Journal of Chromatography A, 1365 (2014) 164–172

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Circuit modification in electrical field flow fractionation systems generating higher resolution separation of nanoparticles

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ARTICLE INFO

Article history:
Received 1 February 2014
Received in revised form 18 August 2014
Accepted 28 August 2014
Available online 8 September 2014

Keywords:
Nanoparticles
Nanoparticle characterization
Field flow fractionation
Electrical field flow fractionation

ABSTRACT

Compared to other sub-techniques of field flow fractionation (FFF), cyclical electrical field flow fractionation (CyElFFF) is a relatively new method with many opportunities remaining for improvement. One of the most important limitations of this method is the separation of particles smaller than 100 nm. For such small particles, the diffusion rate becomes very high, resulting in severe reductions in the CyElFFF separation efficiency. To address this limitation, we modified the electrical circuitry of the ElFFF system. In all earlier ElFFF reports, electrical power sources have been directly connected to the ElFFF channel electrodes, and no alteration has been made in the electrical circuitry of the system. In this work, by using discrete electrical components, such as resistors and diodes, we improved the effective electric field in the system to allow high resolution separations. By modifying the electrical circuitry of the ElFFF system, high resolution separations of 15 and 40 nm gold nanoparticles were achieved. The effects of applying different frequencies, amplitudes and voltage shapes have been investigated and analyzed through experiments.

1. Introduction

Nanotechnology and nanoscience are two fast-growing research fields which involve production and use of substances at the nanoscale (i.e., between 1 and 100 nm). Many nanotechnology-based consumer products are already on the market: cosmetics, nano-medicines, sunscreens, semiconductors, house-cleaning items, and paints, among others. As the necessity of producing specialized nanoparticles increases, new separation techniques are needed to sort particles according to their vast number of properties such as size, shape, charge, density, internal structure, magnetic susceptibility and optical properties. Currently, several analytical methods are used to separate and characterize nanostructures; the three main chromatography techniques are: liquid chromatography, electrophoresis, and field flow fractionation [1]. An electrical version of field flow fractionation will be the focus of this paper.

Field flow fractionation (FFF) is a powerful nanoparticle characterization and separation method first developed by Giddings in 1966 [2]. In FFF, separation occurs in a long, thin channel in which the carrier flow is laminar with a parabolic velocity profile. Perpendicular to this flow, a separation field is applied, which causes the particles to migrate to different mean locations away from the channel walls, giving the particles different velocities down the channel length, and causing the separation to occur.

FFF sub-techniques are differentiated based on the type of the applied separation field. The major sub-techniques are electrical FFF [3], magnetic FFF [4], thermal FFF [5], gravitational FFF [6], and flow FFF [7]. In electrical field flow fractionation (ElFFF), the separation field is produced by applying voltages to the top and bottom walls of an ElFFF channel. In this method, particles are separated based on their size and electrophoretic mobility [8].

ElFFF typically uses static or DC fields, but oscillating fields are showing promise and the technique is referred to as cyclical electrical field flow fractionation (CyElFFF) [9]. Cyclical voltages mitigate the loss of electric field strength in the channel caused by electrical double layer formation (EDL) on the channel walls. In traditional ElFFF, static voltages are applied to the walls of the channel, and typically the EDL is fully formed on the surface of the channel walls in about 1-min. As a consequence of EDL formation, the electric field inside the channel drops to 3% or less of its initial value [8]. This major drawback gives rise to a considerable reduction in the separation efficiency. In CyElFFF, since the electric

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http://dx.doi.org/10.1016/j.chroma.2014.08.097
0021-9673/

field polarization changes with each cycle, insufficient time exists for an EDL to be formed completely and EDL effects are reduced.

Compared to other FFF techniques, CyElFFF is a relatively new method [10–13] with significant opportunities remaining for performance improvement. In previously reported CyElFFF studies, separations have been achieved only for particles larger than 100 nm [11,12]. For particles smaller than 100 nm, diffusion rates become very high, resulting in severe reductions in CyElFFF separation efficiency. Essentially, particle diffusion yields a greater particle distribution across the CyElFFF channel with corresponding increases in both the mean and the distribution of down-channel velocities. The result is lower retention times and greater particle dispersion, both of which reduce separation resolution.

In an attempt to help mitigate the effects of diffusion, Tasci et al. [14] demonstrated a new method, Biased Cyclical Electrical Field Flow Fractionation (BCyElFFF) achieving the separation of nanoparticles smaller than 100 nm by utilizing high duty cycle voltage waveforms. Even though separation capabilities are improved by use of the BCyElFFF method, the required voltage amplitude to achieve quality separations is increased, which may lead to the electrolytic breakdown of the carrier. Furthermore, it was shown that BCyElFFF produces low resolution at frequencies higher than 10 Hz and it is only applicable to square voltage waveforms (i.e., not suitable for sinusoidal, triangular and sawtooth waveforms). In this work, we demonstrate a method resolving the diffusion challenges in the CyElFFF systems while avoiding the drawbacks of the BCyElFFF method.

The primary innovation is an electric circuit designed to create a non-decaying, unbalanced field that opposes the effects of diffusion while also reducing the impact of the EDL in the ElFFF channel. Essentially, a diode is placed parallel to the separation channel, which causes current to flow preferentially in one direction, creating an electric field bias in the channel. In all previous ElFFF efforts [3,8–13,15–21], electrical power sources have been connected directly to the ElFFF channel walls and no alterations have been made in the electrical circuitry of the system, other than minor changes to enable measurement of the electric field in the channel [18]. In this work, adding discrete electrical components such as resistors and diodes to the overall ElFFF circuit generates an overall bias that suppresses the effects of nanoparticle diffusion, which allows baseline separation of sub 50 nm particles. Moreover, the designed circuit allows application of voltage waveforms other than a square wave (i.e., sinusoidal, sawtooth and triangular) and works effectively at high frequencies, which permits utilization of much shorter ElFFF channels. The improvements implemented in this work can be used to make CyElFFF a more effective tool in the separation and characterization of nanoparticles and macromolecules.

2. Theory

An ElFFF system consists of a wide, thin channel between 2 flat electrodes. The flow inside the CyElFFF channel is laminar with a parabolic velocity profile. When a cyclical voltage is applied to the channel walls (electrodes), particles susceptible to the electric field oscillate back and forth between the electrodes. In each electrical cycle, depending on their electrophoretic mobilities, particles spend more or less time in the faster fluid regions, which are near the center of the flow channel. Essentially, particles that spend more time close to middle of the channel elute earlier, whereas particles that spend more time close to the channel wall elute later.

The operational principle of CyElFFF is shown in Fig. 1, where the trajectories of two particles having different electrophoretic mobilities are presented for 3 cycles of an applied square wave voltage. In each cycle, the particle having a higher electrophoretic

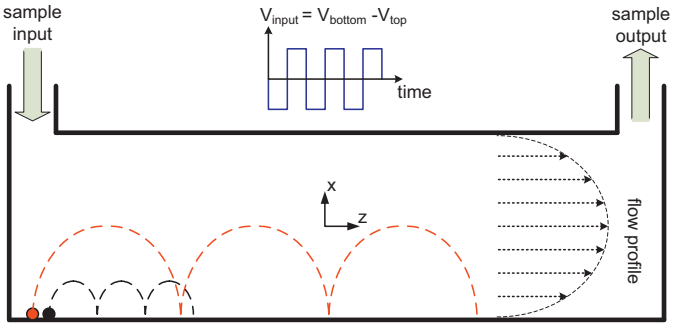

Fig. 1. Operational principle of a typical CyElFFF system. The cartoon shows the motion of two particles having different electrophoretic mobilities for 3 cycles of an applied square wave voltage. (Figure is not to scale, it is rescaled for better visualization of particle motions. In ElFFF systems, the channel length is usually at least 1000 times longer than the channel height).

mobility comes closer to the middle of the channel, where the z-direction flow velocity is highest. As a result, that particle moves faster through the channel (in the z-direction) than the particle having the lower electrophoretic mobility which stays closer to the channel walls and the concomitant slow flow regions. Thus, the lower electrophoretic mobility particle moves more slowly in the z-direction and elutes later than the higher mobility particle.

Mathematically, the velocity of a nanoparticle under the influence of an electric field can be represented by the equation

$$v_p = \mu_p \times E_{eff} \quad (1)$$

where v_p (m/s) is the velocity of the particle, μ_p (m^2/V s) is the electrophoretic mobility of the particle, and E_{eff} (V/m) is the effective electric field inside the channel. As shown in Eq. (1), to increase the electrically driven velocity of a nanoparticle, the effective electric field (E_{eff}) should be increased.

As noted earlier, nanoparticles also move as a result of diffusion (Brownian motion). The average diffusion length traveled by a particle in a given time is shown by

$$l_d = \sqrt{2Dt} \quad (2)$$

where D (m^2/s) is the diffusion coefficient of the particle and t (s) is time. The diffusion coefficient of a spherical particle can be calculated using the Stokes–Einstein equation [22]

$$D = \frac{TK_b}{3\pi\eta d} \quad (3)$$

where T (K) is temperature, K_b (J/K) is Boltzmann's constant, η (Pa s) is the dynamic viscosity of the carrier liquid, and d (m) is the particle diameter.

An examination of Eq. (3) shows that the particle diffusion rate increases as particles become smaller. As particle diffusion causes significant degradation of retention and resolution in CyElFFF, separation of very small particles becomes problematic. For CyElFFF, diffusion occurring in the $+x$ direction has an especially negative effect on separation efficiency, retention time, and resolution. The reason for this negative effect is shown schematically in Fig. 2a, which represents the particle trajectory in a typical CyElFFF system for 2.5 cycles of a square wave. As a consequence of the particle diffusion in the $+x$ direction, a particle moves away from the channel wall during each cycle, gaining a faster average velocity downstream. When a particle moves faster along the channel length, its retention time significantly drops and separation efficiency decreases.

To reduce the detrimental effect of particle diffusion on the separation efficiency, diffusion in the $+x$ direction should be countered. An electrical force opposing diffusion in the $+x$ direction can be achieved by applying DC offset voltages along with the cyclical