DETECTION AND CHARACTERIZATION OF NANOPARTICLES IN THE SURFACE WATER:

CHALLENGES AND FINDINGS

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ABSTRACT

Nanoparticles (particle of <100 nm) in surface waters is a growing concern worldwide. It is estimated that there are more than 1800 consumers products in the use that contain nanoparticles. Due to their ultrafine invisible nature, it is very difficult and highly technical to detect them in the aquatic environment. Limitation of available techniques for complex environmental samples makes the study of the nanoparticles in the environment is challenging. As part of this thesis research a systematic review of the procedures and techniques that are currently used for detecting and quantifying nanoparticles was conducted such that a standard procedure for nanomaterial analysis in environmental samples can be developed. In addition, detection and characterization of nanoparticles using spectroscopic approaches was carried out for the Tennessee River water samples. Also, dispersion and aggression characteristics of selected synthetic metallic nanoparticles in deionized water was examined at discreate time of sonication.

DEDICATION

This thesis is dedicated to my parents.

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At the very beginning, I would like to show my gratitude to Almighty, the most merciful, kindest and generous, who has allowed me to research one of the emerging fields of nano contamination.

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LIST OF ABBREVIATIONS

NM, Nanomaterial

NPs, Nanoparticles

EPA, Environmental Protection Agency

AAS, Atomic Absorption Spectrometry

FAAS, Flame AAS

GFAAS, Graphite Furnace AAS

ICP, Inductively Coupled Plasma

ICP AES, ICP Atomic Emission Spectrometry

ICP MS (SP), ICP Mass Spectrometry (Single Particle)

ICP MS (HR), ICP Mass Spectrometry (High Resolution)

DLS, Direct Light Scattering

UV-vis, Ultraviolet Visible Spectroscopy

FTIR, Fourier transform infrared

XRD, X-Ray Diffraction

EDX, Energy Dispersive X-ray

PL, Photoluminescence (PL)

NTM, Nuclear magnetic resonance

SEM, Scanning Electronic Microscope

TEM, Transmission Electronic Microscope

AFM, Atomic Force Microscope

CHAPTER 1

INTRODUCTION

Background

Different organizations such as Environmental protection Agency (EPA), British Standard Institution (BSI), European Union (EU) have different standards in defining NPs. In principle, nanomaterials are described as materials with a length of 1-1000 nm in at least one dimension (J. Jeevanandam, A. Barhoum, Y. S. Chan, A. Dufresne, & M. K. Danquah, 2018a). According to the United States Environmental Protection Agency (US-EPA., 2017), the ultrafine particles with a size between 1 to 100 nanometer (nm) in at least one dimension are termed as a nanomaterial (NM). Whereas Nanoparticles (NPs) have structural components smaller than 100 nm in at least two dimensions. They are also termed as bridge amid bulk materials and atomic or molecular structures. Nano contamination is a growing concern worldwide. Their presence in the environment is growing day by day due to their increased use in a wide variety of applications including biomedical, optical, electronic fields, water treatment, clothing. More than 1,800 consumer products are containing NMs are available in the market (Vance et al., 2015). While their size may be trivial for their extraordinary performance, but it also has large consequences when it comes to the environment. They may be more harmful to their counterpart bulk material. The release of NPs in the environment has long term bearings on ecology and eventually on human health (E. Kabir, V. Kumar, K.-H. Kim, A. C. Yip, & J. J. J. o. e. m. Sohn, 2018).

Large and most of the coarse particles in water environmental samples are visible by bare eyes and can be detected easily. Micro and colloidal particles can also be detected but with difficulty. But it is taxing to detect NPs in the aquatic environment due to their ultrafine sizes, which is compounded by their expected trace concentrations (in ng/L) (Peters et al., 2018b). There are no straightforward methods to detect and characterize NPs. In general, NPs detection and characterization are a complex tedious process that requires high technical skills for sample collection, preparation, and final analysis. It is not only difficult to collect a representative sample, but also to maintain the original matrix or properties of the sample when dealing with such a sensitive analyte. Any simplification of the NPs analysis process may result in the representativeness of the results. To meet the detection sensitivity of available instruments for NPs detection, environmental samples are preconcentrated as part of the sample preparation. Each step (collection, preparation, and detection) involved in NPs detection and characterization in water environmental samples is still emerging and researchers are yet to settle on a standard method.

Typically, surface water is characterized by turbidity due to the presence of suspended solids, bacteria, viruses, algae, organic/inorganic matters, pesticides generating bad taste and odor. In some areas, like river estuaries, surface water can be brackish, due to the high concentration of salts. The composition of surface water also depends on geographical locations. Rainwater gets contaminated by the atmosphere as well as landcover of the surrounding area. The composition of runoff in the urban area is different than the agricultural area. NPs are ubiquitous in water with greater than atomic structure but less than colloidal structure (N. B.

Hartmann, Legros, Von der Kammer, Hofmann, & Baun, 2012) . In addition to natural NPs, production of artificial NPs is growing with their augmented use in consumer products and reaching the environment at an alarming rate (Proulx, Hadioui, Wilkinson, & chemistry, 2016). When discharged into the surface waters, NMs intermingle with the dissolved or suspended, inorganic or organic components and may start aggregation resulting in the physical changes and chemical transformations. The aggregation can be homo-aggregation (interaction between the same NMs) or hetero-aggregation (interaction between different NMs or between NMs and natural colloids) (Jeevanandam et al., 2018a). The surface water composition also influences the type of interaction of NMs with media parameters. Such interaction in the waters makes NPs detection challenging as the resulting products may behave differently than the original NPs.

While noteworthy advancement has been made in developing analytical techniques for NPs analysis, often such progress has been developed using synthetic sample matrix. Also, the limited research that is available on environmental samples is primarily focused on few case studies. For example, the case studies may focus on many samples to concentrate NPs for the detection or just applied only to selected instrumentation available. Similarly, few review literatures are existing for the case of synthetic samples (US-EPA., 2012). And often, such review literature is focused on the final detection step of the NPs and comprehensive study on the sample collection and preparation. As part of this research, a comprehensive review of more than 100 peer reviewed articles were studied to detail the overall process of NPs detection and characterization in aquatic environmental samples. The review includes the most updated information on sample collection, preparation, and detection of NPs. More importantly, we have presented our review findings on sample collection by category of surface waters (flowing waters, stagnant waters, and runoff waters). However, it is essential to note that the composition and expected concentration of NPs in each category of surface waters makes them unique and requires a unique sample collection technique. Following sample collection, sample preparation processes are detailed in two categories, physical processes, and chemical processes. At the end, the final NPs detection is detailed by spectrometry, spectroscopy as well as imaging approaches.

Objectives

The overall objectives of this thesis research are to understand standard available techniques for ENPs detection and to characterize the ENPs in the surface water environment. The specific objectives included are as follows:

a. Understanding current standards of nano contamination detection and characterization in environmental samples.

Approach: Conduct a comprehensive review of emerging techniques such that a standard technique for analyzing ENPs can be established (Chapter 3)

b. Detection as well as quantification of nano contamination in Tennessee River water.

Approach: Establish sampling protocols, field sampling and laboratory analysis of the river water for nanoparticles. (Chapter 4)

c. Understanding the behavior and interaction of NPs within the environment sample using synthetic NPs.

Approach: Generate protocols to disperse synthetic ENPs in water media and measure dispersion behavior using multiple parallel techniques (Chapter 5)

Organization of the thesis

The thesis is presented in 6 chapters. Chapter 1 presented the background and objectives of the study. Chapter 2 presented literature studies on the collection and preparation of surface water samples for the detection of NPs. Chapter 3 consists of a literature review comprising nano detection instruments, while chapters 4 and 5 presented with the findings of the research in the TN river as well as with the synthetic NPs. Final chapter 6 includes the conclusions of the thesis.

CHAPTER 2

LITERATURE REVIEW

Classification

NMs can be classified in various ways. Sometimes they can be spherical, tubular, flat or any irregularly formed. Or, they can be found as stuck, aggregated or agglomerated forms of organic, inorganic, crystal-like, or amorphous structures. Apart from dimensions and shape, NPs may be classified based on origin, material or electron movement. For example, NPs can be natural (exist naturally) and synthetic (produced by mechanical means for different uses or as a byproduct) or organic and inorganic or combination of both (J. Jeevanandam, A. Barhoum, Y. S. Chan, A. Dufresne, & M. K. J. B. j. o. n. Danquah, 2018b). Virus, Protein, DNA or ATP are examples of natural NPs (L. Chen, Bazylinski, & Lower, 2010). Whereas quantum dots and dendrimer are examples of the synthetic NPs. Carbon nanotube and metal oxides can be both natural or artificial or termed as composite NPs. Another popular name of synthetic NPs/NM is the Engineered NPs or ENPs/ Engineered NM or ENM (US-EPA., 2017). Sometimes NPs are produced by anthropogenic methods like diesel exhaust, welding fumes, industrial effluents, etc. are termed as incidental NM. Based on electron movement, it can also be categorized into 0 D, 1 D, 2 D and 3 D NPs. When an electron is entrapped in a dimensionless space is termed as 0 D NPs. Likewise, 1 D, 2 D and 3 D NPs have electron movement along the x, x-y, and x-y-z axes. Multi-metallic NPs like poly elemental NP can be formed which can be used in the various field (P.-C. Chen et al., 2016).

Environmental Release and Behavior

The ultimate destiny of the ENPs, whether intentional or not, will be at the water/sediment interface after following a variety of pathways. ENPs can flow into the environment after a long-life cycle. Three emission scenarios may be visualized: (i) release during production; (ii) release during usage; and (iii) release after discarding of products containing NMs (waste management). Emissions of NM can be direct to the environment or indirectly through technical means such as wastewater treatment plants (WWTPs) or landfills. Indirect emissions take place in the form of the effluent of WWTPs, or application of biosolids to earth, or leachates released from landfills. ENM in the technical means such as WWTPs may be of bare, coated, chemically or physically transformed. The NPs can simply adhere metals and other water-borne contaminants due to their large surface areas. The existence of other natural species can also modify the surface charge on the NPs. It may undergo aging processes like chemical transformation, aggregation, and disaggregation. In short, dissolution, passivation, aggregation, adsorption, sedimentation, and deposition may be termed as relevant fate and transport processes of ENMs (Bundschuh et al., 2018) .

Health impact

Nano contamination is a growing concern worldwide. Their size may be tiny but may have large consequences. Release of NPs has far-reaching effects on natural ecosystems and ultimately human health (E. Kabir, V. Kumar, K.-H. Kim, A. C. Yip, & J. R. Sohn, 2018). Many NM may consist of non- biodegradable inorganic chemicals such as metals, metal oxides, and ceramics that are not anticipated to biodegrade (US-EPA., 2017). Under low or no Ultra Violet (UV) exposure, Titanium Dioxide (TiO_2) NPs was found to accelerate mortality as well as reduce growth (Haynes, Ward, Russell, & Agrios, 2017). Nanosilver was observed to induce a stress response on fish (Murray, Rennie, Enders, Pleskach, & Martin, 2017). The growth rate of the algae was affected by Zinc Oxide (ZnO) NPs and it was found that ZnO NPs were more toxic than marine algae and bulk ZnO (Manzo, Miglietta, Rametta, Buono, & Di Francia, 2013).

NPs Analysis

It is very difficult to detect ENPs in the environment due to its ultrafine sizes. Large and most of the coarse particles are visible by bare eyes and can be detected easily. Micro and colloidal particles can also be detected but with difficulty. But ultrafine particles like NPs are more challenging to detect, because of the tiny environmental concentrations which may be in the ng/L range. Many authors followed variety of methods directly or indirectly to identify NPs in the surface water. Often it requires multiple technologies in tendon including ultrafiltration, sonication, centrifugation, ionization to identify NPs. In general analysis of ENM in waters is a three-step process: (1) Sample Collection, (2) Sample Preparation, and (3) Sample detection. While the sample collection and sample preparation methods are closely aligned with techniques used for other analytes (example, suspended solids, metals, nutrients, etc.), the detection of ENM is an emerging area at present. Sample collection and sample preparation are discussed in the following sections of this chapter, whereas NM detection is discussed in Chapter 3.

Sample collection

Peters and his coworker carried out a study on the detection of NPs in the rivers Meuse and IJssel of the Netherland. In this study, samples were collected in duplicate from 15 spots along the river. Polyethylene containers (each of 1 L size) were used for the collection of field samples. The container was placed just underneath the water surface for the collection of water from the middle of the stream or a minimum of 2 m from the shoreline. From the container, two amber colored 20 ml glass bottles were also filled without headspace, sealed with a screw cap including a Teflon lining and stored at 4^0C till the experiment. A few blank samples with or without spiked n-Ag were also carried during the sampling of the surface waters. Samples were investigated within 24 hours of collection (Peters et al., 2018b). For more representativeness, the technique of composite sample collection could be followed. Another study was performed to trace the dissolution of Ag NPs in the clear creek at Golden, Colorado, USA. Surface water was also collected from the clear creek just beneath the water surface. But distance approximately 1 m from the shoreline was maintained and passed through a 0.45-micron filter. The samples were preserved in a polyethylene bottle at 20 ^{o} C before use. As a measure of the sensitivity of the instrument and a check standard, acidified samples (with 2 % HNO_3) were prepared (Mitrano et al., 2014). For better representativeness, the sample could be collected throughout the width of the river like bank as well as middle of the stream. Polycyclic aromatic hydrocarbon (PAH) can act as a carrier of contaminants on suspended particles, which was demonstrated on the water of Hamilton Harbor, Canada. Subsurface water samples from this harbor were collected in

September 1995 and was stored in a 50 L polyethylene carboy, which was transported instantly to the laboratory for investigation. Suspended particles were separated using differential cascade sedimentation and centrifugation (Leppard et al., 1998).

An investigation on citrate -capped 20 nm Ag NPs was carried out in lake water at Maryland, United States. Three samples of surface waters from the lake were collected using a 500 ml wide-mouthed polyethylene bottle at NIST (National Institute of Standards and Technology), Gaithersburg campus. Samples were collected from the western bank of the northern pond, southern pond, and creek connecting the ponds. Containers were submerged slowly in a horizontal position around 2 ft away from the edge of the bank. Cares were taken to avoid bubbles as well as strong flowing currents directly into the container. The containers were gradually immersed to the bottom to prevent dislocating bed sediments, turned vertically, then raised out of the water and capped. Samples were preserved under room temperature until further use. Before the experiment, samples were shaken to dilute any sediment that had settled during storage. Visible Cloudiness was visible in the sample, resembled the presence of significant amounts of natural organic matter (NOM). (Chinnapongse, MacCuspie, & Hackley, 2011). Similarly, wastewaters were sampled at different stages of wastewater treatment using containers made of PTFE origin (Behbahani et al., 2013) and polypropylene centrifuge tubes (G. Hartmann & Schuster, 2013) and 60 ml polystyrene bottles (Markus et al., 2018a).

Sample preparation method

There are many intents or purposes of sample preparation. As surface water contains material or particles of various sizes like coarse, fine and ultrafine, etc. Without removing the particle (> Nano sizes) that may interfere with other components and will develop a complex matrix state. Thereby, sample preparation before analysis is a challenge. There should be a right modality between simplification of the matrix as well as maintaining the representativeness of the sample (Oetjen et al., 2017). These purposes are traditionally met by reducing the complexities of the sample and retaining ultrafine particles to detect NPs. There is various procedure available for sample preparation.

Physical methods

Dilution

Dilution aids in reducing the concentration of a solute in the solution. It lessens the viscosity of the sample and as a result reproducibility increases. Viscous samples may not fill the syringe (that are commonly used to load sample to instruments in the detection of ENPs) due to tiny openings and thus causing volumetric errors. However, dilution is often chosen in the non-targeted investigation because of its less biased. Sometimes, series dilutions of samples may give a better result. This approach was found suitable to detect surfactants in the effluent from a wastewater treatment plant (Getzinger et al., 2015).

Filtration

The most popular and mandatory sample preparation for many of environmental samples is filtration. Filtration separates solid from a suspension. Removing particulate material above nano-size makes the sample compatible and shields the instrument from clogging and high backpressure. However, filtration does not concentrate or alter the dissolved fraction of the sample matrix. There is a likelihood of biasing the sample, once the chemical components that are adsorbed to the suspended solids in the matrix are also removed (Mitra, 2004). In case of produced water, filtration has been used as a widespread method for sample preparation, particularly for analysis of High-Resolution Mass Spectrometry.

Centrifugation

Centrifugation is another sample preparation technique that involves centrifugal force to separate particles from a suspension according to their shape, size, density, viscosity. The rotor speed of the pump also plays a vital role in this segregation method. Here sedimentation principle is used, where denser substances moves outward or accumulated at the bottom and lighter particle moves toward the top or center of the rotor. Centrifugation has been used as a common technique for separating NPs of different shapes and sizes. Gold Nanorod was easily segregated using this method. Byproducts like nanospheres and others can also be separated by multiple rounds of centrifugation. A three-phase system of centrifugation can separate three types of products like nanorod, nanospheres, and large particles. It is challenging to demarcate a line of boundary between the denser and lighter substances. For the detection of Ag and Au NPs in River water and sewage treatment plant, centrifugation was used for the segregation after adding necessary capping agent (Y. Yang, C.-L. Long, H.-P. Li, Q. Wang, & Z.-G. Yang, 2016a). Viens and his team used centrifugation (5 mins with 3000 rpm) for the separation of a sample containing NPs in the river as well as rainwater (Fréchette-Viens, Hadioui, & Wilkinson, 2019).

Sonication

Sonication, which uses sound waves to agitate to disperse NPs inside the liquid and to break down the aggregation of the particles. The frequency of sound waves is beyond the upper audible limit of human hearing or ultrasonic frequency (> 20 kHz). Thereby it is also termed as ultrasonication. In the laboratory, two types of sonicators are used. One is an ultrasonic bath, where energy is transmitted through water. Another is the ultrasonic probe, where energy is transmitted directly inside the sample. Where direct contact ultrasonic homogenization is inappropriate, ultrasonic baths allow gentle homogenization (sonication) through the walls of, for instance, a plastic or glass tube. Sonication is a common prerequisite before any laboratory experiment. Yang and his team have used ultra-probe sonication (with ice) of river water and sewerage treatment effluent for homogeneous dispersion of NPs (Yang et al., 2016a). For detection of $TiO_{2,}$ samples were ultrasonicated for 3 mins before being placed in TEM and ICP MS (J. Vidmar, R. Milačič, & J. Ščančar, 2017a).

Evaporation

Evaporation is one of the simple techniques for preconcentration of NM. Here the concentration of ENPs is increased to gain sensitivity for the subsequent determination. In this method, NPs are segregated after evaporation of the solvent and particle dryness. A broad range of solvents, from volatile organic solvents to water are appropriate for this method. For example, a miVac duo concentrator (centrifugal vacuum concentrator and freeze driers) was used for preconcentration after migration experiment of Ag NPs from plastics into food simulants (Artiaga, Ramos, Ramos, Cámara, & Gómez-Gómez, 2015).

Chemical Methods

Chromatography

Chromatography (C) is a laboratory method for the extraction of components in a mixture based upon the distribution of particles between a mobile and a stationary phase. The component dissolved in a liquid act as a carrier of the particles termed as a mobile phase while the other component does not move termed as a stationary phase. The stationary phase is confined in a column or a plane (plate or paper etc.). The various components of the mixture move at various speeds, triggering them to discrete. There are various types of C, can be used for sample preparation of surface water. In size Exclusion C (SEC), column filled with porous packing materials, where particles smaller or equal to the pores of packing materials can percolate deep inside the column. The pores will exclude the larger particle first and then will elute. The SEC analysis is fast, simple, reproduceable, and rather economical. Several columns (usually three or four) may be required for a wide range of size distribution of the sample to get a satisfying separation result. A pretreatment step is a prerequisite, as there is a risk of clogging the pores by large particles (J. Liu & Jiang, 2015).

LLE (Liquid extraction) C is one of the commonly used separation techniques. Holt and his team determine the amount of iron (III) employing oxine (8-hydroxyquinoline) in chloroform, which paved the way for detecting NPs using LLE (Holt & Easley, 1965). Presently, this is the most common separation method for wastewater samples. This LLE method can also be used for highly water-soluble sample, where hydrophobic component is removed leaving the hydrophilic compounds behind (Ho, Pedersen-Bjergaard, & Rasmussen, 2002). This can lead to high noise and sensitivity issues, due to its limited amount of choosiness but a growing number of analytes. Another disadvantage is the development of emulsions during the separation. Emulsions can be removed by passing the extract through columns containing silica (Majors, 2013). HPLC (High-Performance Liquid C) is also another type of LLE C, which can segregate finer particles. In this technique, high pressure is imposed through a capillary tube to accelerate the performance of segregation. Ag+ can be successfully eluted from Ag NPs in a single run after addition of thiosulfate with the mobile phase, where recoveries is > 80 % for both of Ag NPs and Ag+ (J. Liu & Jiang, 2015). This method can analyze actual samples, such as extracts from sports socks, could show good reproducible analytical results with a low detection limit.

SPE (Solid-phase extraction) C is a form of liquid C used for sample preparation of the liquid sample. It is a versatile method used for matrix simplification. Many different sorbent and elution conditions are available for different analytes and matrices. This approach has been successfully used in surface water research for Liquid C analysis (Regnery, Coday, Riley, & Cath, 2016) . A major advantage is the elimination of emulsion issues that are arising while dealing with surface waters. This is easier when carrying out targeted analysis, but for non-target analysis, it may be biased. This can be eluded by using multiple sorbents and solvents. SPE was successfully used to quantify Selenium (Abdolmohammad-Zadeh, Jouyban, Amini, & Sadeghi, 2013). For micro-level extraction, a fiber coat is used in an adsorbent material to extract analytes from liquid matrices or headspace gas. A polymer-coated fused silica fiber is submerged into the liquid sample so that analytes are adsorbed. It is an alluring choice as it does not require organic solvent compared to purge-and-trap or headspace analysis. Due to the lesser handling time, it delivers fewer background noise (Oetjen et al., 2017).

Magnetic solid-phase extraction (MSPE)

MSPE is based on magnetic or magnetizable absorbent. Magnetic particles in the nanometer range get separated by an external magnet. Thus, magnetic material was used as new type of sorbents for NPs preconcentration and speciation, which has given rise to the method of magnetic solid-phase extraction (MSPE). Mwilu and his team developed an MSPE approach for speciation and preconcentration of dissolved Ag^+ and Ag NPs using magnetic particle (Mwilu et al., 2014). Coated or uncoated Fe NPs are utilized in this segregation. Uncoated-Fe NPs picked up Ag NPs with only 5% of Ag ions, whereas Fe NPs coated with dopamine or glutathione or a mixture seized Ag NPs with 20–50% of Ag ions (Ayache, Beaunier, Boumendil, Ehret, & Laub, 2010). Palchoudhury and her team developed a similar methodology using magnetic particles for the segregation of Au NPs and ionic Au (Palchoudhury & Lead, 2014).

Cloud-point extraction (CPE)

CPE method based on cloud point temperature. The temperature at which dissolved solids do not remain as solvable and triggering to precipitate with a turbid or cloudy appearance, is termed as cloud point temperature. It was first studied by Watanabe and his co-worker in the late 1970s and involved the application of surfactants as extractants (Watanabe & Tanaka, 1978) . A surfactant was transformed from one liquid to another by heating. When the temperature increases above the cloud point temperature, the surfactant molecules turned into micelles. This property was utilized to combine the analyte of interest with the micelles and activate preconcentration. Few advantages of this technique were high extraction efficiency, high preconcentration factor, less cost, simple handling, and free from toxicity. CPE was applied for extraction/preconcentration of different metallic NPs, such as Ag (Chao et al., 2011) (J.-f. Liu, Chao, et al., 2009) (G. Hartmann, Hutterer, & Schuster, 2013) , Au (G. Hartmann & Schuster, 2013), ZnO (Majedi, Lee, & Kelly, 2012) and CuO (Majedi, Kelly, & Lee, 2014) from environmental samples, antibacterial products as well as wastewaters. Liu and his co-worker developed a segregation process for extraction/ concentration and dispersion of several NM (Cd Se/ZnS, Fe_3O_4, Ag, Au, and TiO_2 NPs) by CPE (cloud point temperature was 23-25 °C) using Triton X-114 (J.-f. Liu, Liu, Yin, & Jiang, 2009). Tsongas and his team developed a sequential extraction/preconcentration method for several types of NPs (Ag, Au, and Fe_3O_4 NPs) from environmental samples (unpolluted river, lake water, and raw sewage) in a single step followed by a back-extraction technique (Tsogas, Giokas, & Vlessidis, 2014).

Field-Flow Fractionation (FFF)

The separation process is very similar to chromatography without the need for a stationary phase. The high resolution and ability to separate wide range of NPs make the FFF popular. It can be used to segregate different types of NPs, such as metals, metal oxides, and SiO_2 (Weinberg, Galyean, & Leopold, 2011). Besides, the nonexistence of a stationary phase avoids the irrevocable interaction with the particles, which ensures high recovery as well as prevent morphology changes. FFF enables fractionation of ENPs with diverse sizes such as macromolecular, colloidal, and particulate materials (Williams, Runyon, & Ashames, 2011) (Von der Kammer, Legros, Hofmann, Larsen, & Loeschner, 2011) (Vickers, 2017). All separation is performed in a thin channel according to their diverse size and velocities. An axial flow of carrier liquid conveyances in the direction of the exit of the conduit, while a field is applied perpendicular to the carrier-driven flow. The particles were driven toward the accumulation wall from where they also diffused back into the channel and as a result, the separation of the particles takes place. Depending on the “fields” utilized, FFF can be divided into different types, such as thermal FFF (ThFFF), sedimentation FFF (SdFFF), crossflow FFF (FlFFF), electrophoretic FFF (DEP-FFF), and magnetic FFF (MgFFF) (J. Liu & Jiang, 2015).

Functionalization

Functionalization is the method of enhancing the properties and characteristics of the NPs. It can be done through the modification of the surface chemistry of the material. It is one of the fundamental methods used throughout biology, chemistry (organic/inorganic), materials science, textile engineering, nanotechnology, etc. After functionalization quality images with viable information can be obtained. NPs, when coated with small molecules of polymer-like dextran, starch, citrate polyethylene glycol (PEG) show larger biodistribution. Functionalization plays a vital role in the detection of NPs using Nuclear Magnetic Resonance, Fourier Transform Infra-Red, Raman Spectroscopy, Transmission electronic Microscopy, etc. Before TEM analysis, Ag NPs capped with citrate and Au NPs capped with tannic acid and as a result, better detection could be made (Yang et al., 2016a).

CHAPTER 3

REVIEW FINDINGS OF ENPs DETECTION

Introduction

The major objective of this research activity is to develop a comprehensive review of emerging analytical techniques to detect ENPs in water matrices such that a standard method can be developed for ENPs analysis in environmental water samples. There is numerous analytical equipment available to analyze surface waters for determining the composition, concentration, size, surface charge, adsorption, agglomeration of NPs. However, most of such techniques are primarily focused on control media where the samples are generated in a laboratory using DI waters or organic solvents. Environmental samples are expected to be complex and often the laboratory methods developed using controlled samples may not work with the same accuracy for environmental samples. Commonly, the laboratory techniques for detecting ENPs are based on the interaction between energy and NPs are based on the interaction between energy and NPs. Light or ray is used as energy. Plasma, laser, ultraviolet, x-ray, infra-red, fluorescence, and other light sources are used as energy. Interaction between light and NPs may take place in the form of absorption, emission, scattering, reflection, refraction, radiation, etc. From the interaction, a spectrum is created which is used for the analysis of NPs. There are two popular methods of analysis based on spectra, such as spectrometry and spectroscopy. Usually, concentration can be measured in spectrometry. On the other hand, size and other auxiliary data can be visualized with spectroscopy. The interaction may provide images, from where the topography of NPs can be visualized.

Spectrometry Approaches

Spectrometry is a powerful analytical approach to quantify unknown material using the known compounds within a sample. It also elucidates the structure and chemical properties of various NPs. In this technique, liquid samples are ionized into chemical components, which are identified according to their mass-to-charge ratio and sorts the ions based on this ratio. That is why the term “mass” is often included in the term mass spectrometry or MS. In easier terms, a spectrum quantifies the masses within a sample. A mass spectrum is a graphical representation of the signal (coming from ion) as a function of the mass-to-charge ratio. These spectra are used to detect the masses of particles and molecules, the elemental or isotopic signature of a sample, and the chemical structures of molecules and other chemical compounds.

Absorption Based: Atomic Absorption Spectrometry (AAS)

In AAS, the concentration of elements is measured from the spectrum, developed after the absorption of radiation. The sample was then atomized at a high temperature. Atoms of different elements absorb characteristic wavelengths of light. The quantity of light absorbed is proportional to the number of atoms. The reduction of light in the detector is perceived as a measure of the concentration of that element. Two methods are generally used to produce atoms from the sample. One is Flame AAS (FAAS) and another is Graphite Furnace AAS (GFAAS).

Flame AAS (FAAS)

Flame AAS (FAAS) is a type of spectrometry that uses a flame to evaporate the sample. Air/acetylene or nitrous oxide/acetylene is utilized to yield a flame. It can produce temperature as much as 2800°C. Due to the high temperature, the liquid sample is evaporated, as well as dissociates into its chemical components. When light from a lamp (different material sensitive to different bulb) passes through, the atoms of interest absorb the light. This is measured by a detector, which can compute the concentration. Metal compounds such as lead or cadmium and transition metals like manganese or nickel are atomized easily in the sub-ppm range. However, there are several refractory elements like vanadium (V), zirconium (Zr), molybdenum (Mo), and Boron (B) which do not perform well with FAAS, as they do not dissociate at this temperature. For example, Behbahani and his co-worker developed an efficient and economical method for the preconcentration of trace amounts of Pb (II), Cd (II) and Cu (II) in environmental samples (Behbahani et al., 2013). Using FAAS, they managed to detect concentrations 0.14, 0.19 and 0.12 $\mu g\ L^{-1}$ for Pb (II), Cd (II) and Cu (II) ions, respectively. Also, trace amounts of Pb, Zn, Cd and Cu ions were measured in marine samples using FAAS (Ghanemi, Nikpour, Omidvar, & Maryamabadi, 2011). The detection limits of Cd, Zn, Cu, and Pb ions were 0.30, 0.21, 0.24, and 0.63 $\mu g\ L^{-1}$ respectively.

Graphite Furnace AAS (GFAAS)

Graphite Furnace AAS (GFAAS) is a type of spectrometry, that uses a graphite coated furnace to evaporate the sample. Instead of a flame, samples are heated electrically with graphite tubes or rods. Results depend on the accuracy of the sample injection. Argon gas is used to produce high temperatures. As much as 3000°C can be achieved by the procedure. Due to the inert nature of argon gas, it can be safely run unattended. The higher the atom density, the longer the residence time in the tube, which makes the GFAAS detection 1000 times better than FAAS. The working life span of graphite tubes is short, and it requires frequent setup. The measurement of metallic NPs in aquatic samples necessitates pretreatment that preferably combines pre-concentration and species selectivity (G. Hartmann & Schuster, 2013). After necessary extraction, a low limit as little as 5 ng L^{-1} is achieved using GFAAS for quantification. Using GFAAS, Jahromi and his co-worker could detect Cd up to 0.6 ng/L in a water sample (Jahromi, Bidari, Assadi, Hosseini, & Jamali, 2007).

Plasma Based: Inductively Coupled Plasma (ICP)

An ICP, also known as a transformer, coupled plasma (TCP), is a type of spectrometry that uses plasma for atomization or excitation. Plasma is formed once the argon gas is "coupled" in an induction coil (time-varying magnetic field). When a spark is applied by the ICP torch to the argon, electrons are stripped off the argon atoms and as a result, argon ions are formed. Here elements experience hardly any chemical interference within the sample. All chemical bonds below 3000 °C are completely dissociated. Due to the high temperature, better detection is also achieved for refractory elements. This technique can provide qualitative, as well as quantitative information about the sample. Aqueous samples are usually introduced in the ICP instruments by using various types of nebulizing systems, which vaporize the sample. It can detect metals and several non-metals in aquatic samples at trace amount. It can detect different isotopes of the same element, which makes it a more versatile tool in the detection field.

ICP Atomic Emission Spectrometry (ICP AES)

ICP-AES, sometimes referred to as ICP Optical Emission Spectrometry (OEP), uses a plasma source to excite the ions to a state where they emit light of a characteristic wavelength. A detector measures the concentration of that element according to the intensity of the emitted light. In ICP analysis, the sample undergoes temperatures as high as 10,000° C, which induce the elements to atomize. Therefore, scale measurements as low as ppb levels can also be determined, which is lower than the FAAS limit. ICP instruments can be of two types: radial and axial. Traditionally, in the radial configuration, the plasma source is observed from the side, across the narrow central channel. Recently many systems observe the emitting channel horizontally along its length; it is termed as axial method. Due to increased path length and reduced plasma background signal, the detection limit is lower in axial configuration than radial. Simultaneously, in ICP instruments as many as 60 elements can be detected at one time. Sequential ICPs can run analytical experiments for about five elements per minute. The status of silver nanoparticles (Ag NPs) in the different aqueous environments in Malaysia (two rivers and two sewage treatment plants) were examined with two adsorbents (activated carbons derived from oil palm and coconut shells) and found concentrations of Ag NPs in the rivers and sewage treatment plants (STPs) are in the ranges of 0.13 to 10.16 mg L^{-1} and 0.13 to 20.02 mg L^{-1}, respectively, using ICP-AES (Syafiuddin et al., 2018a).

ICP Mass Spectrometry (ICP MS)

The mechanism of ICPMS is also based on a plasma source, which dissociates the sample into its constituent atoms or ions. After excitation by the plasma, ions are passed through the system. Then a detector (mass spectrometer) can measure the ions themselves rather than emitted light. It is based on their atomic mass-to-charge ratio either by a quadrupole or magnetic sector analyzer or time of flight. Concentration is derived through calibration with certified reference materials. Measurements as low as parts per trillion (ppt) range can be detected. Quadrupole mass spectrometers are the most common in ICP-MS as they are easy to operate and maintain. On the contrary, magnetic sector instruments are inherently more sensitive and have a higher ion extraction potential. As a result, they are used in more specialized applications, where higher sensitivity is needed. Liquid samples are usually passed through different types of pneumatic nebulization systems, the first gateway of ICP-MS instrument. But now a days monodisperse droplet generators (MDG) are being used for the introduction of nanoparticle suspensions. The efficiency of MDGs in nebulization efficiencies is close to 100%, much better than conventional nebulization systems (Laborda, Bolea, & Jiménez-Lamana, 2014)

. There are a lot of variations of ICP MS like Single Particle (SP) ICP MS, High Resolution (HR) ICP MS, etc.

SP ICP MS is an emerging technique based on a single particle mood, capable of measuring NPs size, number and concentration. It is termed as a robust and reliable method for the characterization of tracing elements, which is one of the main challenges of analytical chemistry. Peters and his team used Single Particle (SP) ICP MS to detect Nano-sized Ag and CeO_2 in the river water of Meuse and Ijssel, Netherland (Peters et al., 2018a). Municipal waste as well as river (Des Prairies, Montreal, Canada) water was analyzed using ICPMS and SP ICPMS by Proulx and others (Proulx, Hadioui, & Wilkinson, 2016). In this experiment, Nano Ag was found below detection limits, but Cu NPs could be detected once the separation technology was coupled. A comparative study of ultrapure and natural water was carried out after spiking with Ag and Au NPs by Yang and his team (Y. Yang, C.-L. Long, H.-P. Li, Q. Wang, & Z.-G. J. S. o. T. T. E. Yang, 2016b) . After SP ICP MS analysis, it was found that both (ultrapure and natural water) have a similar level of NPs concentration. ZnO NPs are found more in river water (14.3 nm) and rainwater (17.7 nm) than Milli-Q water (8.2 nm) after a similar amount of spiking with SP ICP MS (Fréchette-Viens et al., 2019)

In the HR- ICP-MS, sensitivity, and resolution can be enhanced by magnetic sector analyzer instead of quadrupoles. It is made for the most flexible and reliable analyses and the best analytical results. It can carry out multi-element analysis at trace level with the highest sensitivity and accuracy. Markus and others collected water samples from River Dommel of the Netherland to analyze seven elements (Ag, Zn, Ti, Au, Ce, Zr, and La) using high-resolution (HR)

ICP MS (Markus et al., 2018a). Silver was found with the lowest concentrations of 0.03 µg/ L, which is in the range of the limit of quantification of 0.02 µg/ L. Seven fullerenes (C60 and C70 fullerenes and five functionalized fullerenes) have been examined in river samples collected near Barcelona (Catalonia, Spain) with HR ICP MS (Sanchís, Bosch-Orea, Farré, & Barceló, 2015). In surface waters, C60 fullerene was the most ubiquitous component and was detected 100% with a concentration from 31 pg/l to 4.5 ng/l, while C70 concentrations ranged from less than these limits (which is 1.5 ng/l).

Spectroscopy approaches

Spectroscopy is another powerful analytical tool based on the interaction between light and matter. Light may be visible or invisible such as IR, UV, X-ray, etc. It can transmit through, reflect, or scattering off the materials. Initially, the study was based on the dispersion of visible light through a prism according to their wavelength. The portion of the visible spectrum enter our eyes determines the colors we perceive. A substance might appear green, once it absorbs the green parts of the spectrum. This method is further enhanced by the interaction between matter and electromagnetic radiation. Emission occurs when the atoms of a molecule move from one energy state to another in the presence of light. In short, spectroscopy is the measurement of light after interaction with the materials.

Laser Ray Based-Direct Light Scattering (DLS) and Raman Spectroscopy

Dynamic Light Scattering (sometimes referred to as Photon Correlation Spectroscopy or quasi-elastic Light Scattering) is the most popular spectroscopy tool used for a size distribution profile of a small particle typically in the sub-micron region. Scattered lights are emitting light, which does not follow the angle predicted by the law of reflection. Once scattered light interacts with the Brownian motion (the erratic movement of particles) of the trace particles, the size distribution profile developed. The larger the particle, the slower the Brownian motion will be. Smaller particles move more rapidly. Temperature also performs a vital role, which is related to viscosity. Without the stability of temperature, convection currents will develop and in turn will ruin the correct interpretation of sizes. The velocity of the Brownian motion is termed as the translational diffusion coefficient. The diameter of a sphere that has the similar translational diffusion coefficient as the particle. The translational diffusion coefficient will depend not only on the size of the particle core, but also on concentration, surface structure, and type of ions in the medium. Any modification to the surface of a particle, will influence the diffusion velocity and accordingly will change the apparent size of the particle. An absorbed polymer layer projecting out into the medium will lessen the diffusion speed more than the flat lying polymer. The nature of the surface, as well as the ionic concentration of the medium, can affect the particle apparent size by several nanometers. Due to its comparatively low cost and ease of operation, DLS is the primary choice of instrumentation for analyzing the size and distribution of NPs. The size distributions of TiO_2 NPs calculated by DLS as 117 ± 22 nm for rutile, 42 ± 30 nm for anatase (J. Vidmar, R. Milačič, & J. J. M. J. Ščančar, 2017b).

Raman Spectroscopy is another light scattering technique that provides detailed information about chemical structure, phase, crystallinity, and molecular interactions. Here light interacts with the chemical bonds within a material. Once the laser light is incident on a molecule, light is emitted with a scattering fashion. Most of the scattered light is of similar wavelength (or color) to the laser source, is termed as Raleigh Scatter, which does not provide useful information. However, a small amount of scattered light (typically 0.0000001%) is of different wavelengths (or colors), is defined as Raman Scatter. A Raman spectrum features several peaks, which correspond to a specific molecular bond such as C-C, C=C, N-O, C-H, etc., and groups of bonds such as the benzene ring breathing mode, polymer chain vibrations, lattice modes, etc. The advanced types of Raman spectroscopy include resonance Raman, tip-enhanced Raman, surface-enhanced Raman, stimulated Raman, polarized Raman, offset Raman, transmission Raman, and hyper Raman. Arsenic (As) could be detected easily by Raman Scattering in developing nations such as Bangladesh, where Arsenic contamination in the groundwater was increasing alarmingly. In this case, a highly sensitive platform utilizing surface-enhanced Raman spectroscopy was used to quantitatively detect Arsenic in water up to 1 ppb (Mulvihill, Tao, Benjauthrit, Arnold, & Yang, 2008).

Ultraviolet Ray Based- Ultraviolet-Visible Spectroscopy (UV-Vis)

UV-vis is a widely used technique to characterize trace material using the interaction between UV rays and the sample material. It is also termed absorption spectroscopy or reflectance spectroscopy. Detection, as well as quantification (size and concentration) of a sample, can be determined using UV-vis. Usually, wavelengths of peak absorbance (i.e., GO NPs at 230 nm, Ag NPs at 438 to 450 nm, Au NPs at 450 nm, etc.) are unique. Electronic transitions of atoms and molecules occurs in the region of the electromagnetic spectrum. Using the Beer-Lambert law, concentration can be calculated from absorbance. Sikder and his team showed that UV–vis is an easy and fast method for detection and quantification of sterically stabilized PVP (Polyvinylpyrrolidone) coated Ag NPs (Sikder, Lead, Chandler, & Baalousha, 2018). They found PVP-Ag NPs have a single plasmon resonance peak, which drops with time. In both synthetic and natural seawaters, PVP-Ag NPs have a single plasmon resonance peak, which decreases with time in synthetic seawater compared to natural seawater (Ellis, Baalousha, Valsami-Jones, & Lead, 2018).

IR Ray Based: IR Spectroscopy

It is a technique used to determine the functional group in the molecule or structure of different chemical groups. Different functional groups bend, stretch and wag at different frequencies. A functional group will absorb light, once the frequency of light merges with the frequency of stretching, wagging or bending. IR spectrum is the graphs of IR light absorbance or transmittance, that gives a hint to the existence of a certain molecule. Individual and multiple peaks of the spectrum are the fingerprint of different molecular structures. The Fourier transform infrared (FTIR) spectrometer is the most popular type of IR spectrometer. The structure of the magnetite NPs was confirmed using FTIR spectra by Bagheri and his team (Bagheri, Afkhami, Saber-Tehrani, & Khoshsafar, 2012). Functional molecules grafted on CNTs (carbon nanotube) could be identified by Baudot and his co-worker (Baudot, Tan, Kong, & technology, 2010). The attachment of organic functional groups on the surface of inorganic nanoparticles can be analyzed using FTIR. The concentration of TiO_2 NPs was examined with five different chemical functionalities ($-CH_3$, $-OH$, $-COOH$, $-NH_2$, and $-CONH_2$). The fastest and maximum deposition mass were observed on $-NH_2$, followed by $-COOH$, $-CONH_2$, $-CH_3$, and $-OH$ (Wang et al., 2017).

X-Ray Based: XRD (X-Ray Diffraction) and Energy Dispersive X-ray (EDX)

Invisible X-rays can be used in characterizing NPs. It can be used to spot the chemical and elemental properties of a sample. There are two main X-ray spectroscopy techniques: XRD and EDXS. X-Ray Diffraction is used for the identification of any crystalline structure of the solid compound. An analysis is based on the spectrum, derived from the scattering of X-rays after imposing them on the crystal. It is not appropriate for amorphous materials and the XRD peaks are too wide for particles with a size below 3 nm. Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is the same technique that are used for the elemental investigation or chemical characterization of a sample. The analysis is based on the peaks from the X-ray emission spectrum. Each element has a unique atomic structure shows a unique set of peaks on its electromagnetic emission spectrum and thereby facilitating the detection. To excite the emission of X-rays from an object, a high-energy beam such as electrons, protons or X-rays, is focused on the sample. The energy of the X-rays emitted from the specimen can be measured by an EDX. In many cases, experiments are carried out using both methods to confirm components and thus they complement each other. To confirm the identity of TiO_2, an EDX scan was carried out and the resulting EDX graph shows the presence of titanium and oxygen, a clear indication of titanium dioxide (Markus et al., 2018b).

Fluorescence-based: Photoluminescence (PL) Spectroscopy

Fluorescence is a kind of light emitted from the molecule. It is also termed as photoluminescence. It is a special type of luminescence from where spontaneous radiation takes place. Fluorescence light emission starts under the optical excitation of a molecule. Different types of lamps like Xenon, tungsten, etc. are used as an excitation source. PL is used for characterization of fluorescent nanoparticles, such as quantum dots, as well as metal nanoclusters. Gong and co-workers studied a highly branched plasmonic nanostructure as like as the PL behavior of a single Au nanoflower (Zhang et al., 2014). The PL tests and emission determinations comprised a complementary approach to the optical scattering method (Petkov et al., 2005). On the other hand, quantum dots such as metal chalcogenide NPs have widely been studied by PL. (Saliba, Coppel, Mingotaud, Marty, & Kahn, 2012).

Nuclear spin-based: Nuclear Magnetic Resonance (NMR)

NMR is a type of spectroscopy used for the quantitative and structural determination of nanoscale material. It depends on the phenomenon displayed by nuclei when placed under a strong magnetic field. A proton inside the nuclei tends to spin due to the influence of the magnetic field. As a result, there are some differences in energy and accordingly, spin up as well as spin-down states are exhibited. The transition between the states can be verified by electromagnetic radiation in the radio wave range. Marbella and Milestone have inscribed a comprehensive article on the NMR techniques for noble metal NPs. They showed that NMR can be utilized for analysis of NPs formation in solution (Marbella & Millstone, 2015). Usually, it is helpful for analyzing the development of metallic NPs. It can also derive information about capping agent density, arrangement, and dynamics. As a result, properties of the particle core like electrical structure, atomic composition or computational architecture can be easily determined (Scheid et al., 2016) (Vowinkel, Paul, Gutmann, & Gallei, 2017).

Imaging approaches

Microscopy is the technique used to visualize objects that cannot be seen by the bare or naked eye. The range of the microscope can be anything between mm and nm. There are various types of microscope such as optical, scanning, electronic, etc. A common optical microscope consists of lens, tube, stage, and reflector. A specimen positioned on the stage is magnified by manifold through the lens. Electron microscopes have superior magnifying power than optical microscopes because of shorter wavelength electrons. Magnifications in electronic microscope can be up to one million times larger than the size of a specimen, while optical microscopes can achieve a magnification of no greater than 1000x. There are various types of electron microscope

– the transmission Electron Microscope (TEM), the Scanning Electronic Microscope (SEM), atomic force microscopy (AFM).

Scanning Electronic Microscope (SEM)

A Scanning Electronic Microscope is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons (as a substitute for sunshine or photons). After the interaction between the electron (a component of a beam) and sample, this, in turn, forms the shape of an image. The focused beam is of high-energy electrons which produces a variety of signals at the surface of solid specimens. After hitting the specimen with the probes, 2 types of electrons come out. The first type of electron is termed secondary or surface electron, which forms the image of a surface feature. The second type of electrons is backscattered electrons, which comes from the deep inside the sample and accordingly form the inner image. But few backscatter electrons get trapped in the specimen and cause X-ray to be given off, which can assist in elemental analysis. Thus, it reveals information about chemical composition, crystalline structure, morphology, and orientation of materials comprising sample. The range of the area is around 1 cm to 5 microns in width, which can be imaged in a scanning mode (magnification ranging from 20 to approximately 30,000 times, a spatial resolution of 50 to 100 nm). In Netherland, SEM was utilized as a technique for the detection of titanium dioxide and gold NPs in influent and sludge samples from the wastewater treatment plant. Diameters TiO_2 was measured in the range of 50 to 300 nm and gold NPs were in the range of 10 to 20 nm

(Markus et al., 2018b). The diameter (70 nm) of the metallic core of Ag NPs could be determined using SEM, which was much precise than DLS analysis (Ahlberg et al., 2014).

Transmission Electronic Microscope (TEM)

Transmission Electronic Microscope is a type of electron microscope, where a beam of electrons is transmitted through a specimen to produce an image. The size of the specimen is tiny, usually it is a ultrathin section less than 100 nm thick or a suspension on a grid. Electrons are scattered, once passing through the specimen and accordingly, an image is formed from this interaction. The image is then magnified and focused onto a fluorescent screen or a scintillator attached to a charge-coupled device. TEMs are capable of magnifying at higher resolution in comparison to other microscopes. Fine details as small as a single column of atoms can be captured, which is thousands of times smaller than an object seen in a light microscope. Information derived from these mechanisms depends not only on the contrast but also on the settings of lenses, apertures, and detectors. Thus, a TEM can provide an extraordinary variety of nanoscale resolution information. In idyllic cases, it not only reveals locations of the atoms but also type of atoms. That is why, TEM is considered as an essential tool for technology in both biological and materials fields. The size distributions of TiO_2 NPs calculated by TEM as 96–106 nm for rutile, 21–38 nm for anatase (Vidmar et al., 2017b).

Atomic Force Microscope (AFM)

Atomic Force Microscope is used as a microscopy technique for generating three-dimensional images of any object. AFM is founded on the interacting forces amid a fine probe and the sample. The probe is a sharp tip, made of silicon or silicon nitride attached to the end of a cantilever. When the AFM examines the sample, the cantilever gets deflected due to the attractive or repulsive forces between the tip and the sample surface. The probe scans the surface of the sample so closely that electrons can flow uninterruptedly between the probe and sample, which generates a flow of current from the surface to probe. Three different modes of scanning like contact, non-contact and tapping mode (also known as an intermediate or oscillating mode) depending on the degree of proximity between the probe and the sample. It forms the pictures pixel by pixel hitting from left to right and top to bottom. The lens is magnetic. Once the electron beam hits the specimen, two major types of electron come out. One type is secondary electrons, which usually give the images of surface features. Another type of electron is termed as backscattering electrons, which come out from deeper inside and accordingly, give the inner image. Backscattering electrons trapped in the specimen cause an x-ray to be emitted and in turn provide a more analytical image. AFM does not require any surface modification or coating before imaging. Low-density materials can also be characterized by AFM. (Qiu et al., 2016). Furthermore, it has a similar resolution like SEM and TEM, but cost is less. It also occupies comparatively less space in the laboratory. On the other hand, AFM demonstrates slower scanning times than other electronic microscope (Oćwieja, Morga, & Adamczyk, 2013).

Characterization of PVP coated Ag NPs in seawater was carried out and found that small NPs dissolved quickly than large NPs (Sikder et al., 2018).

Conclusion

No single instrument is adequate to detect NPs. Often multiple technologies in tandem are utilized for detection as well as characterization of NPs. There were a lot of instances in the literature that used ICP blended with SEM and EDX, TEM followed by ICP (Yang et al., 2016b). HRMS with NTA (Sanchís, Bosch-Orea, Farré, Barceló, & chemistry, 2015), FAAS with FTIR, XRD, TEM (Bagheri et al., 2012) etc. However, the use of ICP blended with TEM is found to be a commonly used detection technique for ENPs in water samples (Syafiuddin et al., 2018b) (Fréchette-Viens et al., 2019).

CHAPTER 4

TN RIVER NANO CHARACTERIZATION

Introduction

The primary objective of this study was to develop a better understanding of the presence of NPs in surface water. Among the major rivers of the south-eastern USA, Tennessee River is the largest which also covering large drainage areas in the southeast region of the United States. It is approximately 652 miles (1,049 km) long and is in the southeastern United States in the Tennessee Valley. Tennessee River is the largest tributary of the Ohio River. Since surface water of the upper TN river basin passed through the Chattanooga towards lower TN river basin, a portion of the TN river around the Chattanooga taken as the study site. This portion of the river is also easily accessible due to its proximity to UTC. As discussed in Chapters 2 and 3, there are no straightforward analytical methods were available for the detection of NPs in the water environmental samples. Most of the available methods for ENPs detection rely on inductively coupled plasma mass spectroscopy (ICP-MS) requiring complex sample preparation procedures and trained personnel for operation. However, as part of this research use of DLS for characterizing NPs is demonstrated by quantifying NPs in Tennessee River.

River water sampling

Samples were collected just below the water surface from a minimum distance of 2 meters from the shoreline. Samples were tested within 24 hours of collection. The area was stretched along the Tennessee river around Chattanooga downtown starting from downstream of Chickamauga Dam up to Moccasin bend (Figure 1). Table 1 is listed with location physical address along with the source area near the sampling locations. Wastewater discharge point and national pollution discharge elimination system are abbreviated as WWDP and NPDES respectively.

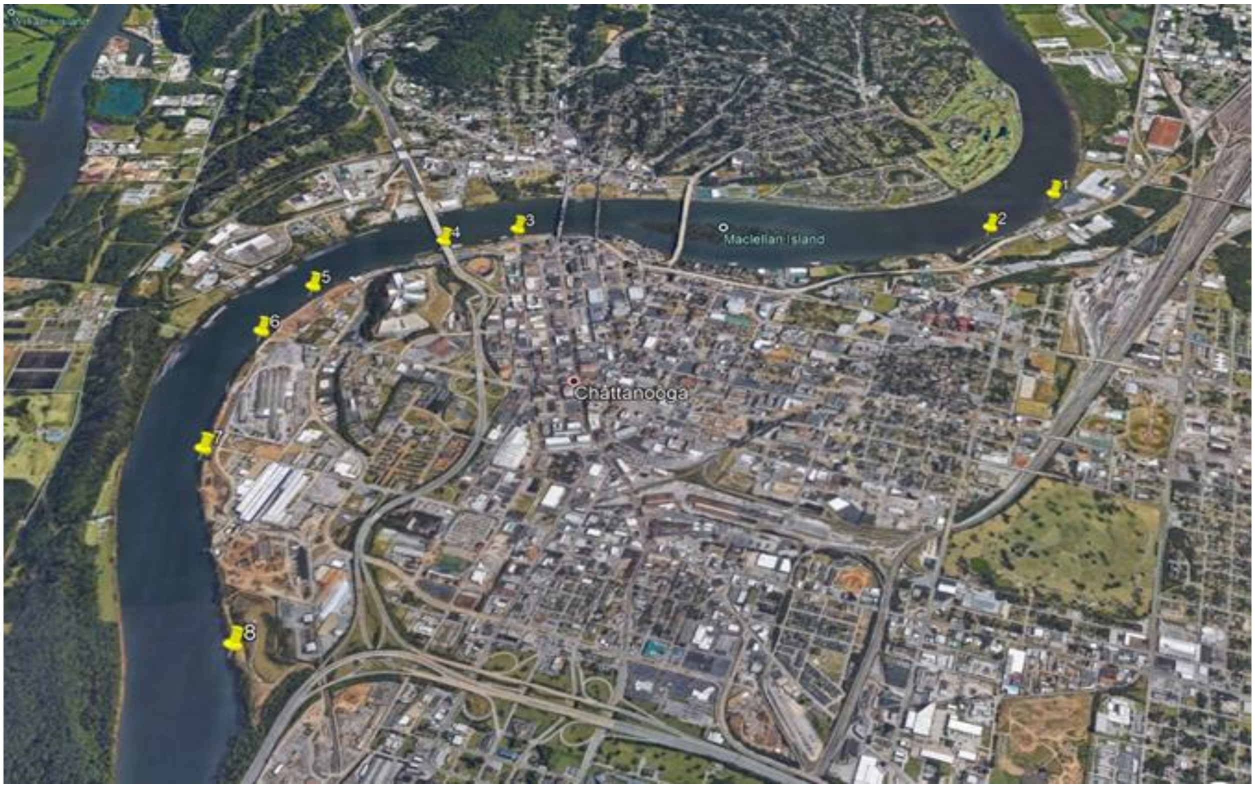

Figure 4. 1 Sample collection locations in Tennessee River around the City of Chattanooga

Table 4. 1 Summary of the sampling location along Tennessee River

No.	Location	Grid	Distance between consecutive collection points in the mile (starting point-endoscopy hospital)		Description
			Distance in between	Cumulative distance	
1	Endoscopy Hospital (DS)	35.057216 N 85.281554 W	0	0	There were a lot of rainwater discharges points at this location
2	WWDP 0.004 (DS)	35.053573 N 85.292158 W	0.8	0.8	There were several spots of rain and treated sewage water discharge points at this location. The location was assigned NPDES permit no TN 0024210 by the City of Chattanooga.
3	Aquarium	35.057064 N 85.312173 W	1.3	2.1	This is a heavily populated tourist attraction spot. Therefore, there might be concerns about anthropogenic pollution.
4	Erwin Mariners	35.055211 N 85.318776 W	0.5	2.6	Several tourist boats were anchored here. Therefore, there was a possibility of fuel pollution.
5	WWDP 462.7 (US)	35.050940 N 85.324704 W	0.4	3.0	Rain and untreated sewage discharge points were there at this location.
6	WWDP 462.7 (DS)	35.049989 N 85.325261 W	0.2	3.2	Rain and untreated sewage discharge points were there at this location.
7	WWDP 462.7 (700 m DS)	35.042930 N 85.327126 W	0.8	4.0	Rain and untreated sewage discharge points were there at this location.
8	WWDP 0.008 (DS)	35.036697 N 85.325627 W	0.6	4.6	This location had a lot of rain and treated sewage water discharge points. Location was denoted as NPDES permit no TN 0024210 by the City of Chattanooga.

Filtration

The 0.22 u filter is one of the smallest filters useful for segregating ultrafine particles. Each sample was filtered through a 0.22 µm polyethersulfone (PES) membrane filtration unit (Fisher Scientific) within 24 hours after collection from the TN River at normal atmospheric pressure and room temperature (Figure 2a).

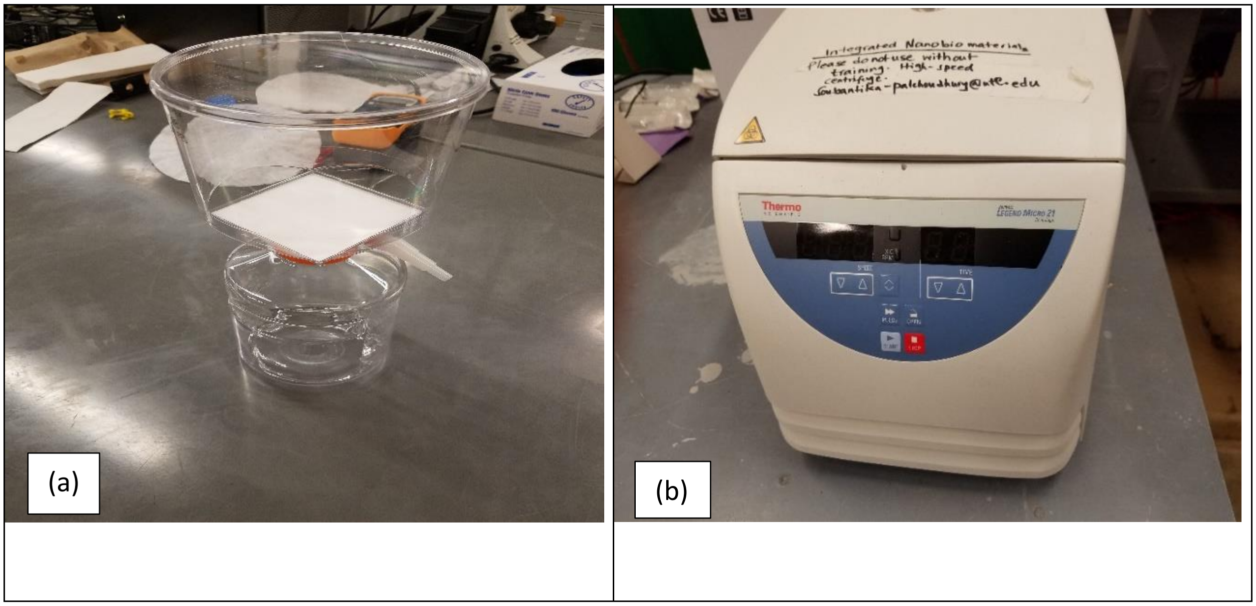

Figure 4. 2 Sample preparation (a) Filter and (b) Centrifugation

Centrifugation

Particle suspended in liquid media can be separated under the influence of the centrifugal field. Due to the ultrafine nature of the particle, a high-speed centrifuge is preferred. The samples were separated via high-speed centrifugation (Fisher Scientific) at 15000 rpm for 5 min and 15 min at room temperature (Figure 2b).

Sonication

Sonication is an effective tool used for mixing particle or disaggregation into a particle in a liquid media. It uses sound waves to agitates particles in a solution. Finally, the treated river water samples were dispersed via sonication (Branson 1800, Fisher) at room temperature for 30 min to render them suitable for various nanomaterial characterization methods (Figure 4.3).

Figure 4.3 Ultra-Sonication (Bath)

DLS

The average size and surface charge of the particles present in the Tennessee river water samples were investigated using a Litesizer 500 Particle Analyzer (Anton Paar) equipped with zeta potential capability (Figure 5). The hydrodynamic sizes were determined as an average of three consecutive measurements conducted at room temperature for the reliable representation of the samples. Zeta potential of the water samples was measured at a reference temperature of 25 °C in Omega cuvettes. An average from three consecutive measurements was used to represent the zeta potential of the sample for reliability (Figure 4.4).

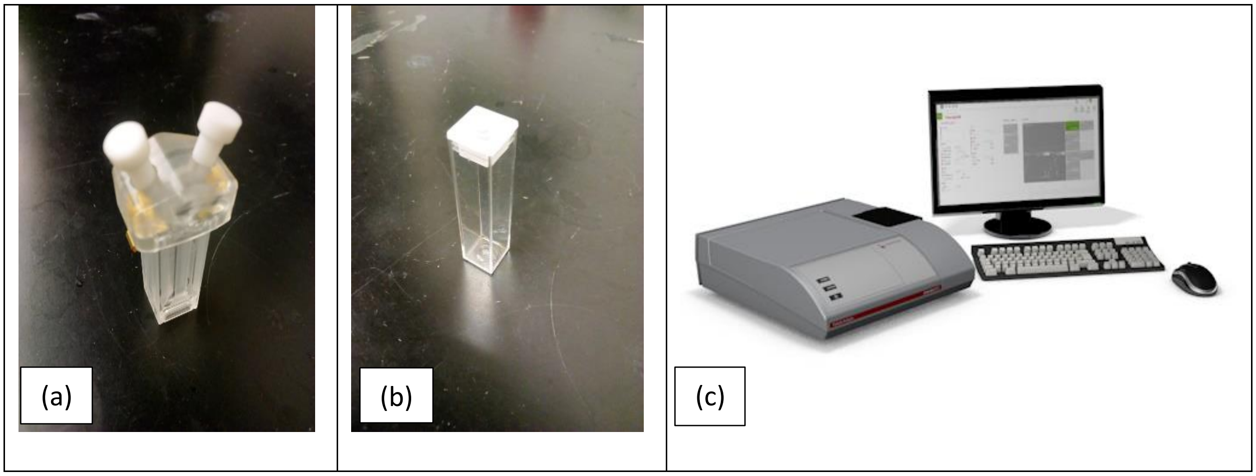

Figure 4.4 Cuvette for zeta potential (a), Cuvette for Size (b), DLS (c)

UV-vis

The river water samples were characterized via a Spectronic 200 ultraviolet-visible (UV-vis) spectrophotometer (Thermo Scientific) to detect the presence of nanomaterials (Figure 4.5). Absorption spectra of the different river water samples were measured over a wavelength range of 340 -1000 nm at room temperature. An average of three consecutive runs was reported as the representative absorption spectra for each sample. Graphical representation, data analysis and comparison of the different adsorption spectra were conducted in Excel.

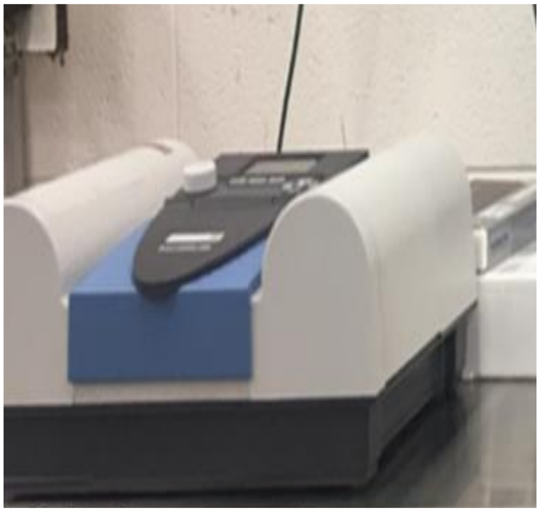

Figure 4.5 UV-vis Spectroscopy

SEM

A Hitachi S3400 SEM was used to investigate the presence of nanomaterials in the different river water samples and to understand the size and morphology of these dissolved nanomaterials. Representative samples for SEM analysis were prepared by a facile drop dry method to prevent any image artifacts from staining or fixation. In a typical sample preparation process, aliquots of the river water sample were added to an adhesive carbon tape mounted on a 15 mm SEM sample stub. The liquid was gently absorbed from the edge using Kimwipes and the sample could dry in a desiccator for 30 min, before imaging. SEM imaging of the water samples was conducted at a lower voltage of 3 kV to prevent artifacts from beam damage. ImageJ and graphical software (e.g., Excel and Kaleidograph) were used for image processing and analysis of the particle size of the samples. SEM provides a wider area scan compared to transmission electron microscopy and is more suitable in this case for gaining insights on the overall size and morphology of particles present in the entire sample (Figure 4.6).

Figure 4.6 SEM

Sample analysis

Filtration Vs Centrifugation

The average size of the untreated sample 2143 nm with two peaks at 160 nm and 1977 nm according to figure 11. The untreated river sample was polydisperse, as expected with a polydispersity index (PDI) of 0.50. This data suggested that nanomaterials might be present in this water sample along with larger particles and aggregates. Therefore, filtration and centrifugation were used as two different non-invasive treatment processes to separate the larger sized particles and thereby detect the nanomaterials in this water sample. The filtered river water sample showed an average particle size of 174 nm with a PDI of 0.26, like the samples treated via centrifugation for 15 min (average size: 161 nm, PDI: 0.27). However, the particle sizes were larger (282 nm, PDI: 0.37) for samples centrifuged for 5 min due to incomplete separation of larger aggregates in this treatment method. All treated samples were more monodisperse compared to the collected river water sample. These results suggested that filtration through a 0.22 µm PES membrane and high-speed centrifugation for 15 min were comparable separation strategies for environmental water samples such as river water (Figure 4.7- 4.9).

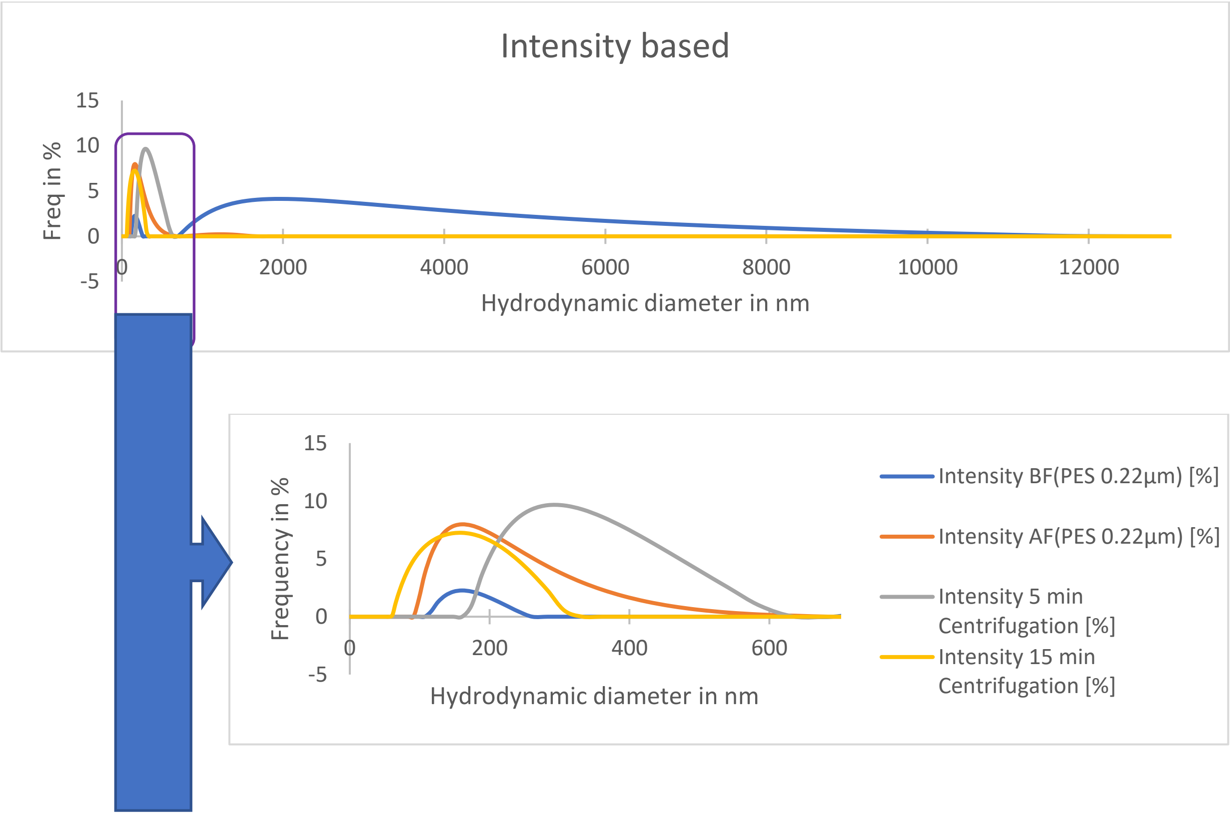

Figure 4.7 Impact of Centrifugation and filtration on NPs detection (intensity)

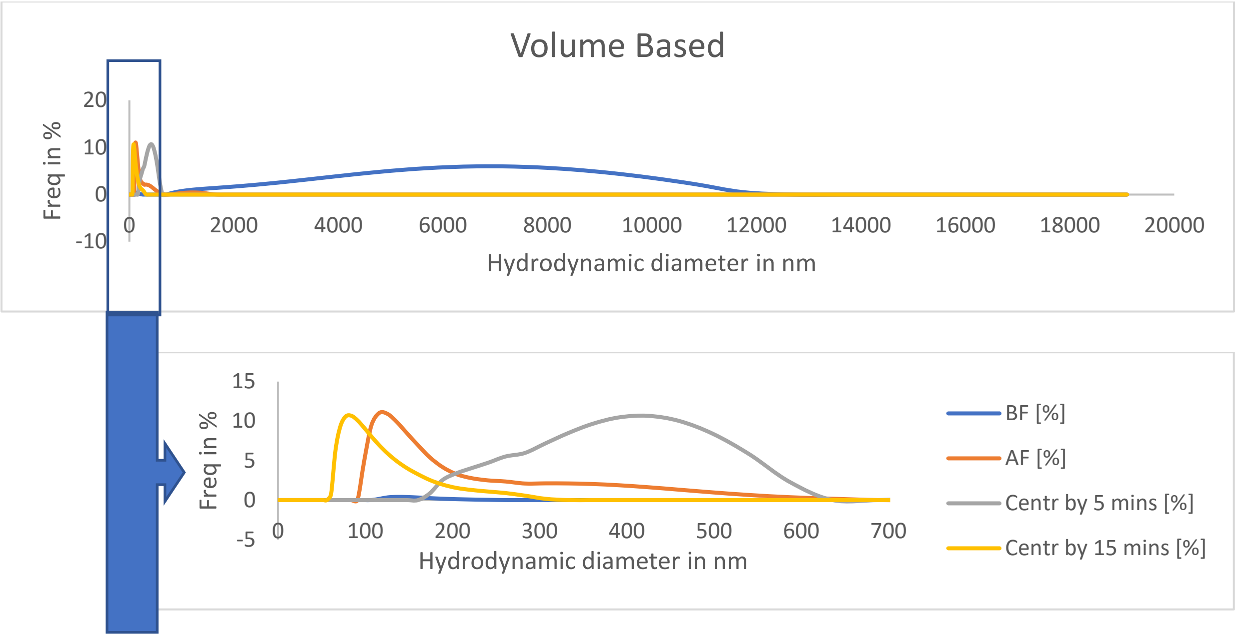

Figure 4.8 Impact of Centrifugation and filtration on NPs detection (volume)

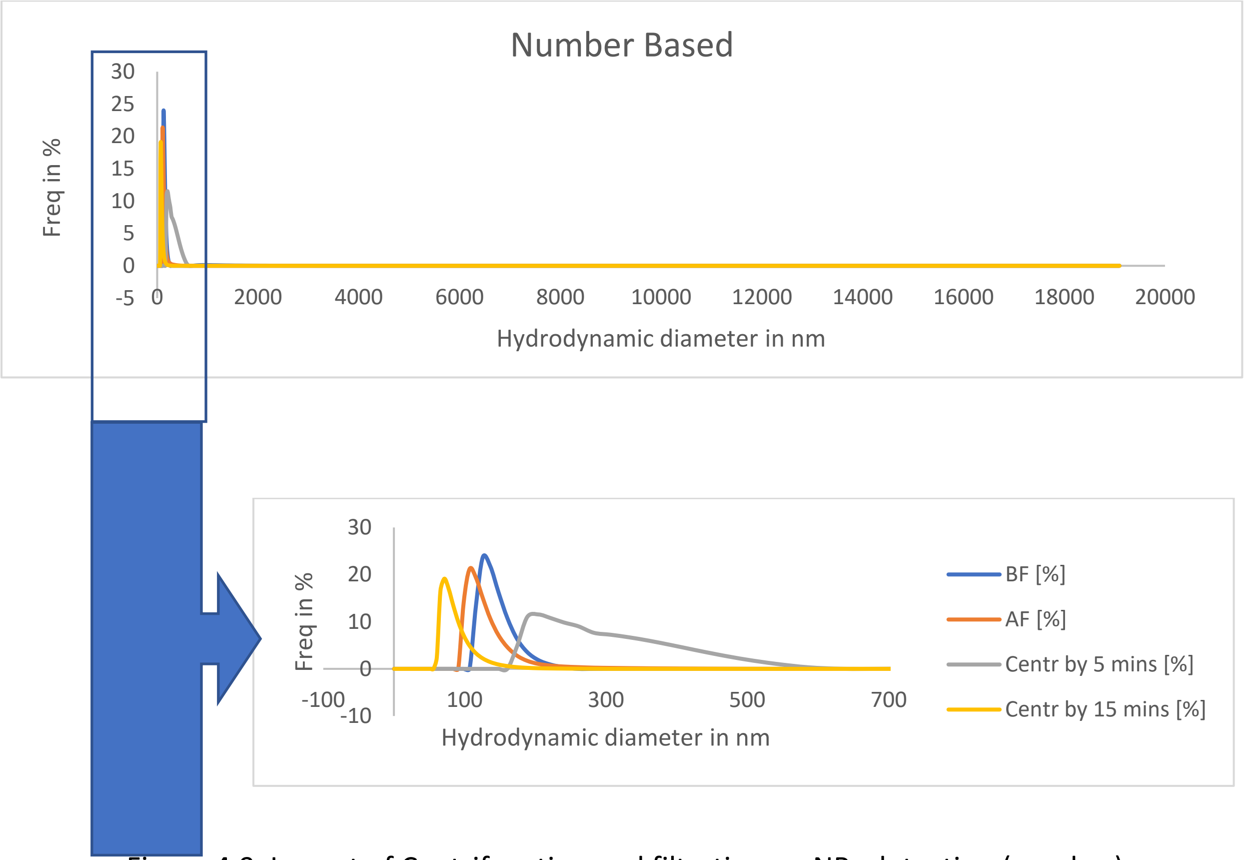

Figure 4.9 Impact of Centrifugation and filtration on NPs detection (number)

Hydrodynamic size

DLS size measurements based on intensity are skewed towards larger particles. A number-based measurement is considered most suitable for detecting the smaller particle sizes. Measurements based on volume also indicate the smaller particle sizes but are less weighted towards small particles compared to the number-based results. An untreated river water sample from location 1 (Endoscopy hospital) showed an average particle size of 188 nm with a PDI of 0.39. The average size is reduced to 66 nm (PDI: 0.22) after separation via a PES membrane filter. This result confirmed that nanomaterials were present in the Tennessee river water at this location. The possible source of these nanomaterials could be the multiple discharge points for rain and sewage water at this spot. In the corresponding volume-based size plots, both the small and larger-sized particles were detected. For example, the untreated water sample showed a small peak at 232 nm and a broader and more prominent peak at 7855 nm and PDI of 0.39. After filtration, the average size of this sample reduced to 83 nm (PDI: 0.22), but the broad tail in the size plot captured the aggregation and presence of larger particles in the sample. Therefore, the combined intensity, number, and volume size plots obtained from the DLS provide an overall representation of the water sample and serve as a clear indicator for the presence of nanomaterials. The summary of the river water sample analysis for hydrodynamic size is presented in Table 4.2 and Figure (4.10-4.11).

Table 4.2 Average hydrodynamic sizes, PDI, and zeta potential of NPs present in the river water samples

No.	Location	Size (nm)						Zeta potential (mV)	
		Untreated			After filtration			Untreated	After filtration
		Intensity	No.	Vol.	Intensity	No.	Vol.		
1	Endoscopy Hospital (DS)	5225 PDI: 0.39	188.7 PDI: 0.39	7855 PDI: 0.39	125 PDI: 0.22	66 PDI: 0.22	83 PDI: 0.22	-1.11	-4.17
2	WWDP 0.004 (DS)	4444 PDI: 0.18	222.95 PDI: 0.18	12833 PDI: 0.18	126 PDI: 0.24	56 PDI: 0.24	75 PDI: 0.24	-10.16	-4.52
3	Aquarium	2495 PDI: 0.34	175 PDI: 0.34	2083 PDI: 0.34	294 PDI: 0.25	48 PDI: 0.25	305 PDI: 0.25	-17.25	-13.44
4	Erwin Mariners	2521 PDI: 0.37	170 PDI: 0.37	8495 PDI: 0.37	108 PDI: 0.25	51 PDI: 0.25	52 PDI: 0.25	-11.82	-10.96
5	WWDP 462.7 (US)	4106 PDI: 0.32	175 PDI: 0.32	13000 PDI: 0.32	133 PDI: 0.25	14 PDI: 0.25	69 PDI: 0.25	-19.95	-5.05
6	WWDP 462.7 (DS)	1034 PDI: 0.32	67 PDI: 0.32	1146 PDI: 0.32	125 PDI: 0.24	64 PDI: 0.24	78 PDI: 0.24	-12.92	-7.85
7	WWDP 462.7 (700 m, DS)	460 PDI: 0.84	427 PDI: 0.84	500 PDI: 0.84	122 PDI: 0.22	60 PDI: 0.22	75 PDI: 0.22	-12.31	-11.18
8	WWDP 0.008 (DS)	2143 PDI: 0.50	83 PDI: 0.50	7225 PDI: 0.50	174 PDI: 0.26	81 PDI: 0.26	111 PDI: 0.26	-14.73	-12.40

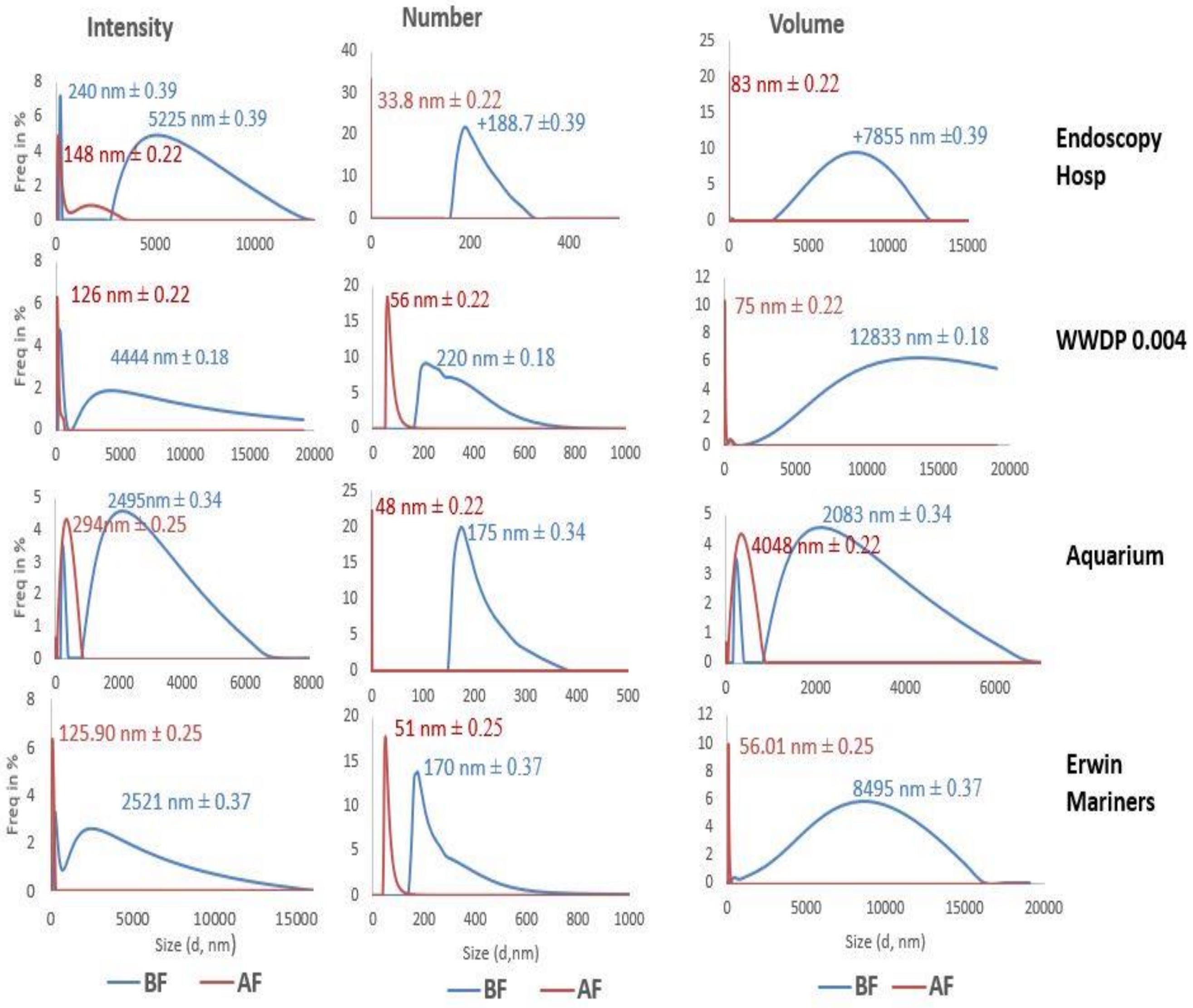

Figure 4.10 Hydrodynamic size of water samples for 1 to 4 locations

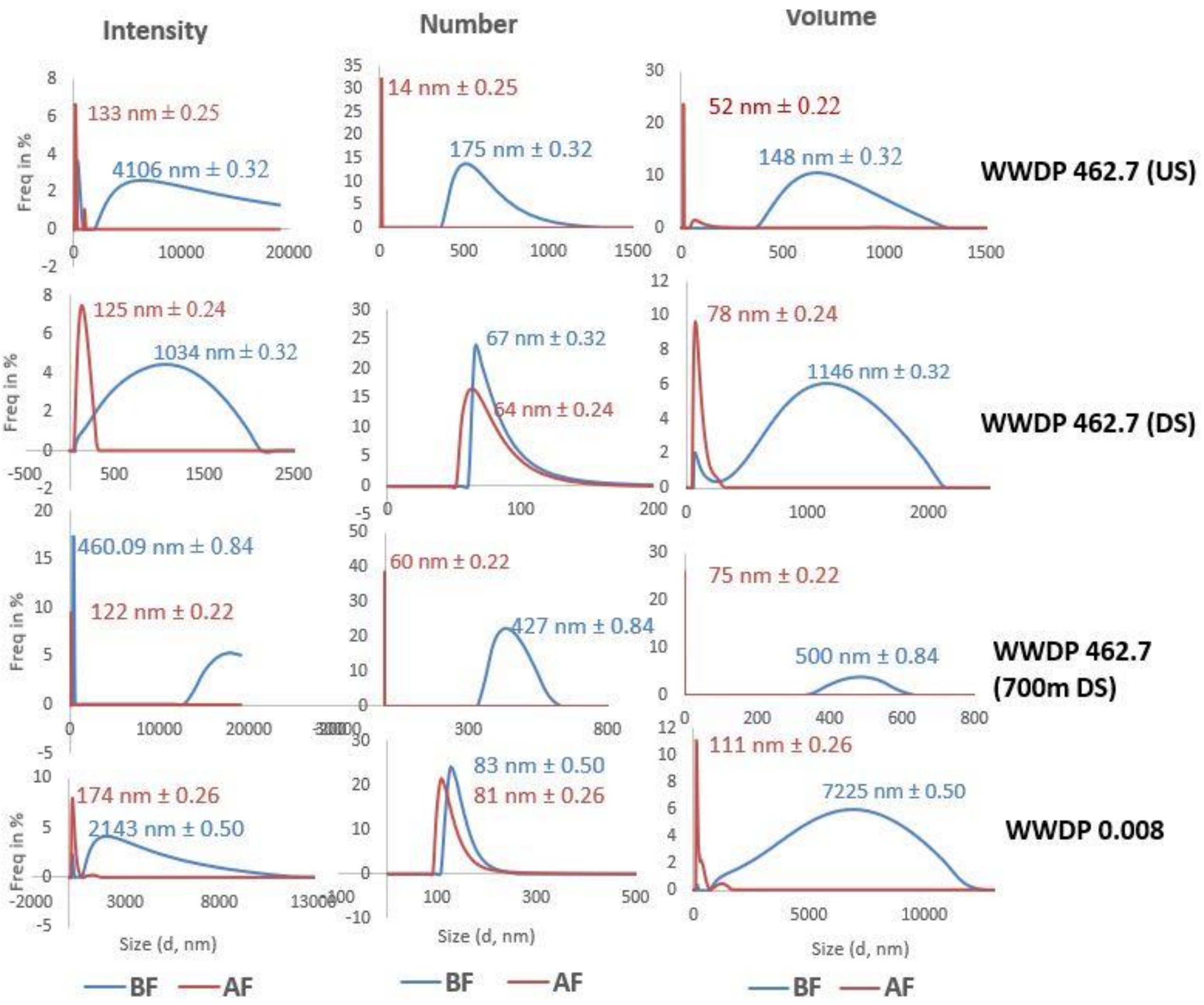

Figure 4.11 Hydrodynamic size of water samples for 5 to 8 locations

Zeta potential

In general, it was observed that the particles were negatively charged with a low absolute zeta potential value. Particles with an absolute value of zeta potential > 30 mV are ionically stabilized while |ξ|< 30 mV indicates steric stabilization and possible aggregation. The zeta potential of particles in untreated Tennessee river water samples ranged from -1.11 to -19.95

mV, speaks about the steric stabilization of these particles. Zeta potential of water samples after treatment via filtration ranged from -4.17 to -13.44 mV. A general trend of decrease in |ξ| of the water samples with treatment was observed for all the Tennessee river water samples. Such a trend in surface charge is expected because the treated river water samples contained more nanosized particles and nanomaterials (Figure 4.12 and 4.13).

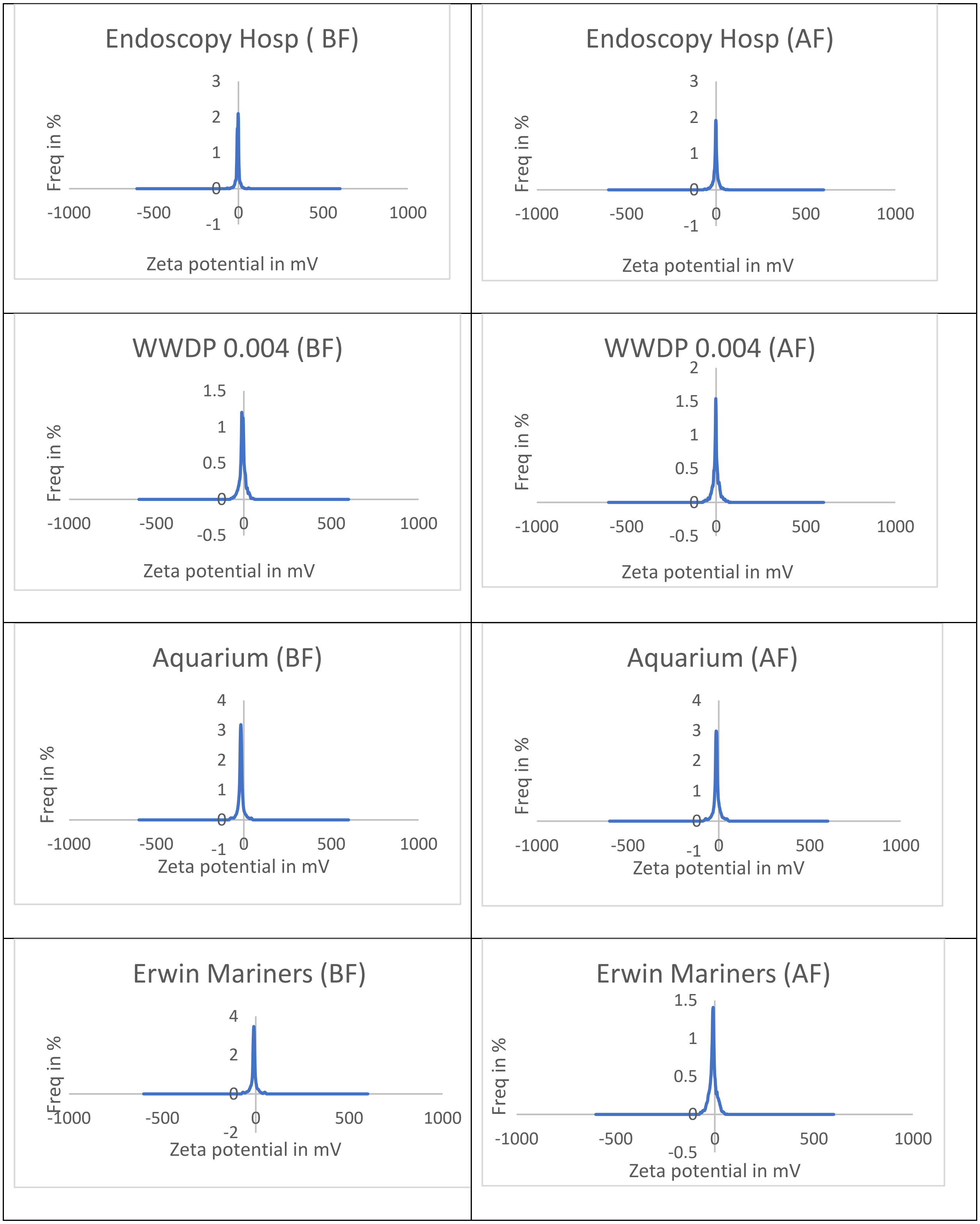

Figure 4.12 Zeta potential of TN River water sample from location 1 to 4

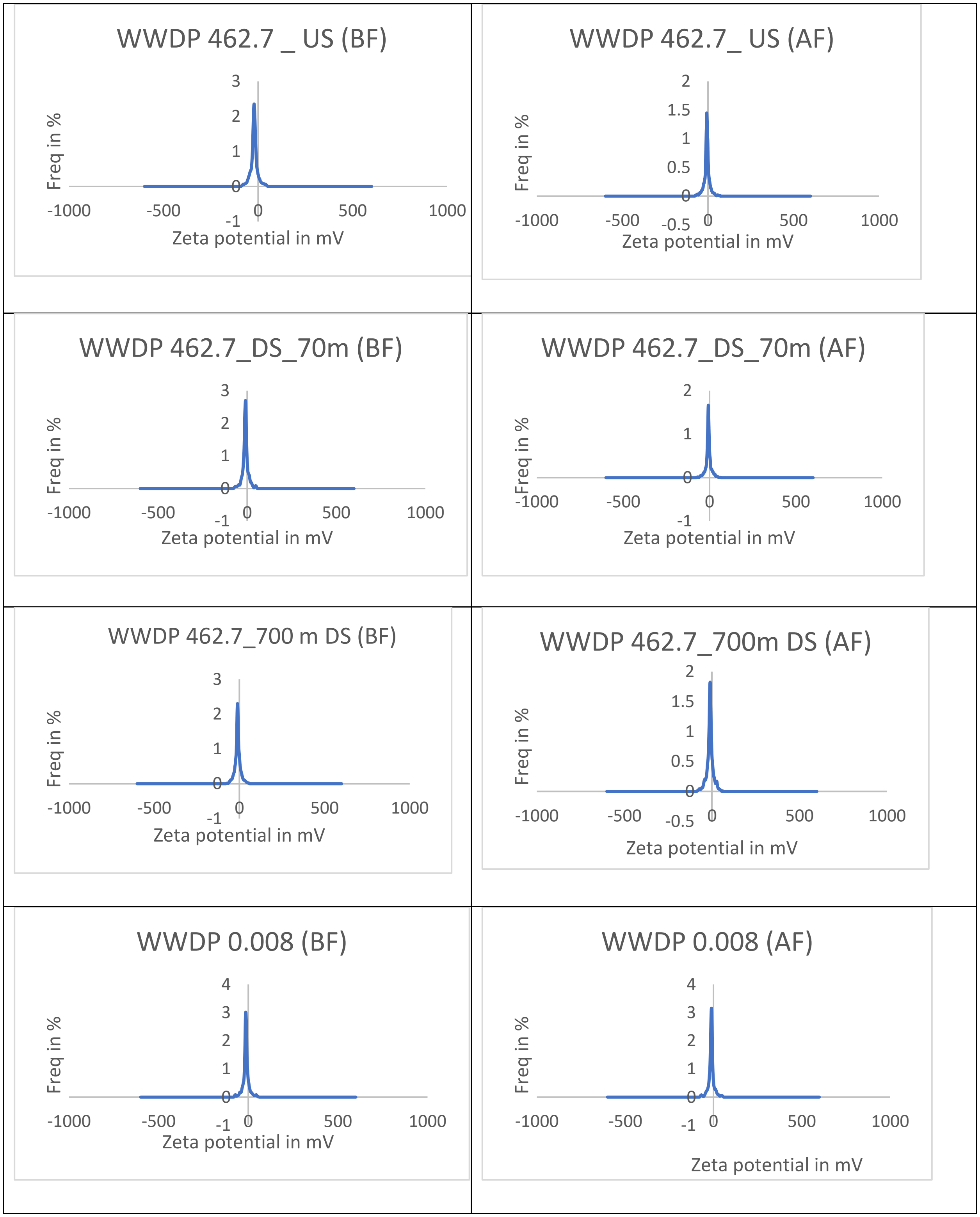

Figure 4.13 Zeta potential of TN river water samples from location 5 to 8

UV-vis

In addition to the DLS, the water samples after filtration were characterized via a UV-vis. The broad peaks observed in the UV-vis plot suggested a likelihood of dissolved nanomaterials in these water samples. Broad absorption peaks were observed around 400-500 nm and 700-800 nm, which were highlighted within the UV-vis plots (Figure 4.14).

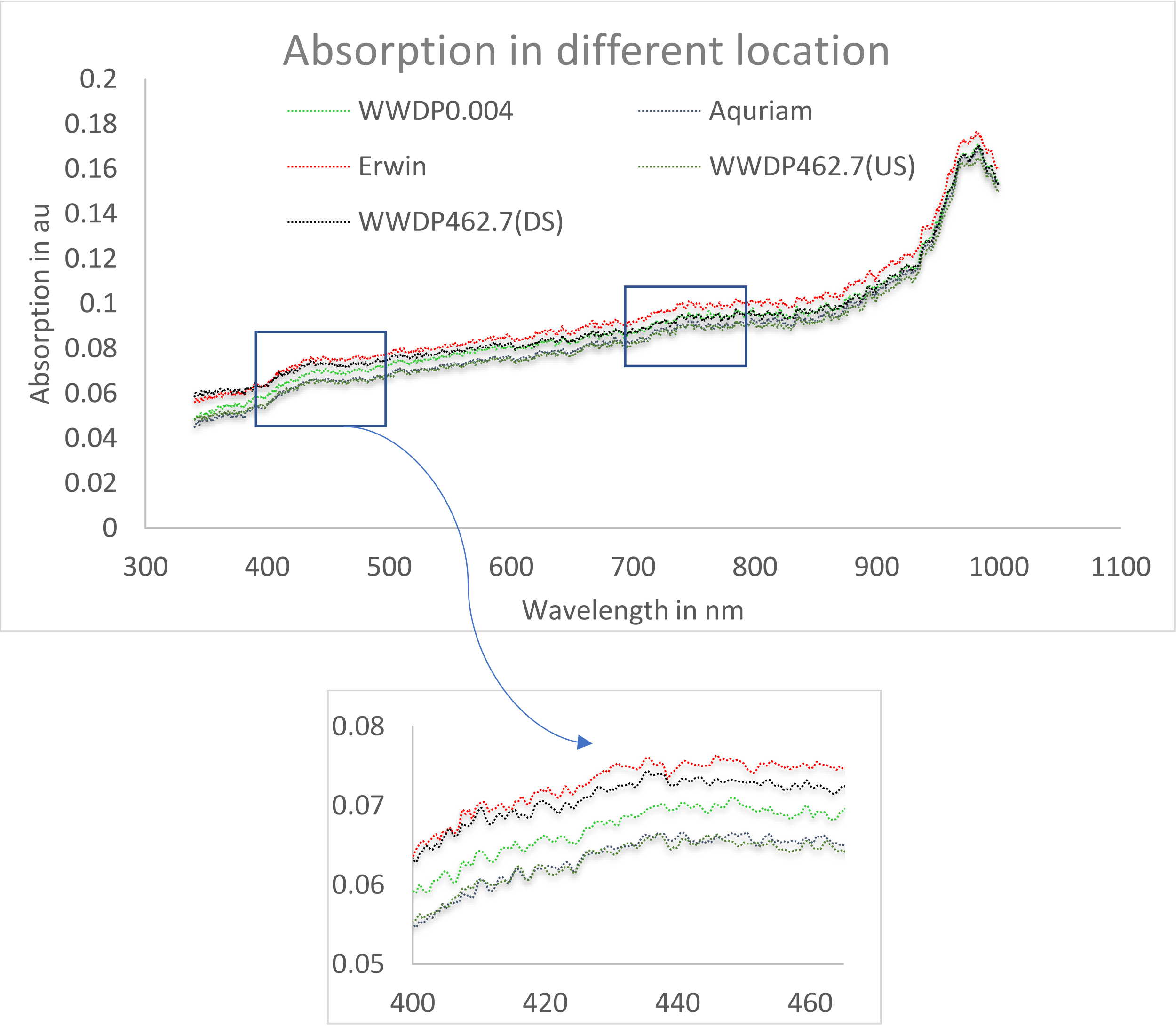

Figure 4.14 Analysis of river water samples using UV-vis

SEM Analysis

River water samples were further characterized via SEM to confirm the presence of nanomaterials. Figure 4.15 shows representative SEM images of the river water samples collected from different locations in the Tennessee River after the larger particles were separated via filtration through the PES membrane. A large concentration of nanomaterials and a few larger particles were observed in these SEM images, as was predicted from our DLS analysis. Comparative SEM images of the water samples before and after filtration also confirmed the effective separation of larger particles using this sample treatment technique. Therefore, the SEM characterization complemented our DLS results for the detection of nanomaterials in river water (Figure 4.16).

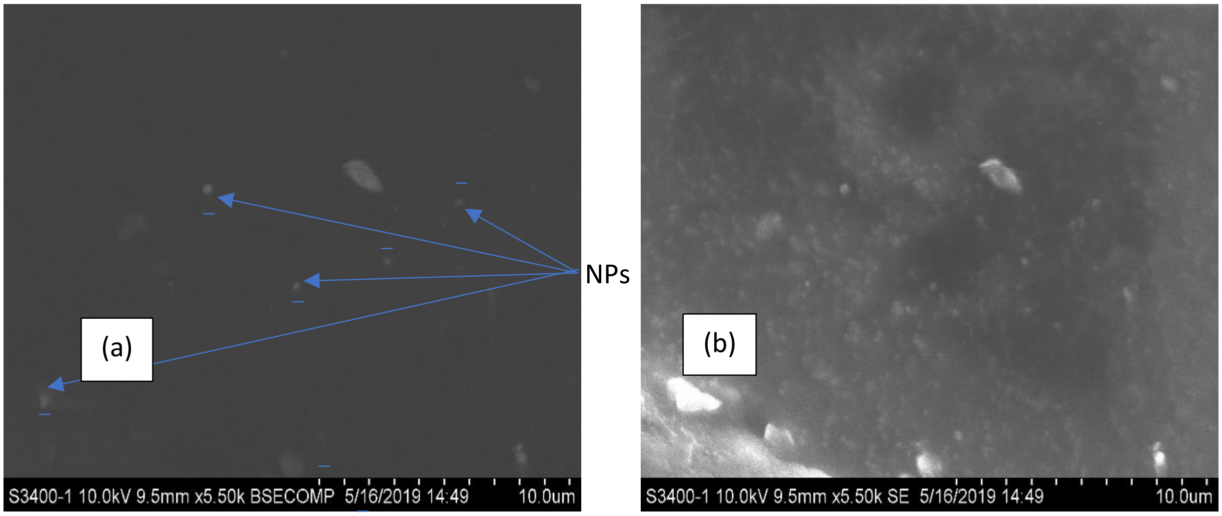

Figure 4.15. SEM images of river water sample at WWDP 462.7, (a) without background, (b) with background, a blue bar indicating NPs<400 nm.

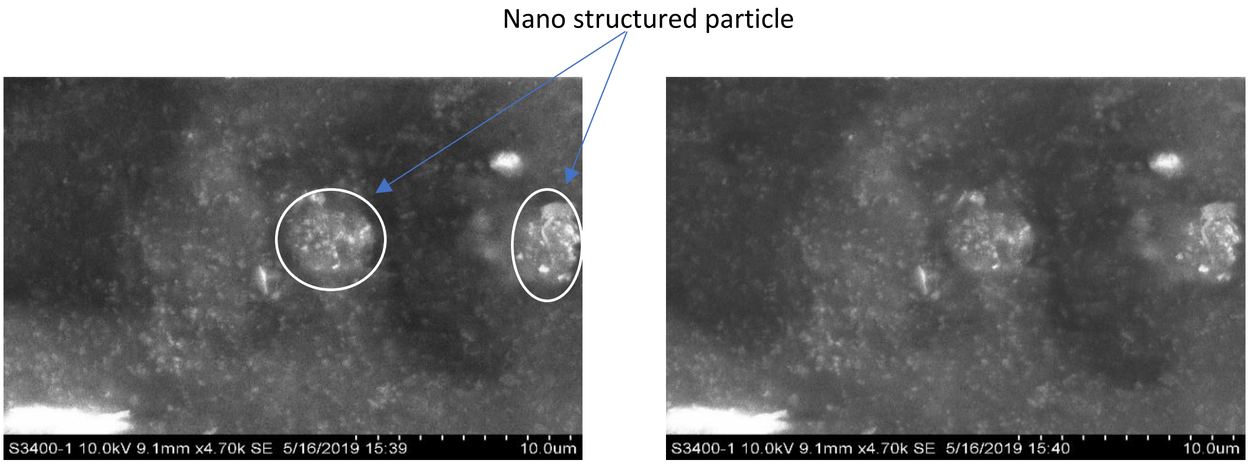

Figure 4.16 SEM images of TN river water samples at WWDP 0.004, left image is more contrast than the right one.

Conclusion

Filtration through 0.22 µm PES membrane and a 15 min high-speed centrifugation was found to be comparable and best suitable sample treatment techniques for the DLS based river water analysis. The average particle sizes of treated river water samples in the different locations ranged from 108 – 294 nm based on the intensity metric and 14 - 81 nm based on the number metric of the DLS. The results indicated the presence of nanomaterials in the Tennessee River. It was found that a combination of intensity, number, and volume based DLS size measurements provided insights on the overall size and distribution of nanomaterials. These nanomaterials were stabilized via steric forces, based on zeta potentials of the treated river water samples (-1.11 to -19.95 mV).

CHAPTER 5

SYNTHETIC SAMPLE CHARACTERIZATION

Introduction

When released into the environment, NPs interact with the variety of dissolved or particulate, inorganic or organic compounds influencing NP aggregation dynamics and thus colloidal stability. Ultimately, exposure conditions are controlled by NP aggregation. There may be homo-aggregation (interaction between the same NP) and hetero-aggregation (interaction between different NP or between NP and natural colloids such as montmorillonite, maghemite, kaolinite but also microorganisms, algae, and proteins as well as disaggregation (Bundschuh et. al., 2018). It may be influenced by several physicochemical properties (e.g., size or aggregation), which will vary significantly across aquatic systems and between materials. Aquatic chemistry dictates that interactions between natural water components and ENPs might result in the formation or break-up of aggregates based on the surface properties of the NPs. Moreover, because of their large surface areas, the NPs are most likely to bind metals and other water-borne contaminants and the presence of these other natural species can also change the surface charge on the NPs. An effort has been taken to feel the dynamics of the complex environmental matrix, a good number of synthetic NPs are collected commercially, which were diluted in the DI water. Accordingly tested in ICP-AES, DLS as well as UV-vis to determine their behavior in terms of dispersion into water.

Sample preparation

Synthetic sample and weighing machine

The ENPs studied include iron (Fe), silver (Ag), titanium (Ti), silicon (Si), copper (Cu), and nickel (Ni), which were purchased from Skyspring NMs, Inc. Their size, content percentage and other relevant properties of interest are shown in Table 5.1. A known amount of ENPs is weighed and diluted into a known volume of water such that the concentration of the ENPs in the samples can be calculated. Such samples were prepared for individual ENPs as well as a combined sample that has all selected ENPs mixed with water. NPs in powder form purchased from Sky Spring nanomaterials were shown in Figure 5.1 and weighing machine shown in Figure 5.2a.

Figure 5.1 NPs in powder form from Sky Spring Nanomaterials

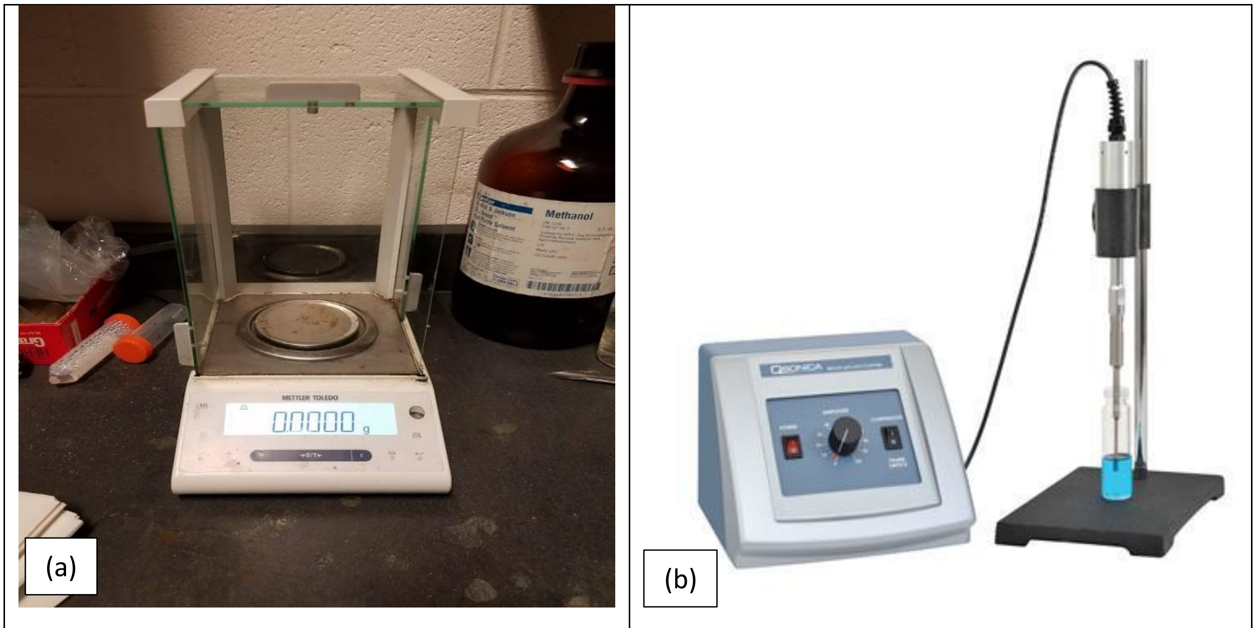

Figure 5.2 Sample preparation using (a) Weighing Machine, (b) Probe sonication

Probe Sonication

Probe sonication has got a high localized impact comparing to bath sonication. In some cases, it is more than 100 times effective than bath sonication. Synthetic NPs are difficult to disperse in the DI water. For better dispersion probe sonicator is recommended over bath sonicator (Figure 5.2b). Samples are subjected to varying time sonication and for every selected time interval the samples were examined using ICP-AES.

Table 5. 1 Synthetic NPs used during Experiment

Serial	**Name of NPs**	**Size in nm**	**Weight in gm**	**% of purity**	**Conc in ppm**
1.	Copper (Cu)	60-80	0.0001	99.0	2
2.	Iron (Fe)	40-60	0.0002	99.7	4
3.	Nickel (Ni)	25	0.0003	99.9	6
4.	Silver (Ag)	20-30	0.0001	99.9	2
5.	Titanium (Ti)	40-60	0.0001	99.95	2
6.	Mix		0.0006	99.9	12

ICP AES

The ICP AES used in this experiment was of Horiba Jobin-Yvon, (France, Ultima model) equipped with a 40.68 MHz RF generator, Czerny-Turner monochromator with 1.00 m (sequential), autosampler AS500 and CMA (Concomitant Metals Analyzer) (Figure 5.3). Before analyzing the samples, the CP-AES was calibrated with a calibration standard prepared in-house. The calibrated performance was shown in Table 5.2 and Figure 5.4. Here LOD stands for a limit of detection and LOQ stands for a limit of quantification.

Figure 5.3 ICP- AES

Table 5.2 LOD and LOQ of NPS in ICP AES

NPs	**Wavelength in nm**	**LOD in ppm**	**LOQ in ppm**
Ni	231.064	0.004829	0.016096
Fe	259.940	0.000166	0.000554
Cu	324.754	0.001182	0.003942
Ag	328.668	0.000563	0.001876
Ti	334.941	0.000419	0.001398

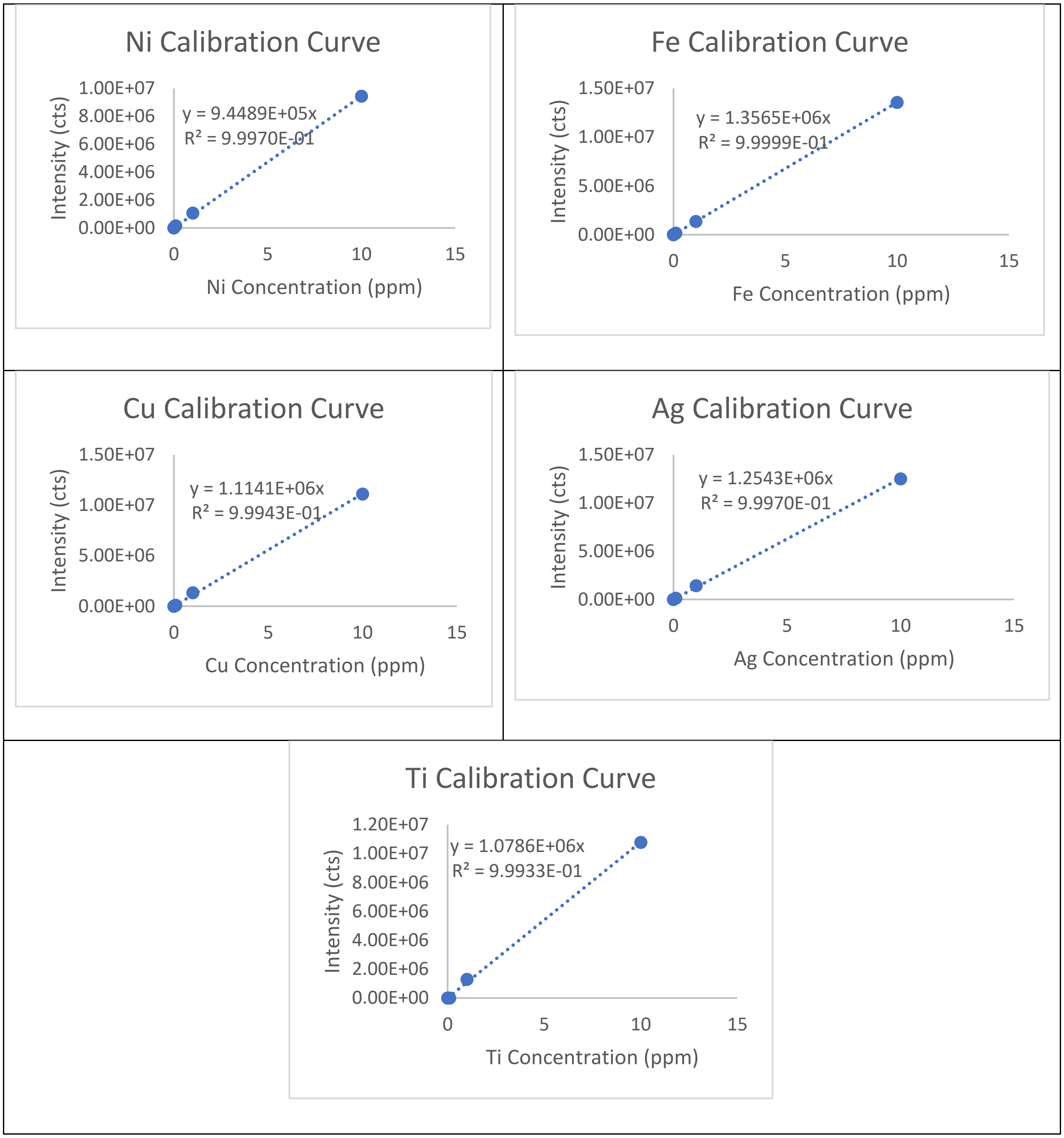

Figure 5.4 Calibration Graph of ICP AES

Sample Analysis

Detection using ICP AES

a. Copper NPs

The size of the Cu NPs was 60 to 80 nm, 0.0001 gm was spiked into DI water and as a result, a concentration of 2 ppm calculated theoretically. After 15 minutes of sonication, no copper NPs could be detected. It may be improper dispersion of NPs due to the hydrophilic growth of NPs. But after 30 mins NPs were being started detected (34% recovered). It shows an increasing pattern except for 3 hours sonication, where detection is slightly attenuated. Detection value greater than LOD (0.001182 ppm) as well as LOQ (0.003942 ppm), which speaks about the reliability of the result. Cu in the mixed sample was detected after 1 hour with an increasing trend (Figure 5.5 a).

b. Iron NPs

The size of the Fe NPs was 40 to 60 nm, 0.0002 gm was spiked into DI water and as a result concentration of 4 ppm appeared. After 15 minutes of sonication, no iron NPs could be detected. It may be improper dispersion of NPs due to the hydrophilic growth of NPs. But after 30 mins NPs were being started detected (0.24 % recovered). It shows an increasing pattern except 1 to 2 hours sonication, where detection is attenuated. Detection value greater than LOD (0.000166 ppm) as well as LOQ (0.000554 ppm), which speaks about the reliability of the result. Fe in mix samples showed a similar pattern of increasing and decreasing trend of detection (Figure 5.5 b).

c. Nickel NPs

Size of the Ni NPs was 25 nm, 0.0003 gm was spiked into DI water and as a result, a concentration 6 ppm appeared. After 15 minutes of sonication, no Ni NPs could be detected. But after 30 mins sonication, detection could appear as 0.0303 ppm and 0.3316 % could be recovered. It was kept on increasing but after 3 hours slight desecrating pattern observed. Detection value greater was than LOD (0.000166 ppm) as well as LOQ (0.000554 ppm), which speaks about the reliability of the result. Ni in mix same showed a similar pattern of increasing trend (Figure 5.5 c).

d. Silver NPs

The size of the Ag NPs was 20 to 30 nm, 0.0001 gm was spiked into DI water and as a result concentration of 2 ppm was measured theoretically. After 15 minutes of sonication, 0.009 ppm Ag NPs could be detected. But after 30 mins NPs were being started detected (34% recovered). It shows an increasing pattern except for 3 hours sonication, where detection is slightly attenuated. Detection values were greater than LOD (0.000563 ppm) as well as LOQ (0.001876 ppm), which speaks about the reliability of the result. Ag in mix sample showed an irregular pattern with hardly any detection (Figure 5.5 d).

e. Titanium NPs

The size of the Ti NPs was 40 to 60 nm, 0.0001 gm was spiked into DI water and as a result, a concentration of 2 ppm was measured theoretically. Detection started appearing from 15 mins sonication. There are both increasing and decreasing pattern of detection. Two peak detection were observed one at 30 mins and another at 3 hours. At 3 hours sonication, Ti was detected as 0.3167 ppm (15.835% recovery). Detection value greater than LOD (0.000419 ppm) as well as LOQ (0.001398 ppm), which speaks about the reliability of the result. Ti in the mixed sample showed similar trends of increasing and decreasing pattern (Figure 5.5e).

f. Combined ENPs sample

Cu, Fe, Ni, Ag, and Ti NPs were mixed in DI water and a concentration of 12 ppm appeared theoretically. Only Ti could be detected (0.291 ppm equivalent to 1.455 % recovery)) from the beginning at 15 mins sonication. In mix samples, Fe NPs detection found better at 3-hour sonication than individual Fe NPs. In other cases, detection becomes more difficult in the mixed sample. Separation or segregation may be required for better detection of NPs. In mix sample, Ag detection is very meager. Maybe it gets agglomerated with other NPs and makes the detection challenge. After 15 mins bath sonication only Ag and Ti could be detected. But the amount of detection is very negligible. The concentration of Fe was 4 ppm, but detection is very less. Only 0.2375 % could be detected after 30 mins of sonication. Fe might be very hydrophobic. The dispersion was not proper. May be by probe sonication better dispersion might be possible. Detection of Cu was highly remarkable, but value more than 100 % speaks about the nonreliability of the results. Contamination from a spatula or during measurement might have taken place. Moreover, it is difficult to take weight using an analytical balance. The less weight, the more possibility of error (Mix sample in red color in Figure 5.5).

g. Recovery of ENPs after spiking

The percentage of recovery of ENPs seems to be very less. Before the experiment ICP AES, all samples had to filter via a 0.22 um filter. Due to a lack of dispersion as well as filtration, all NPs might not pass through the filter. Thus, detection, as well as recovery, were very less (Table 5.3 and Figure 5.6).

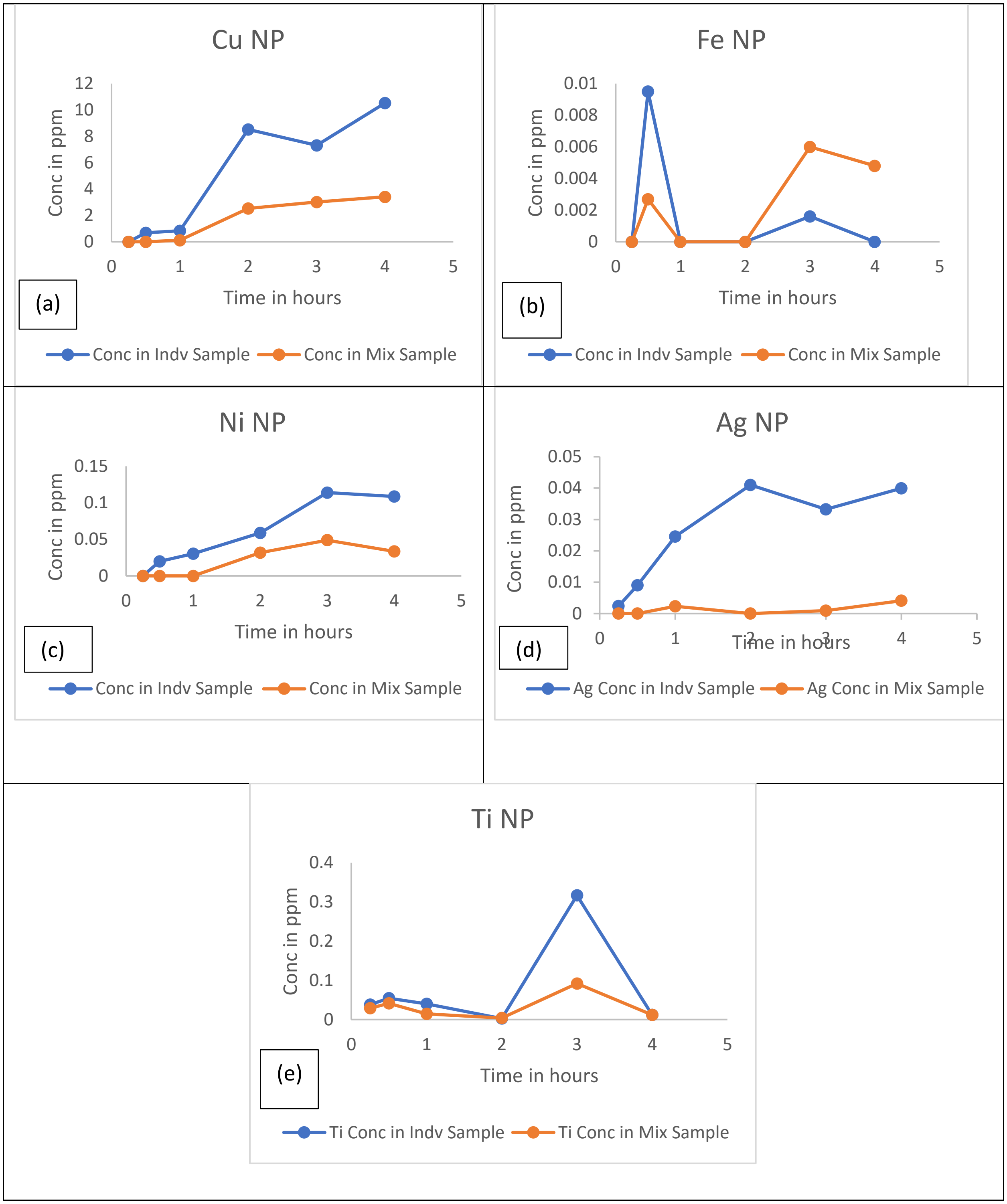

Figure 5.5 NPs dispersion in DI water using ICP-AES, (a) Cu, (b) Fe, (c) Ni, (d) Ag, (e) Ti

Table 5.3 Percentage of NPs recovery

NPs	0.25 hrs	0.5 hrs	1 hrs	2 hrs	3 hrs	4 hrs	Conc in ppm
Fe	0	0.2375	0	0	0.045	0	4
Ni	0	0.3316	0.505	0.98	1.9	1.81	2
Ag	0.12	0.45	1.23	2.05	1.66	1.995	2
Ti	1.905	2.725	2.015	0.125	15.835	0.58	2
Cu	0	34	42.205	426.205	365.84	526.1	2

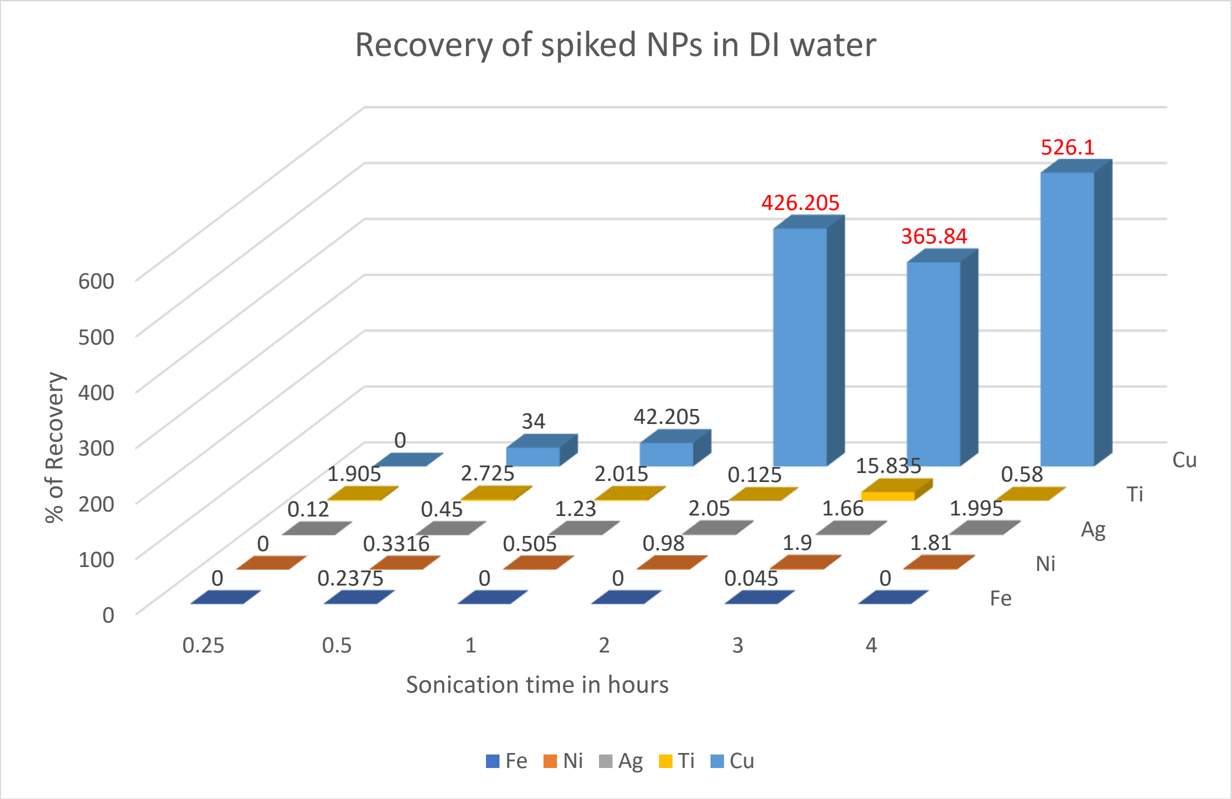

Figure 5.6 Recovery percentage of ENPs using ICP AES

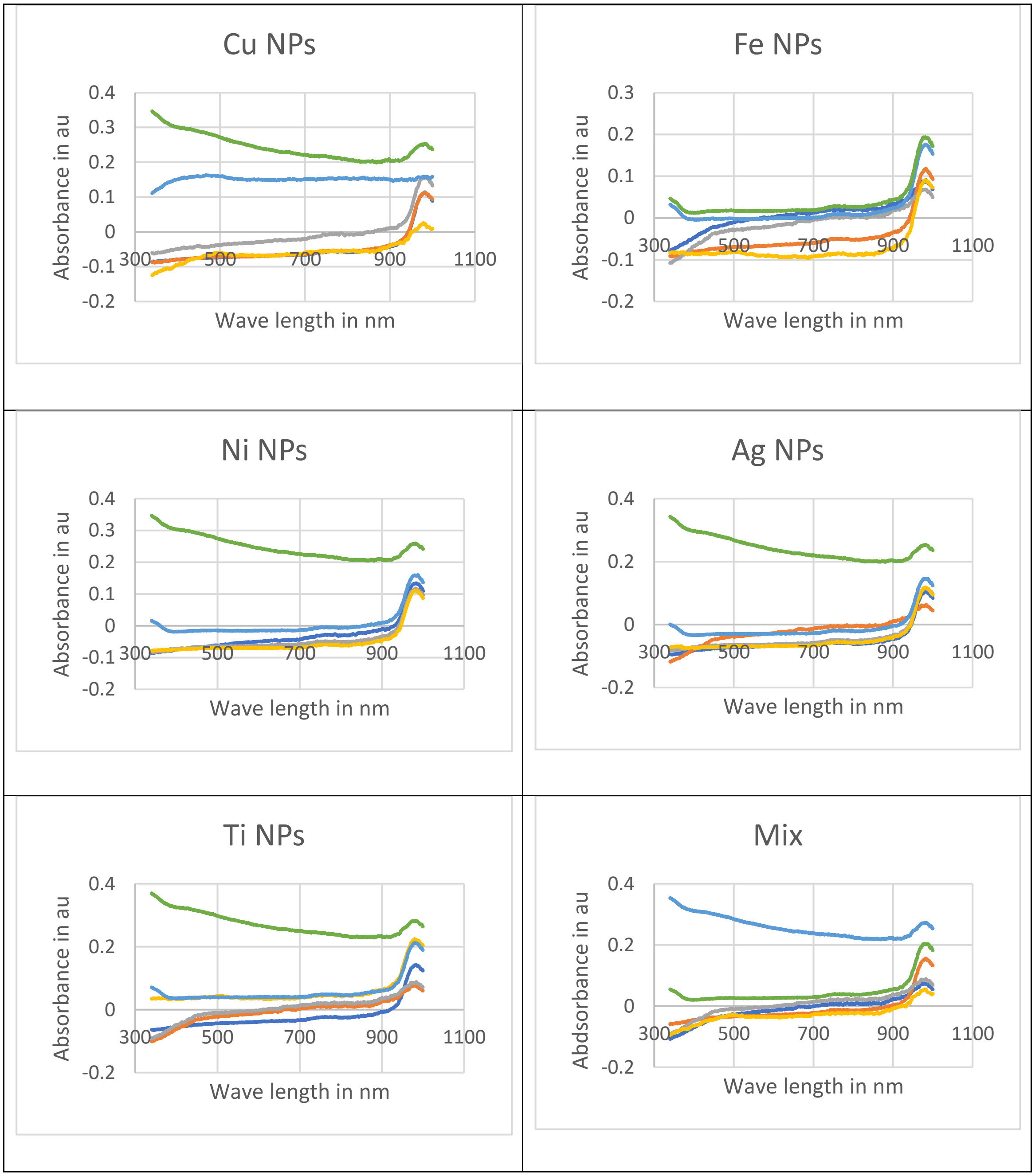

Figure 5.7 UV-vis analysis above synthetic NPs

DLS analysis of Synthetic NPs

DLS is a valuable tool for determining and measuring the agglomeration state of nanoparticles as a function of time or suspending solution. In an agglomerated suspension, the DLS measured diameter will be similar or slightly larger than the TEM size. If the particles are agglomerated, the DLS measurement is often much larger than the TEM size and can have a high polydispersity index (large variability in the particle size). All the particle is hydrophilic. Once they encounter water the pristine nature of the particle lost and start getting agglomerated. PDI of Fe and Ag (more than 30 %) speaks about the greater tendency of agglomeration. Nano powder dispersion by bath sonicator seems to be very difficult. Only 10 to 30 % particle could be made available within nano sizes after 4 hours of sonication. Transmittance more than 76% confirms its diffusion of nature and movement towards agglomeration. Multiple peaks speak about bimodal or multimodal solutions (Figure 5.8 to 5.13).

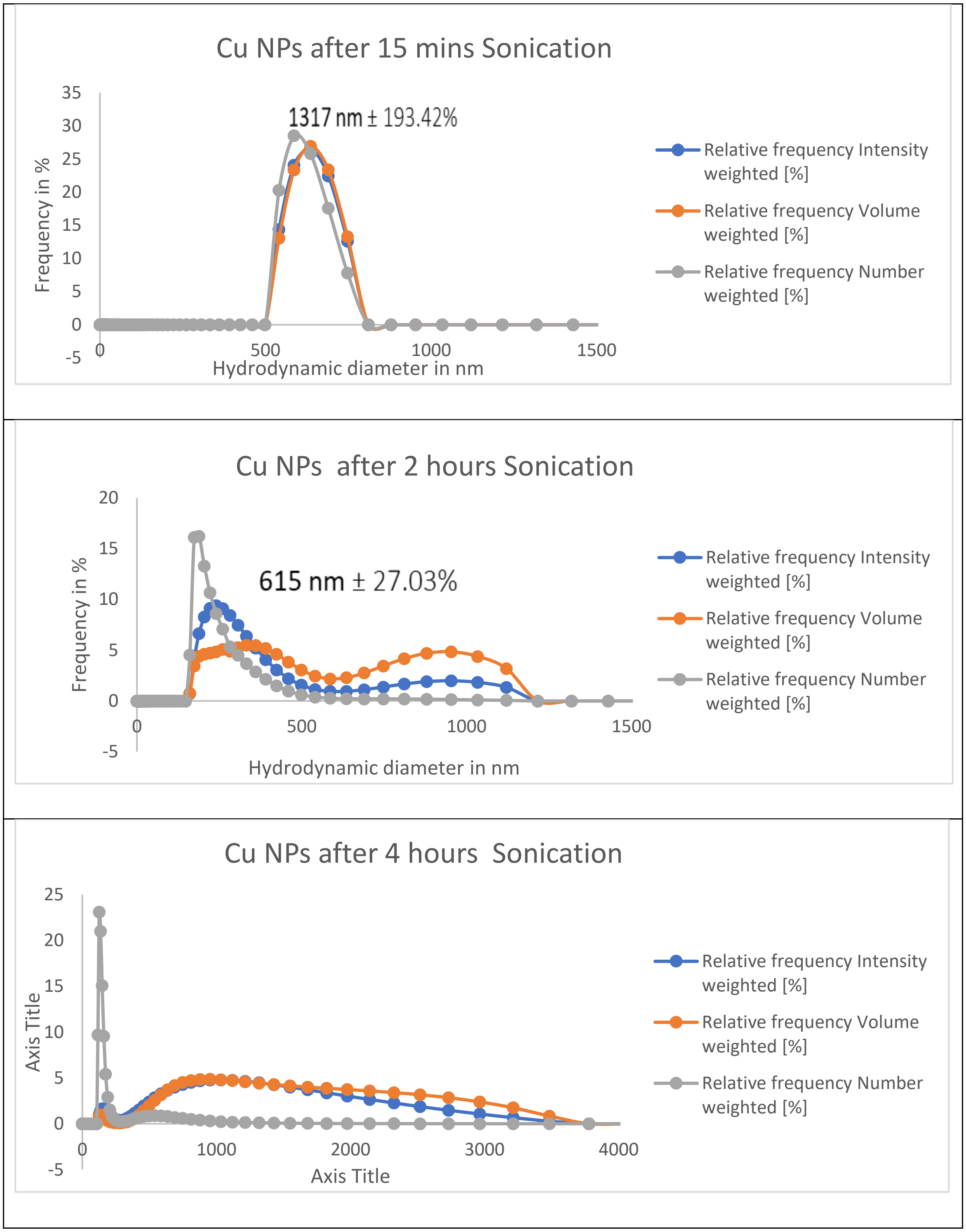

Figure 5.8 DLS analysis Cu NPs

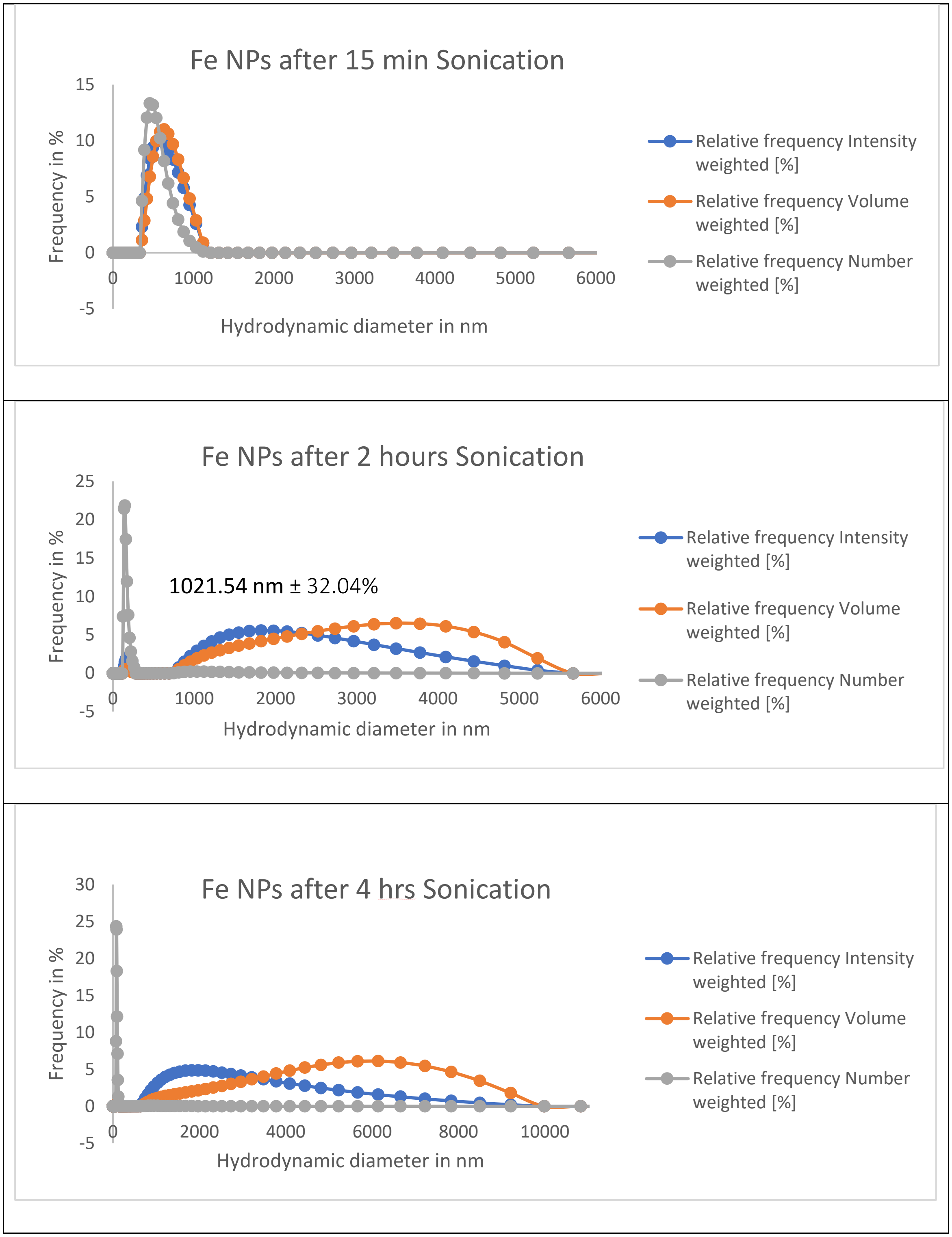

Figure 5.9 DLS analysis Fe NPs

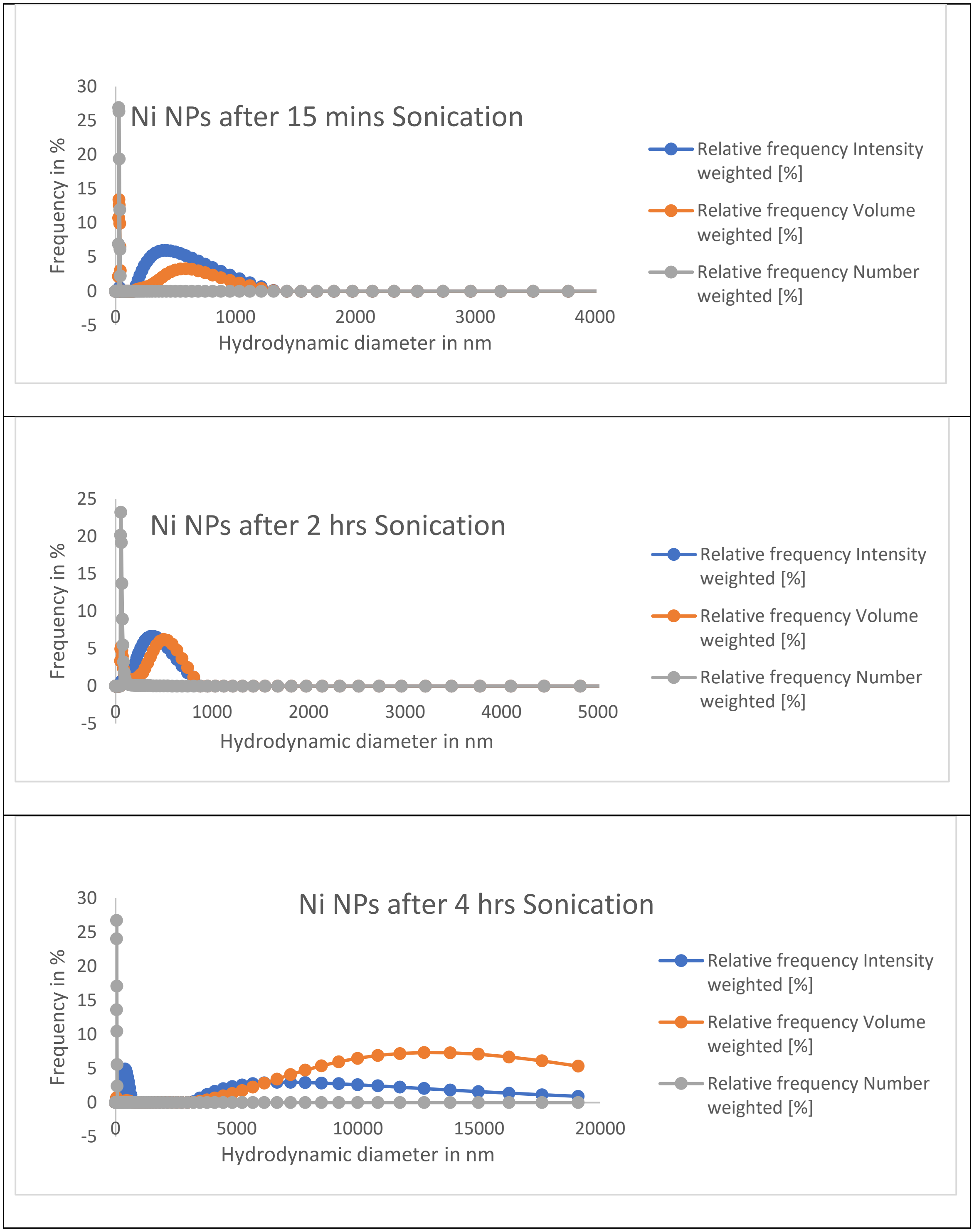

Figure 5.10 DLS analysis Ni NPs

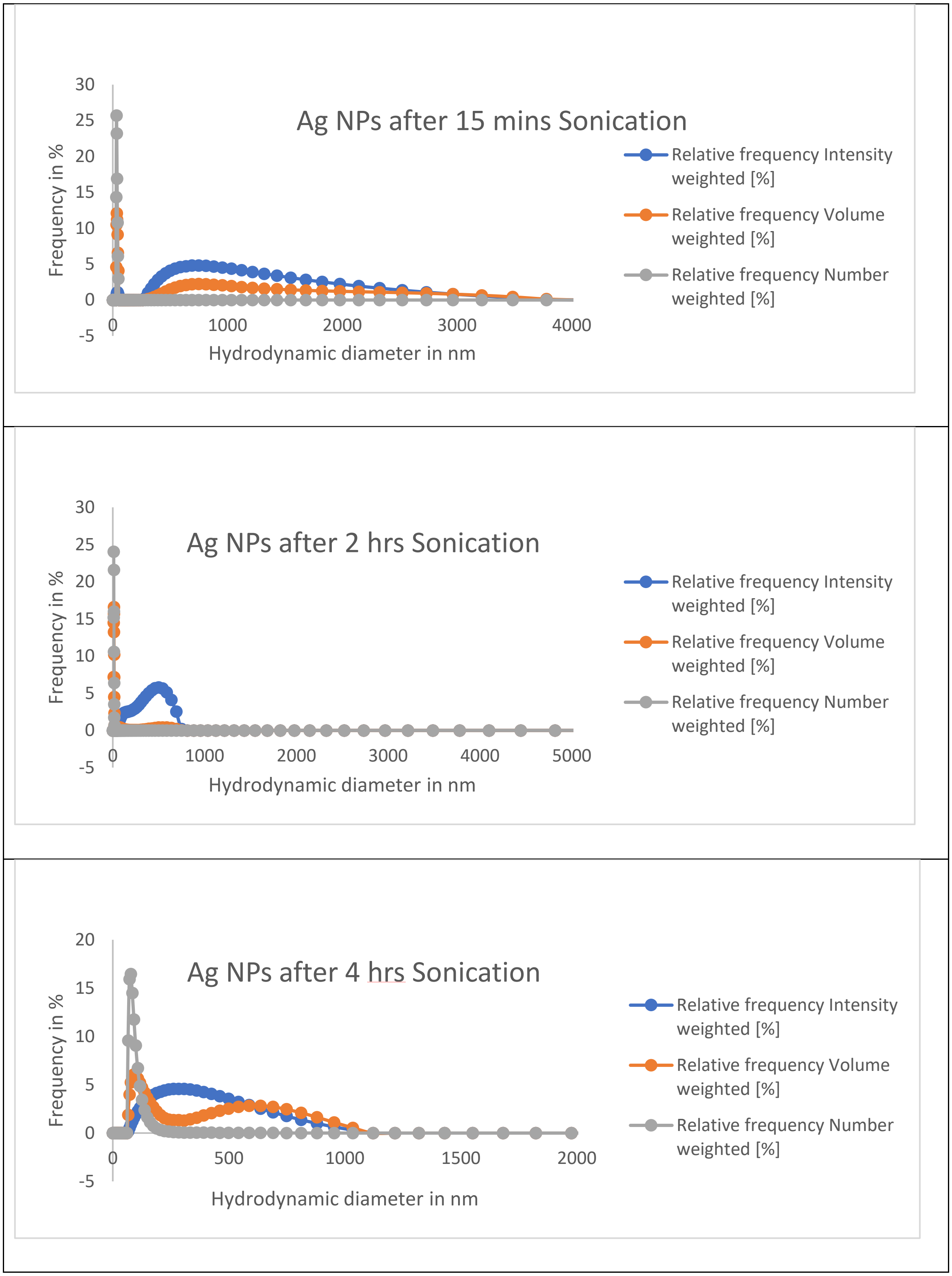

Figure 5.11 DLS analysis of Ag NPs

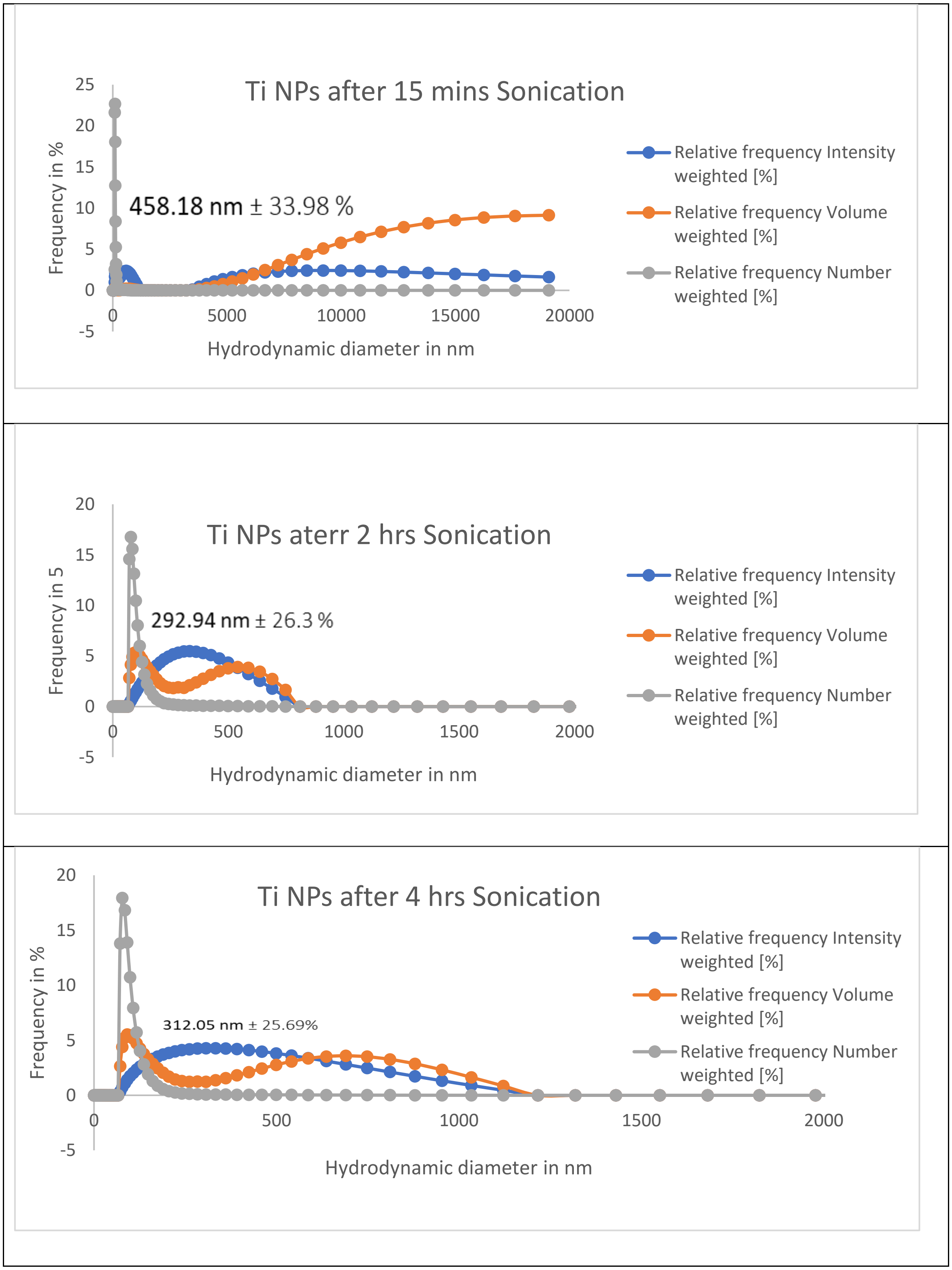

Figure 5.12 DLS analysis of Ti NPs

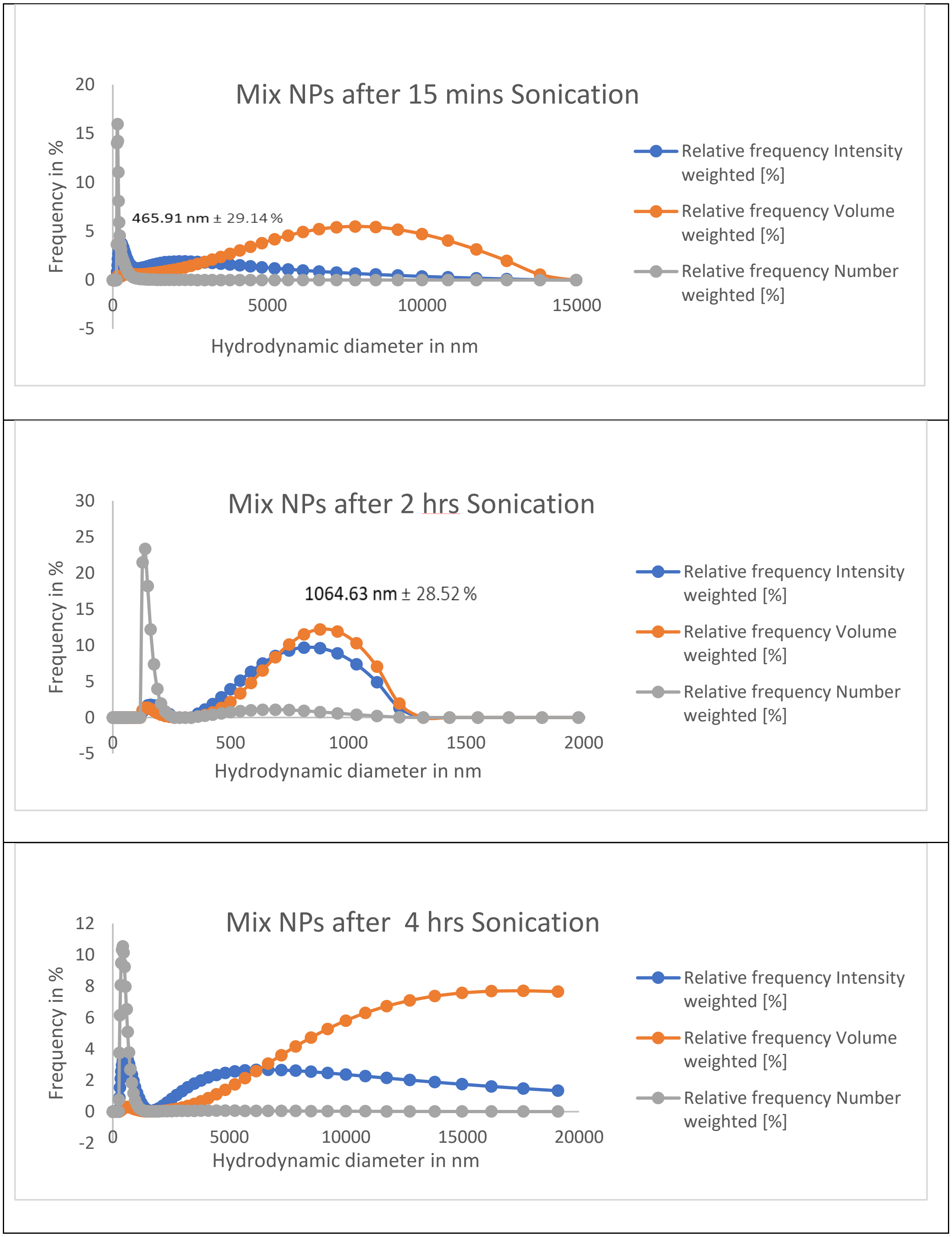

Figure 5. 13 DLS analysis of Mix sample

Comparative Analysis

NPs have got a strong affinity for water. The moment they dispersed into the water they tend to aggregate. Hydrodynamic size seems to higher in the initial stage of the dispersion when compared to their aggregation on longer times of dispersion. Longer sonication leading to dis-aggression and hence better dispersion.

a. Copper

The percentage of NPs at 2 hours sonication was 16 %, which is increased to 23 % at 4 hours sonication. The more sonication, the more particle will be dissolved in the water. The initial aggregated size will be destabilizing and will try to gain the pristine size of NPs. Similarly, absorption, as well as detection rate, also increasing. Due to a lack of strong sonication (preferably probe sonication), all the NPs could not dissolve. Moreover, with a 0.22 u filter, particle size greater than 200 nm is trapped. Thus, the number of NPs detected is very less (Figure 5.5 and 5.8).

b. Iron

Percentage of NPs after sonication at 15 mins 13 %, 2 hours 22 %, and 4 hours 25 %. Thus, it speaks that the more sonication, the more particle will be dissolved and the more is the number NPs. The moment it meets water started aggregated due to affinity with water and then agglomerated. That is why the initial size of the particle was as large as 615 nm. After sonication, it starts breaking down into its pristine size of NPs. Similarly, absorption, as well as detection rate, also increasing. Due to a lack of strong sonication (preferably probe sonication), all the NPs could not dissolve. Moreover, with a 0.22 u filter, particle size greater than 200 nm is trapped. Thus, the number of NPs detected is very less (Figure 5.5 and 5.9).

c. Nickel

PDI (10.89%) nearer to 10 % speaks about a solution close to monodisperse (Polydispersity indices less than 0.1 are typically referred to as "monodisperse"). The percentage of NPs at 2 hours sonication was 23 %, which is increased to 27 % at 4 hours sonication. The more sonication, the more particle will be dissolved in the water. A particle will come out from initial aggregated as well as agglomeration size to gain the pristine size. Similarly, absorption, as well as detection rate, also increasing. Due to a lack of strong sonication (preferably probe sonication), all the NPs could not dissolve. Moreover, after filtration with 0.22 u filter, particle size greater than 200 nm is trapped. Thus, the number of NPs detected was very less (Figure 5.5 and 5.10).

d. Silver

PDI was more than 30 % up to 2 hours sonication and thus solution remains sterically unstable. Particle sizes were more due to initial aggregation and agglomeration. After 4 hours of sonication, the percentage of NPs was found 17 % and will tend to move towards greater dispersion. The more sonication, the more particle will be dissolved in the water. Similarly, absorption, as well as detection rate, also increasing. Due to a lack of strong sonication (preferably probe sonication), all the NPs could not dissolve. Moreover, with a 0.22 u filter, particle size greater than 200 nm is trapped. Thus, the number of NPs detected was very less (Figure 5.5 and 5.11).

e. Titanium

PDI was 33% (>30%) speaks about the unstable solution tending aggregation and agglomeration. But after more sonication time particles tried to return its pristine size. Percentage of Nanosized after 2 hours sonication was 16 %, which is increased to 18 % at 4 hours sonication. The more sonication, the more particle will be dissolved in the water. Similarly, absorption, as well as detection rate, was also increasing. Due to the lack of strong sonication (preferably probe sonication), all the NPs could not be dissolved. Moreover, after filtration with 0.22 u filter, particle size greater than 200 nm is trapped. Thus, the number of NPs detected was very less (Figure 5.5 and 5.12).

Conclusion

All the samples with known concentrations were studied subjected to sonication. Then the study of dispersion and aggression was carried out using DLS as well as ICP-AES at discrete times of sonication. Results clearly showed that the dispersion of the ENPs is very small but increased with time of sonication. Copper had better dispersion when compared to the rest of the ENPs studied. In general, aggregation of the particles increased initially, but later after 3 hours of sonication, it started decreasing. The detection of NPs in a single mix sample is comparatively significant than mix sample. After mixing all NPs in the same DI water makes the matrix complicated. It becomes more difficult to detect due to aggregation, reaction, adsorption or absorption (Figure 5.5 and 5.13).

CHAPTER 6

CONCLUSION

The ability to detect and to quantify NPs in the environment is highly critical. The initial review has covered the experiences and efforts of many researchers across the world. Then nanoparticle is tried to detect from the aquatic natural environment. Filtration through 0.22 µm PES membrane and a 15 min high-speed centrifugation was found to be comparable and best suitable sample treatment techniques for the DLS based river water analysis. The average particle sizes of filtered river water samples ranged from 108 – 294 nm based on the intensity metric and 14 - 81 nm based on the number metric of the DLS. The results indicated the presence of NMs in the Tennessee River. It is found that a combination of intensity, number, and volume based DLS size measurements provided insights on the overall size of nanomaterials as well as the presence of smaller sized nanomaterials and aggregates in the sample. These nanomaterials were stabilized via steric forces, based on zeta potentials of the treated river water samples (-1.11 to -19.95 mV). The DLS results for the detection of nanomaterials was supported through the SEM micrographs of the river water samples.

The complex environmental behaviors of NPs were also replicated while working with synthetic NPs. Detection of individual NPs from a spiked sample was found significant, but from a mixed sample appeared critical. The detection will be more critical in the case of a natural sample. Commercial NPs were received as powder aggregates, and in water neither ultrasound nor chemical dispersants could break them up into primary NPs. The study of dispersion and aggression was carried out using DLS as well as ICP-AES at discrete times of sonication. Results clearly showed that the dispersion of the ENPs was very low but increased with time of sonication. Copper had better dispersion when compared to the rest of the ENPs studied. In general, aggregation of the particles increased initially, but after 3 hours of sonication, it started decreasing.

The approach used to quantify NPs in the river water has demonstrated a possible analytical procedure for analyzing ENPS in water samples. Such quantifications are also useful in understanding location-specific fate and transport of NM. Additional sampling from different locations, as well as multiple samples from the same locations, can provide statistical significance to the results and help researchers understand nano pollution in surface waters. While this research has provided a means to analyze surface water samples for NPs, additional work is required to distinguish natural NPs from engineered products. Distinguishing between natural NPs and ENPs is extremely limited and remains one of the most critical priorities for the advancement of the NMs industry. There are no simple methods to characterize the exact molecular structure of an unknown nano pollutant in a complex matrix (e.g., water). The inability to determine the presence and/or chemical structure of ENPs will hinder efforts to evolve treatment technologies. However, further instrumentation will bring prospects in the future for the detection methodology of nano pollutants.

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VITA

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