



Using light scattering to evaluate the separation of polydisperse nanoparticles



Anne A. Galyean^{a,*}, Wyatt N. Vreeland^b, James J. Filliben^c, R. David Holbrook^d,
Dean C. Ripple^b, Howard S. Weinberg^a

^a Gillings School of Global Public Health, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, NC 27599, USA

^b Biomolecular Measurement Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

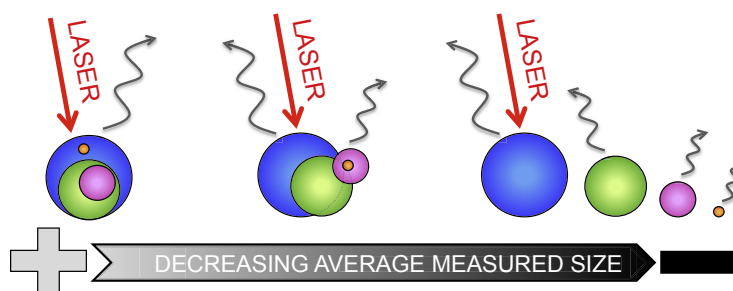
^c Statistical Engineering Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

^d Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

HIGHLIGHTS

- We present a tool to assess relative accuracy among separation protocols.
- This metric can be applied to any techniques using light scattering detection.
- An improved separation protocol minimizes the average measured particle size.
- A protocol with the smallest average measured particle size is the best separation.
- Metric is demonstrated by improving AF⁴ cross flow protocols for polystyrene beads.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form

3 June 2015

Accepted 7 June 2015

Available online 7 August 2015

Keywords:

Separation

Multi angle light scattering

Quasi-elastic light scattering

Polydisperse

Nanoparticle

Flow field flow fractionation

ABSTRACT

The analysis of natural and otherwise complex samples is challenging and yields uncertainty about the accuracy and precision of measurements. Here we present a practical tool to assess relative accuracy among separation protocols for techniques using light scattering detection. Due to the highly non-linear relationship between particle size and the intensity of scattered light, a few large particles may obfuscate greater numbers of small particles. Therefore, insufficiently separated mixtures may result in an overestimate of the average measured particle size. Complete separation of complex samples is needed to mitigate this challenge. A separation protocol can be considered improved if the average measured size is smaller than a previous separation protocol. Further, the protocol resulting in the smallest average measured particle size yields the best separation among those explored. If the differential in average measured size between protocols is less than the measurement uncertainty, then the selected protocols are of equivalent precision. As a demonstration, this assessment metric is applied to optimization of cross flow (V_x) protocols in asymmetric flow field flow fractionation (AF⁴) separation interfaced with online quasi-elastic light scattering (QELS) detection using mixtures of polystyrene beads spanning a large size range. Using this assessment metric, the V_x parameter was modulated to improve separation until the average measured size of the mixture was in statistical agreement with the calculated average size of

* Corresponding author.

E-mail addresses: galyean@live.unc.edu (A.A. Galyean), wyatt.vreeland@nist.gov (W.N. Vreeland), james.filliben@nist.gov (J.J. Filliben), dave.holbrook@nist.gov (R.D. Holbrook), dean.ripple@nist.gov (D.C. Ripple), howard_weinberg@unc.edu (H.S. Weinberg).

particles in the mixture. While we demonstrate this metric by improving AF⁴ V_x protocols, it can be applied to any given separation parameters for separation techniques that employ dynamic light scattering detectors.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Field flow fractionation (FFF) and specifically, flow field flow fractionation (F₄FFF), has become one of the most favored methods for separating complex colloidal samples. F₄FFF is a type of chromatography that does not require the use of a stationary phase and relies on hydrodynamic principles to separate particles in an open fluidic channel [1–4]. F₄FFF can be directly interfaced with a wide variety of standard chromatography detectors, such as multi-angle light scattering (MALS) for particle sizing, quasi-elastic light scattering (QELS) for measuring particle diffusion coefficients, concentration detectors, fluorescence, or inductively coupled plasma-mass spectrometry for elemental analysis, among others [5]. F₄FFF has been applied to particle separation of very small particles, such as humic substances in the 1 nm range, natural colloids in the 20 nm–450 nm range, and larger particles, such as clay, in the 5 μm–100 μm range [3]. F₄FFF has been widely applied to nanoparticle analysis, such as metals, metal oxides, SiO₂, and carbon black. Additionally, it has been used to analyze complex sample matrices such as soil suspensions and colloids in fresh and marine water samples [6] while simultaneously reducing sample complexity and fractionating colloidal materials by size. There is a growing body of literature on how to optimize and define asymmetric flow field flow fractionation (AF⁴) separation parameters for various applications and types of nanomaterials, based on theory and experimental parameters that influence AF⁴ [3,7–13].

The development of separation techniques operated in tandem with MALS and QELS detectors allows for size and molar mass distribution measurements of arbitrary polydisperse mixtures of particles and in some cases, information about molecular conformation [14]. While the angular dependence of scattered light can provide information about particle size as measured by MALS, QELS directly measures the translational diffusion coefficient, and computes hydrodynamic radius (R_h) using the Stokes–Einstein equation. When light scattering is combined with a non-destructive separation technique that presents the light scattering detector with scattering from an essentially monodisperse particle size at each measured fraction, the size distribution of the original sample can be calculated [15,16]. Because the relationship between particle size and scattering intensity is highly non-linear ($I \propto r^6$, where I is the scattering intensity and r is the particle radius; light scattering theory has been described in detail elsewhere [15–17]), the measured size can be heavily biased to being erroneously large in insufficiently separated mixtures. In other words, a few large particles may obscure the detection and accurate measurement of much greater numbers of small particles. Therefore, obtaining an accurate measurement of a polydisperse distribution requires a separation of sufficient resolution, and the optimum separation will result in the smallest average size (Fig. 1).

Separations of various natural, environmental, biological, or otherwise complex samples are less defined and contain a higher level of variability [14,18–20] when compared to the separations of mixtures of monodisperse or distinct particle sizes. Currently, to our knowledge, there is no metric to establish whether the separation optimization is complete and the separation is the best

possible given the available experimental conditions. Experience and FFF theory can provide tools for choosing separation conditions based on a certain range of particle sizes. However, in the case of unknown or complex mixtures spanning a large size range, these conditions may be much less obvious. Similarly, extremely polydisperse mixtures, such as environmental or natural samples, may not yield sufficient resolution between sample components to judge separation quality by observing the raw data in fractograms alone. Therefore, the analysis of a single separation and its data may not provide adequate information about the accuracy of the measurement. Thus, a rigorous characterization requires multiple separation protocols and comparison among them.

To address the challenges described above, we compare the average measured particle size for a distribution of particles with various separation parameters, and demonstrate that the best separation possible is obtained when the average size is at a minimum. In this work, the separation parameter of cross flow in an AF⁴-QELS system is used as a simplified example to represent changing separation conditions. This separation metric is described and subsequently applied to mixtures of polystyrene nanoparticles of several known mean sizes to mimic complex mixtures.

2. Materials and methods¹

2.1. Instrumentation

AF⁴ was performed using an Eclipse DualTec separation module (Wyatt Technologies Corp., Santa Barbara CA) with OpenLab CDS Chem Station edition software (Agilent Technologies, Santa Clara, CA). Injections were made with an Agilent 1260 Infinity series isopump and autosampler with a 900 μL injection loop. The run buffer was degassed by a Gastorr TG-14 (Flom USA, San Diego, CA) at 10 kPa directly from solvent bottles, and filtered in series by a polytetrafluoroethylene frit (RESTEK Corp., Bellefonte, PA) and a 0.1 μm Durapore[®] membrane filter (Millipore Inc., Billerica, MA). Separation was performed with an outlet channel flowrate of 1 mL min⁻¹ and a 1 min focusing time using a Wyatt Technologies “short channel” containing a 350 μm spacer and a regenerated cellulose ultrafiltration membrane with 5 kDa cutoff (Wyatt Technologies Corp.). AF⁴ instrumental parameters held constant for each protocol are provided in Table 1.

Quasi electric light scattering (QELS) measurements were made with a WyattQELS™ detector through a QELS fiber attached to the Wyatt DAWN[®] II MALS detector at a nominal angle of 140° with a 2.0 s collection interval (Wyatt Technologies Corp.). Multi angle light scattering (MALS) measurements were not included in this work. Polystyrene samples were prepared in the ammonium nitrate buffer and placed in amber glass vials sealed with PTFE/silicone septa (Chemglass Life Sciences, Vineland, NJ). Data were

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Download English Version:

<https://daneshyari.com/en/article/1163745>

Download Persian Version:

<https://daneshyari.com/article/1163745>

[Daneshyari.com](https://daneshyari.com)