

Chapter 1

Evaluation of Currently Available Techniques for Studying Colloids in Environmental Media: Introduction to Environmental Nanometrology

Allan Philippe
University Koblenz-Landau, Germany

ABSTRACT

Engineered nanoparticles are emerging pollutants with poorly known environmental fate and impact. Studying the fate of engineered colloids in the environment is highly challenging due to the complexity of their possible interactions with environmental components and to the need of dedicated analytical methods. Many relevant processes like e.g. agglomeration and dissolution can be studied by monitoring the size of colloids. Techniques dedicated to the determination of the size of colloids in environmental media are thus required. Such techniques should remain accurate at low concentrations and be specific, widely matrix independent and free of artefact due to sample preparation. This chapter aims at evaluating and comparing systematically the currently used tools (e.g. microscopy, light scattering, particle counters) for sizing colloids considering these requirements. As an example of a highly promising solution, the current development of separation techniques coupled to (single particle) ICP-MS is described in more details.

DOI: 10.4018/978-1-5225-0585-3.ch001

INTRODUCTION

Numerous studies have addressed the fate of engineered colloids in the environment due to the strong need for societal and environmental risk assessment (Batley, Kirby, & McLaughlin, 2012; Nowack et al., 2012). Furthermore, colloids are increasingly used in water purification or soil remediation processes (Karn, Kuiken, & Otto, 2009), where prediction of the long-term effects of their application requires understanding their fate in those media. This implies monitoring their most relevant properties being: size, shape, mass, density, crystalline phase, charge, and elemental composition. For instance, understanding agglomeration requires being able to distinguish between agglomerates formed by different mechanisms such as reaction or diffusion limited agglomerates, flocs and hetero-agglomerates, which were all observed under simulated environmental conditions and are characterized by different structures and shapes (Hotze, Phenrat, & Lowry, 2010; Allan Philippe & Schaumann, 2014b). Thus, distinguishing them requires information on their mass, size, shape and elemental composition. Over the years, various techniques were developed for determining these parameters (Hassellöv, Readman, Ranville, & Tiede, 2008; Jimenez, Gomez, Bolea, Laborda, & Castillo, 2011; López-Serrano, Olivas, Landaluze, & Cámara, 2014; Simonet & Valcárcel, 2009; Singh, Stephan, Westerhoff, Carlander, & Duncan, 2014; K. Tiede et al., 2008).

This chapter attempts to systematically evaluate and compare the most used analytical methods for determining the size and the shape of colloids in environmental media and propose a systematic approach for future selection or development of analytical techniques. Only methods with a broad applicability are addressed. Some techniques like UV-visible-, Raman-, IR-, EPR-, NMR-spectroscopy, HPLC, ESI-, MALDI-, TOF-mass spectrometry, can be applied to some specific samples (K. Tiede et al., 2008) but lack of versatility and, therefore, are not considered here. For further comprehensive reviews on nano-analytical techniques, the reader is invited to refer to published reviews (Burleson, Driessen, & Penn, 2005; Fedotov, Vanifatova, Shkinev, & Spivakov, 2011; Hassellöv et al., 2008; Jimenez et al., 2011; López-Serrano et al., 2014; Simonet & Valcárcel, 2009; Singh et al., 2014; K. Tiede et al., 2008; Frank von der Kammer et al., 2012). This chapter focuses on aqueous samples; methods dedicated to pedogenic or aerial particles are beyond the scope of this work. The largest part of the discussions presented in this chapter was already addressed in author's PhD work (Allan Philippe, 2015).

The following section described the specific challenges raised by environmental samples. In the next sections, common techniques are described, evaluated and compared on the basis of these criteria. Considering this current analytical toolbox for colloids, the remaining challenges and needs for the development of new techniques are described followed by an example of a recent answer to this needs: hydrodynamic chromatography coupled to single particle ICP-MS.

REQUIREMENTS FOR ENVIRONMENTAL SAMPLES

Detection Limit

During the second half of the XXth century, biologists and polymer scientists leaded the analytics of colloids. Environmental scientists focused mostly on the characterization of natural colloids (Buffle, Wilkinson, Stoll, Filella, & Zhang, 1998). Natural colloids are mainly composed of organic matter, iron oxides, and aluminosilicates with concentrations in the mg L⁻¹ range (J. R. Lead & Wilkinson, 2006). The

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