industries [1,2]. The stationary phase in TLC consists of sorbent particles that are attached to a solid support, typically an aluminum or glass plate. The analytes of interest are spotted directly onto the stationary phase, the edge of which is brought into contact with the mobile phase. The mobile phase proceeds up the plate via capillary action. Separation of analytes occurs due to interactions with both the mobile phase and the stationary phase. A number of different materials have been applied as the stationary phase in TLC, including alumina, cellulose, ion-exchange resins and, perhaps most commonly, silica gel [3–6]. More recently, nanostructured surfaces have been developed for TLC applications [7,8].

In 2001, ultra-thin layer chromatography (UTLC) was developed. This technology, which typically utilizes a stationary phase with a 5–20 μm thickness (compared to 100–400 μm thick stationary phases for commercial TLC devices), represented a significant improvement in analysis time and sensitivity over traditional

Abbreviations: AE-UTLC, aligned electrospun ultra-thin layer chromatography; E-UTLC, electrospun ultra-thin layer chromatography; PAN, polyacrylonitrile.

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http://dx.doi.org/10.1016/j.aca.2012.11.028

TLC devices [4,9]. Our lab previously demonstrated that electrospinning can be utilized to generate a mat of nanofibers that can be used as a UTLC sorbent [10,11]. Electrospinning is a simple and cost effective method of generating nanofibers by placing a high electric field between a syringe containing a polymeric solution and a conductive surface. At a critical voltage, the surface tension of the polymer solution at the syringe tip is overcome, and polymeric nanofibers are splayed from the droplet and are collected on the conductive surface [12]. To date, electrospinning has been used in a variety of applications including use in sensors [13], tissue scaffolds [14], and in solid phase microextraction [15,16].

Electrospun UTLC (E-UTLC) plates are particularly attractive for a number of reasons: no binder material is required in fabrication [2]; the solid support and mat thickness are readily variable; the small dimensions of the fibers provide a support with high surface area, and the chemical functionalities in the stationary phase can be easily modified [10,11]. Electrospun polyacrylonitrile (PAN) UTLC plates not only demonstrated a decreased time of analysis, but also vastly superior separation efficiencies for steroidal compounds relative to a commercially available cyano phase TLC plate [10]. Cyano-modified phases are frequently utilized as a stationary phase in the separation of steroidal compounds, as well as alkaloids and derivitized amino acids [17]. The PAN E-UTLC plate demonstrated 500 times greater separation efficiency and a decreased time of analysis by up to 50% when compared to the conventional cyano TLC phase [10].

The previous E-UTLC studies used electrospun mats with randomly oriented nanofibers. The work reported herein marks the first use of aligned electrospun UTLC (AE-UTLC). Aligned electrospun fibers have been utilized in a variety of applications, often demonstrating a profound impact due to the ordered structuring of the nanofibers [18]. For example, aligned nanofibers have been utilized as cell scaffolds. With this fiber configuration, cells propagate in the direction of the nanofibers' orientation [19]. It was hypothesized that UTLC with aligned electrospun nanofibers may show an increase in chromatographic performance relative to non-aligned electrospun UTLC plates.

While there are many different techniques that have been applied to generate aligned electrospun fibers [20], the two most commonly used models are: the parallel electrode and rotating drum models (Figure S1) [18]. While the parallel electrode model is both simple to use and capable of generating highly aligned nanofibers, the electrodes can only be placed about 1–5 cm apart, thus limiting the length of the nanofibrous mat that can be generated [18,21]. Furthermore, it is very difficult to obtain electrospun mats that are sufficiently thick to use as a chromatographic support; the wider the distance between the two electrodes the thinner the electrospun mat [18,22].

A rotating drum apparatus is capable of giving much larger surface areas of aligned nanofibers than the parallel electrode configuration [18,23,24]. Thicker nanofibrous mats are also possible with the rotating drum. However, it is more challenging to generate mats that are as highly aligned as those generated with parallel electrodes. Additionally, the rotational speed must be optimized to produce the highest alignment possible while preventing fiber breakage [18]. Due to the increased mat areas and thicknesses possible with the rotating drum, the AE-UTLC plates utilized in this study were fabricated using this method.

Herein, the use of a newly configured rotating device to generate PAN AE-UTLC plates is described. These plates were applied to the analysis of both laser dyes and a mixture of β-blockers and steroidal compounds. The performance of the AE-UTLC plates was compared to that of the previously published PAN E-UTLC devices [11].

2. Materials and methods

2.1. Experimental

2.1.1. Reagents

Polyacrylonitrile (PAN), molecular weight ~150,000 g mol^{-1}, was purchased from Sigma Aldrich (Atlanta, GA). *N*,*N*-Dimethylformamide, utilized as the solvent for PAN, was also purchased from Sigma Aldrich. The laser dyes studied were purchased from Exciton Inc. (Dayton, OH) and included kiton red, sulforhodamine 640, rhodamine 610 chloride, and rhodamine 610 perchlorate. Acebutolol, propranolol, and cortisone were purchased from Sigma Aldrich. Tetrabutylammonium bromide (99+%) was purchased from Arcos Organics (New Jersey). Acetone, heptane and 2-propanol were acquired from Fisher Scientific (Fair Lawn, NJ). Chloroform (EMD Chemicals, Gibbstown, NJ), ethanol (Decon Labs, Inc., King of Prussia, PA), and methanol (Avantor Performance Materials) were also utilized. Commercially available thin-layer chromatography plates were purchased from Macherey-Nagel (Bethlehem, PA) catalog number 818184. The plates contain a 0.15 mm layer on an aluminum sheet. The layer is composed of cyanopropyl modified silica particles ranging from 2 to 10 μm in size.

2.1.2. Instrumentation

A Hitachi S-4300 (Hitachi High Technologies America, Inc., Pleasanton, CA) scanning electron microscope was utilized to obtain all the SEM images of the electrospun nanofibers. ImageJ (Available from the National Institute of Health at http://www.rsbweb.nih.gov/ij/index.html) software was employed for all measurements of SEM images, including those utilized to determine the degree of alignment of the electrospun nanofibers.

2.1.3. Aligned electrospinning

The spinning drum apparatus used in this experiment is shown in Fig. 1. The drum itself consisted of a 33.02 cm diameter × 3.18 cm wide piece of aluminum, which was drilled out to reduce weight. The drum is supported by a bearing-containing support on each end via 27.94 cm axles. The supports are bolted to rails at the base; the rails were slotted to provide easy adjustment to meet electrospinning conditions. On one side, the mandrel was attached to a ¾ horsepower, air-actuated stirrer with a chuck (Mixer Direct, Inc., Jeffersonville, IN). This was used to rotate the drum relative to the electrospinning syringe. The motor was powered by house air, at a pressure of approximately 90 psi. The motor was capable of providing speeds of 0–3000 rpm; the rotational speed of the drum was determined using a NIST-certified, Monarch Instrument PLT200 pocket laser tachometer (Cole-Parmer, Vernon Hills, IL). During electrospinning experiments, the surface of the drum was wrapped with 0.003" stainless steel shim stock (McMaster-Carr, Robbinsville, NJ) to serve as a solid support for the nanofibers. The rest of the apparatus consisted of the equipment necessary to electrospin the polymer: the syringe pump, a Harvard Model 33 dual syringe pump (Holliston, MA), and the power supply, a Spellman CZE 1000R high voltage source (Hauppauge, NY).

2.1.4. Thin layer chromatography

AE-UTLC plates were fabricated by removing the shim stock, now covered by aligned electrospun nanofibers, from the drum and cutting the material into plates that were appropriately sized for UTLC experiments (~2 × 5 cm). Analytes were spotted on the plates utilizing a fused silica capillary with an internal diameter of 250 μm; the volume of analyte spotted was ~50 nL. All UTLC experiments were conducted in a cylindrical glass development chamber (volume = 250 mL) containing 5 mL of mobile phase. The