



# Analysis of single-walled carbon nanotubes using spICP-MS with microsecond dwell time



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## ABSTRACT

Although catalytic metal nanoparticle (NP) impurities in carbon nanotube (CNT) structures are undesirable in a manufacturing context, they can be used as proxies to detect CNTs by single particle inductively coupled plasma-mass spectrometry (spICP-MS). The use of 100  $\mu$ s dwell times, a recent advancement for spICP-MS, increases resolution between pulse events and reduces background signal, improving the detection of low metal-content CNTs. Serial filtration supports the assertion that metal NPs, containing yttrium in this study, are primarily incorporated in CNT structures and remain bound to the tubes throughout analysis. Analysis of both acid-digested and suspended CNTs confirmed that CNTs are fully ablated in the plasma and that all residual metals are ionized. This result, combined with good agreement with UV-Vis spectroscopy analysis, indicates that spICP-MS can provide quantitative CNT mass analysis. Though Nanoparticle Tracking Analysis (NTA) was less accurate than spICP-MS when counting Au-PVP NPs, it gave higher particle number concentrations than spICP-MS for CNTs. The likely undercounting of CNTs by sp-ICPMS is ascribed to the heterogeneous distribution of yttrium NPs among CNTs, and the small diameter of many yttrium NPs ( $\sim 15$  nm), nearing their detection limit. Despite this limitation, its sensitivity and elemental specificity make spICP-MS a powerful nanometrology method for environmental exposure assessment of CNTs. To illustrate this capability, CNT association with *Daphnia magna* was measured at  $\mu$ g/L CNT concentrations. After 48 hours of exposure to a CNT suspension,  $3.48 \pm 0.32\%$  of CNTs were taken up by *D. magna* adults. This simple and direct application of spICP-MS to detect CNTs in organisms can be applied to toxicological investigations to help understand potential bioaccumulation of CNTs in aquatic ecosystems.

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## 1. Introduction

Nanotechnology has grown rapidly in recent decades, driven by the novel properties of nanoparticles (NPs) (Green & Ndegwa, 2011; Mohanraj & Chen, 2006; Schulenburg, 2008). Carbon nanotubes (CNTs) have unique mechanical, electrical, and thermal properties which are beneficial to diverse applications such as energy storage, electronic components, and new material development (Schokrieh & Rafiee, 2010; Lam et al., 2006). With their increasing and potential widespread use, CNT production exceeded several thousand tons in 2013 (De Volder et al., 2013). In addition to beneficial applications, the potential for environmental and human health impacts of NPs have garnered attention (Nanotechnologies, 2006; Fent, 2010; Joner et al., 2008). The large amount of CNTs produced is likely to result in release to the environment during manufacturing, transportation, and use phases across their life cycle (Green & Ndegwa, 2011; Joner et al., 2008; Mueller & Nowack, 2008a; Walser et al., 2012). There are concerns over the safety of CNTs due to their very small size and high aspect ratio, as well as their graphitic properties (Donaldson, 2006). One of the major challenges in

determining the health and safety effects posed by CNTs is detecting and quantifying the extremely low concentrations of CNTs that could be present in complex, heterogeneous environmental matrices (Upadhyayula et al., 2012). For better understanding of a potential CNT risk, sensitive and robust nanometrologies are therefore needed to evaluate exposure.

Most predictions of aqueous environmental concentrations of CNTs are in the ng/L range (Mueller & Nowack, 2008a; Walser et al., 2012; Boxall et al., 2007). However, the most commonly used characterization methods for CNTs, such as X-ray photoelectron spectroscopy, scanning electron microscopy, X-ray diffraction, transmission electron microscopy, UV-Vis and Raman spectroscopy, cannot efficiently detect or quantify CNTs in aqueous media at these low concentrations (Belin & Epron, 2005). In contrast, inductively coupled plasma-mass spectrometry (ICP-MS) has detection limits of ng/L or sub-ng/L for most elements. Furthermore, detection of NPs is made possible by using ICP-MS in single-particle mode (spICP-MS) (Jiménez et al., 2011; Pace et al., 2012; Reed et al., 2013; Mitrano et al., 2012a).

Conventional ICP-MS analysis utilizes signal integration over 10 s to 100 s of milliseconds (ms) to average short-term instrumental noise or drift. In contrast, spICP-MS uses individual readings (counts/dwell time) taken at dwell times  $\leq 10$  ms to generate time-resolved data. This short

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dwelt time allows measurement of dissolved metals, present as a background signal, and simultaneous detection of NPs as “pulses”. If the sample transport efficiency is determined (Pace et al., 2011), the intensities of pulse signals can be converted to analyte mass using a calibration curve constructed from dissolved ions of known concentrations. For chemically uniform (metal and metal oxide NPs) spherical NPs the measured masses can be used to obtain a particle size distribution (Pace et al., 2012). The number of pulses can also be converted to particle number concentration (Pace et al., 2011). Direct measurement of CNTs by carbon analysis is not feasible using ICP-MS due to poor ionization and high background, particularly in realistic environmental settings due to the ubiquitous presence of carbon-containing compounds. However, residual metal NPs (e.g. Ni, Co, Y) are commonly embedded in CNT structures as an impurity from the catalytic synthesis, and these metals can be analyzed by spICP-MS (Reed et al., 2013). Purification steps such as acid treatment are frequently applied to CNTs after synthesis to remove metal impurities (Belin & Epron, 2005; Prasek et al., 2011; Kumar, 2011; Meyyappan et al., 2003), but some metal NPs typically remain in the carbon structure. While these metal NPs allow for CNT detection, their quantity is likely to vary between individual CNTs, so size distributions of CNTs likely cannot be determined. Mass concentrations of CNTs can be measured by ICP-MS in samples if the metal content of the CNT is known (Ge et al., 2008; Yang et al., 2010).

In a previous study, spICP-MS with 10 ms dwell times was used to detect single-walled CNTs (SWCNTs) using 89Y as the analyte isotope (Reed et al., 2013). In this previous study a relationship between CNT mass concentration and particle number was established. Determining particle number was based on establishing an intensity cutoff, using the mean and standard deviation, above which particles are quantitatively counted. The effect of varying the cutoff on reported particle number versus CNT mass concentration was examined.

The very small size (~15 nm) of yttrium NPs in CNTs results in pulses of low intensity that must be detected above the background signal. Several spICP-MS studies have suggested that a single particle generates an ion cloud with duration in the ICP-MS quadrupole on the order of 300–500  $\mu$ s (Liu et al., 2014; Gschwind et al., 2011; Olesik & Gray, 2012; Koch et al., 2013). Thus the background intensity contributes to the overall signal for nearly 95% of a 10 ms dwell time. Furthermore, the short duration of the pulse suggests that multiple particles could be detected (coincidence) during individual dwell times of about a microsecond or more. Coincidence is undesirable because it leads to undercounting of particle numbers and overestimation of particle sizes. Recent ICP-MS hardware and software advancements provide the means to shorten dwell times to the  $\mu$ s scale, which can achieve better characterization of NPs by reducing the effects of elevated background and coincidence (Montaño et al., 2014).

Achieving improved analysis of CNTs, both in mass and particle number quantifications, was the major goal of this study. We report the first use of 100  $\mu$ s dwell times to collect spICP-MS data for CNTs. This study also goes beyond the previous work on spICP-MS analysis of CNTs by more fully confirming the association of metal NPs with CNTs and assessing the quantitative analysis of CNT-associated Y NPs. Finally, we demonstrate the ability of spICP-MS to measure biological exposure to CNTs by introducing *Daphnia magna* to a dilute aqueous CNT suspension, ultrasonically digesting the tissue, and measuring biological CNT association. The  $\mu$ s-spICP-MS method developed in this study provides a powerful new means of looking at part of the life cycle of CNTs and addresses some of the limitations of previous analytical approaches (i.e. use of radio-labeled CNTs and high CNT exposure concentrations).

## 2. Materials and methods

### 2.1. Reagents

The CNTs were obtained from Carbon Solutions (Riverside, CA) as a dry powder. Stock CNT solutions were prepared by suspending a

known mass of CNTs in a known volume of ultrapure water (HPLC grade) containing 1 wt% sodium deoxycholate (Sigma-Aldrich, Saint Louis, MO). A bath Branson 1510 ultrasonicator (Danbury, CT) was used to suspend CNTs overnight. Stock solutions were diluted using 18.2 M $\Omega$  cm<sup>-1</sup> Nanopure water (Barnstead Nanopure Diamond, Lake Balboa, CA), on the order of 100 to 1000 times, to concentrations appropriate for spICP-MS. Diluted solutions were placed in 15 mL polypropylene centrifuge tubes and sonicated (Fisher FS60H bath sonicator, Pittsburgh, PA) for 15–20 min after each dilution. Dissolved Au calibration solutions (0, 2, 5, 10  $\mu$ g/L) were prepared using Claritas PPT (SPEX Certiprep, Metuchen, NJ) ICP-MS standards and 2% hydrochloric acid (Optima, Fisher Chemical, Fair Lawn, NJ). Similarly, dissolved Y calibration solutions (0, 1, 2, 5  $\mu$ g/L) were prepared using Claritas PPT ICP-MS Y standards and 2% nitric acid (Optima, Fisher Chemical, Fair Lawn, NJ). A gold NP standard (55 nm, National Institute of Standards and Technology (NIST) RM 8013, Gaithersburg, MD) was diluted to 1  $\mu$ g/L from the stock 50 mg/L ( $\sim 2.98 \pm 0.04 \times 10$  (Upadhyayula et al., 2012) particles/mL) solution and analyzed to determine transport efficiency (Pace et al., 2011). Nanopure water was analyzed by spICP-MS in triplicate at the beginning of each experiment as a blank. Filtration of CNT suspensions was performed using 0.02  $\mu$ m (Whatman Anotop 25 syringe filters, 6809-2002, Pittsburgh, PA), 0.2  $\mu$ m (Whatman Anotop 25 syringe filters, 6809-2022, Pittsburgh, PA), and 2  $\mu$ m (Millex syringe filter units, SLAP02550, Billerica, MA) filters. An Au-PVP NP (40 nm, nanoComposix, AUPN40-25 M, San Diego, CA) was obtained as a powder, suspended in HPLC water and used to determine the accuracy of spICP-MS for particle number-concentration analysis.

Acid digestion was performed on the CNT suspension to determine total metal content. In this experiment, 5 mL of concentrated nitric acid (69.0–70.0%, Baker analyzed A.C.S. Reagent 9601, J.T. Baker, Phillipsburg, NJ) and 15 mL concentrated sulfuric acid (95.0–98.0%, Baker analyzed A.C.S. Reagent 9681, J.T. Baker, Phillipsburg, NJ) were added to ~100 mg CNTs with ~1 mg surfactant. The mixture was placed in an oil bath and refluxed at 70 °C for 5 days. The temperature was raised to 90 °C and refluxing continued for an additional 30 days. The digested sample was diluted with Nanopure water and sonicated using a bath sonicator before being introduced into ICP-MS. All analyses were performed in triplicate.

### 2.2. Instrumentation

All spICP-MS data were collected on a NexION 300Q ICP-MS (Perkin Elmer, Waltham, MA) with an S10 autosampler. The analyte isotope was 89Y and the dwell times used were 0.1, and 10 ms, with 60 s data acquisition time. The sample introduction flow rate was 0.3 mL/min. Data collection and spICP-MS calculations were performed using Syngistix™ Nano Application Module (more information on ICP-MS operating conditions is in SI Table 1). A Varian Cary 50 Conc UV-Visible Spectrophotometer (Palo Alto, CA) was used to obtain UV-Vis data with Cary Varian UV Scan Application 3.00. Imaging of CNTs was carried out using a Philips CN 300 Field Emission gun TEM operating at 300 kV. CNTs were dispersed in tetrahydrofuran/chloroform and followed by 4-hour bath sonication. The CNT was dip cast on a Lacey carbon grid (Lacey, Ted Pella Inc., Redding, CA). Dip-coating was used for grid preparation with several seconds of association time, and then grids was allowed to air dry for approximately 10 min. Low electron voltages were used to minimize beam damage to the CNTs. Images were collected with a bottom mounted Gatan SC200 CCD camera. Elemental composition of the CNTs was measured simultaneously with the images by energy-dispersive X-ray spectroscopy (EDS). Nano Tracking Analysis (NTA) was used to measure particle number concentration for comparison with spICP-MS. A NanoSight LM 10 instrument (Ann Arbor, MI) equipped with a 405 nm laser source, a temperature-controlled chamber, and a scientific CMOS camera, was used (Reed et al., 2013).

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