Analytica Chimica Acta 809 (2014) 9–24

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Review

Rational strategy for characterization of nanoscale particles by asymmetric-flow field flow fractionation: A tutorial

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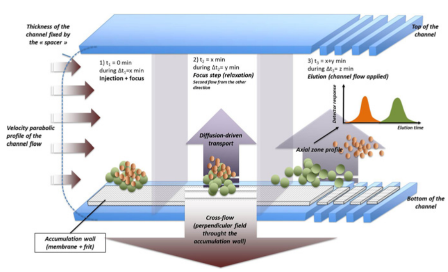
HIGHLIGHTS

- Underlying theory and critical parameters are introduced.
- A rational workflow is proposed to optimize and refine A4F methods.
- Specific optimization steps and validation parameters are delineated.
- Pedagogical examples are provided to demonstrate the process.
- Use and relevance of different detection modalities is addressed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 August 2013
Received in revised form 31 October 2013
Accepted 8 November 2013
Available online 16 November 2013

Keywords:
Field flow fractionation
Nanoparticle
Nanomaterial
Protocol
Optimization
Validation

ABSTRACT

This tutorial proposes a comprehensive and rational measurement strategy that provides specific guidance for the application of asymmetric-flow field flow fractionation (A4F) to the size-dependent separation and characterization of nanoscale particles (NPs) dispersed in aqueous media. A range of fractionation conditions are considered, and challenging applications, including industrially relevant materials (e.g., metal NPs, asymmetric NPs), are utilized in order to validate and illustrate this approach. We demonstrate that optimization is material dependent and that polystyrene NPs, widely used as a reference standard for retention calibration in A4F, in fact represent a class of materials with unique selectivity, recovery and optimal conditions for fractionation; thus use of these standards to calibrate retention for other materials must be validated a posteriori. We discuss the use and relevance of different detection modalities that can potentially yield multi-dimensional and complementary information on NP systems. We illustrate the fractionation of atomically precise nanoclusters, which are the lower limit of the nanoscale regime. Conversely, we address the upper size limit for normal mode elution in A4F. The protocol for A4F fractionation, including the methods described in the present work is proposed as a standardized strategy to realize interlaboratory comparability and to facilitate the selection and validation of material-specific measurement parameters and conditions. It is intended for both novice and advanced users of this measurement technology.

Published by Elsevier B.V.

Contents

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0003-2670/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.aca.2013.11.021

Charlène Schmitt obtained her M.S. in physics and chemistry for polymers and materials at the University of Pau, France in 2012. Her graduate research centered on the synthesis of polystyrene latex using sustainable saponin surfactants. During 2012, she completed a graduate research sabbatical at the U.S. National Institute of Standards and Technology, where she developed field flow fractionation methods to characterize polymer-based nanoparticles. Currently, she is a Ph.D. student in analytical and polymer chemistry at the University of Pau, where her research focuses on new polymers.

John M. Pettibone, received his Ph.D. in chemical engineering from the University of Iowa. He received a National Research Council Fellowship to conduct research at the U.S. National Institute of Standards and Technology in 2009 and is now a staff scientist. His research focuses on detection, characterization and quantification of nanoscale particles over a wide continuum of states and sizes, and exploration of new measurement approaches to examine complex and dynamic formation and transformational reactions that are critical for predicting the impact and fate of nanoscale materials.

Julien C. Gigault graduated in analytical and environmental chemistry at the University of Brest, France in 2008, and obtained his Ph.D. from the University of Pau, France in 2011. His Ph.D. focused on field flow fractionation (FFF) for the characterization of single- and multi-walled carbon nanotubes and the study of their environmental behavior. Since 2011 he has been a postdoctoral Associate at the U.S. National Institute of Standards and Technology, where his research seeks to develop and validate novel measurement methods based on FFF coupled to multiple detectors, in order to qualitatively and quantitatively determine the physico-chemical properties of nanoscale particles for environmental risk assessment.

Vince Hackley obtained a Ph.D. in water chemistry (now environmental chemistry and technology) from the University of Wisconsin in Madison, and has held associate and staff scientist positions at the U.S. National Institute of Standards and Technology since 1991. He leads a project team engaged in applied physical and chemical metrology for the analysis of engineered nanoscale materials and their interactions with biological and environmental systems. He is involved in international standards development for nanotechnology and particle characterization through committees in ISO and ASTM, and the development of particle reference materials at NIST. He received the U.S. Department of Commerce Silver Medal for scientific achievement in 2008, and is the author or coauthor of 95+ publications, including two edited books on particle technology.

1. Introduction

The accurate characterization of nano-object populations (with at least one dimension in the 1 nm to 100 nm range), and, more generally, particles in the submicrometer range (up to 1 μm), is an important and relevant measurement challenge spanning a broad range of applications, including industrial, consumer products, environmental remediation, risk assessment, and biomedical research, among others [1–7]. The rapid growth of interest in nano-object characterization has been driven by the emergence and corresponding commercial penetration of nanotechnology over the past decade. Surface chemistry or functionality in combination with the physical form of nano-objects (i.e., their dimensions, shape and aggregation state) are the primary determinants of their behavior in biological and environmental systems, impacting their transformations, transport, fate, biodistribution, metabolism, clearance and toxicity, among other properties [8–13]. Similarly, commercially exploitable optical, magnetic and photochemical properties of nano-objects are directly impacted, if not entirely determined, by their physical form [1,14,15]. Though primarily defined by their dimensions, nano-objects actually represent many different classes of materials characterized by a broad range of physical and chemical properties, including materials of natural, manufactured and anthropogenic sources [16]. Thus, the characterization of these different nano-object classes according to their specific nature, complexity, and source, represents a relatively new and important scientific challenge. International Organization for Standardization (ISO) defines nano-objects as belonging to one of