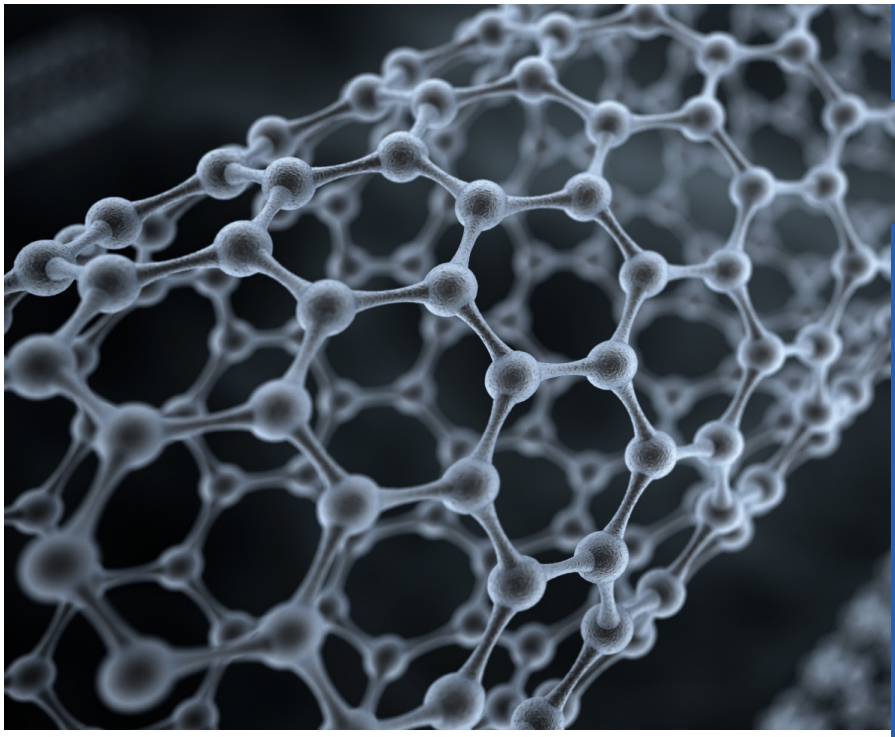

APPLICATION NOTE

ICP - Mass Spectrometry

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Analysis of Single-Walled Carbon Nanotubes with SP-ICP-MS

Introduction

With the growing use of nanotechnology, a wide variety of nanomaterials are being used in all types of products. Carbon nanotubes (CNTs) are among the most widely used nanomaterials, being produced at several thousand tons per year[1]. The production process often involves the use of metallic catalysts, which can result in metal NPs remaining on the CNTs (Figure 1). Although finished CNTs are washed to remove as much of the residual catalysts as possible, there are always remnants. Since residual metals can affect the performance of the CNTs, it is important to determine the level of metallic residue left from the catalysts. Additionally, the metal impurities can be used as a tracer for CNTs in fate and effect studies, thus overcoming the difficulties of measuring carbon in complex environmental and biological media.

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Measuring the amount of metals in CNTs presents a challenge. High levels can be measured directly in the solid by several techniques, including XRF and TEM, while low-level analysis requires complete digestion of the sample prior to analysis by ICP-OES or ICP-MS. The main limitation of XRF is that it measures the total quantity of metal in the sample rather than metal-associated with individual CNTs. TEM can measure individual CNTs and their associated metal NPs, but it is a slow, tedious process. Typical TEM analysis involves finding a particle/area to measure, performing the measurement, and then repeating the measurement a sufficient number of times to obtain a representative result. As a consequence, often only a small number of samples of CNTs can be measured in a day.

The limitation of conventional ICP-OES and ICP-MS analysis is that they require complete digestion of the CNTs, which is a challenge due to their chemical inertness. Digestion processes involve long processing times, dangerous acids, small sample quantities, and long digestion times, which even with closed-vessel microwave digestion, can range from hours to days. While a leaching procedure would be faster, this would only remove metals residing on the surface and not those embedded in the CNTs, thus not providing a complete analysis.

Another option for determining the residual metal content in CNTs is available: single particle ICP-MS (SP-ICP-MS). With this technique, solid nanoparticles (including CNTs) are completely ionized, and the resulting metallic signal associated with each individual CNT or CNT bundle is measured[2]. By monitoring the transient metallic signals, a semi-quantitative measurement of the amount of metal can be determined without the need for sample digestion. SP-ICP-MS provides measurement at lower concentration levels than by EDX or TEM. SP-ICP-MS also provides rapid measurement of thousands of individual CNTs in a minute, which results in the estimation of particle number concentrations.

This work focuses on the determination of yttrium (Y), a commonly used catalyst, in single wall CNTs (SWCNTs).

Experimental

Samples and Standards

SWCNTs were obtained in powder form from Carbon Solutions (Riverside, CA). Stock solutions were prepared by suspending a known quantity of SWCNTs in a known volume of deionized (18.2 MΩ-cm) water containing 1% (w/w) sodium deoxycholate. The CNTs were suspended in solution by sonicating overnight and then further diluted 100 to 1000x. Prior to analysis, the solutions were bath sonicated for 15-20 minutes.

To determine the transport efficiency of the system, 60 nm Gold NPs (SRM 8013, NIST, Gaithersburg, MD) were diluted with deionized water to a final concentration of 1 µg/L. Dissolved gold standards were used to compute transport efficiency using the mass-based approach[3]. Aqueous yttrium (Y) calibration standards were prepared at 1, 2, and 5 µg/L from a 1000 mg/L stock solution.

To determine if the small (20 nm) Y particles were associated with larger SWCNTs, filtration of the CNT suspensions was done through 0.02 µm, 0.2 µm, and 2 µm filters (Whatman, Pittsburgh, PA; Millex, Billerica, MA). To confirm complete ionization of the SWCNTs, a nitric acid digested SWCNT sample was analyzed at the same dilution as the intact SWCNT solutions.

Instrumentation

All SP-ICP-MS analyses were performed on a NexION® ICP-MS (PerkinElmer, Shelton, CT) using the conditions shown in Table 1. Data collection and analysis were done with the Syngistix™ Nano Application Module.

Table 1. NexION Operating Conditions.

Instrument Parameter	Value
Nebulizer	Glass Concentric
Spray Chamber	Baffled Glass Cyclonic
Nebulizer Gas Flow (L/min)	0.85-1.00
Sample Uptake Rate (mL/min)	0.300
ICP RF Power (W)	1600

Results and Discussion

Initial studies were done with transmission electron microscopy (TEM) to determine to what extent Y was associated with the CNTs. Figure 1 shows TEM images of CNTs, which appear as long, grey rods. The dark areas within the CNTs are metals (Ni, Y), as confirmed with TEM. The supplier of the CNTs also states that Ni and Y are used as catalysts in their production, thus providing further confirmation of their presence.

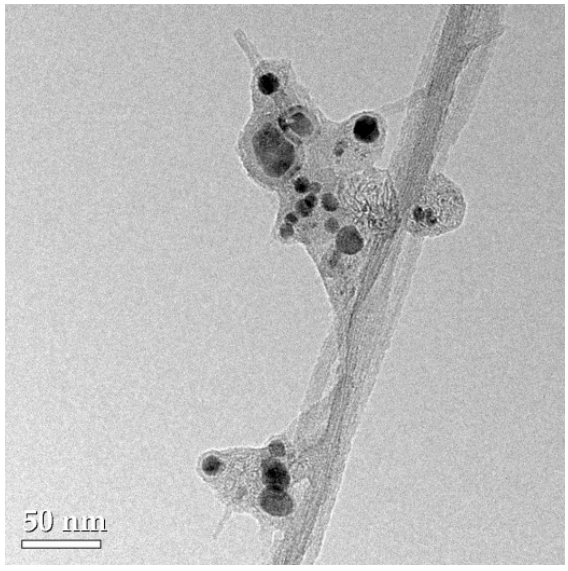

Figure 1. Transmission electron microscopy (TEM) images of CNTs showing electron dense metal NPs associated with amorphous graphitic material and long SWCNTs (Wang et al., 2016).

Figure 2 shows the SP-ICP-MS signals for Y where each spike represents the Y signal from a SWCNT. The signals from the unfiltered and 2 µm filtered samples look very similar, indicating that the CNTs largely pass through the 2 µm pores. These results are consistent with the reported physical dimensions of the SWCNTs: diameters of 3.8 ± 1.8 nm and lengths of 1800 ± 1000 nm. However, with a smaller pore size of 0.2 µm, most of the CNTs were removed, as evidenced by the reduced number of Y pulses. Finally, with a pore size of 0.02 µm, no Y signals are observed, indicating that none of the CNTs have passed through the filter. This work demonstrates that Y NPs are associated with the CNTs: when the CNTs are present, Y signal is seen; however, when the CNTs are removed, the Y signal disappears.

The Syngisitx Nano Application Module automatically counts the number of peaks found in an analysis and displays the average and median intensities of both the background and the Y - generated pulses. Integration of the signal provides the total amount of metal present in the SWCNTs. With knowledge of the density of the analyte, each pulse can be converted by the Syngisitx Nano Application Module into an equivalent spherical diameter. However, it is likely that multiple metallic aggregates are attached to each of the SWCNTs (Figure 1). Thus the reported diameter is likely to larger than the true diameter of an individual metal NP. Using the transport efficiency, the number concentration of the SWCNTs in solution can also be calculated.

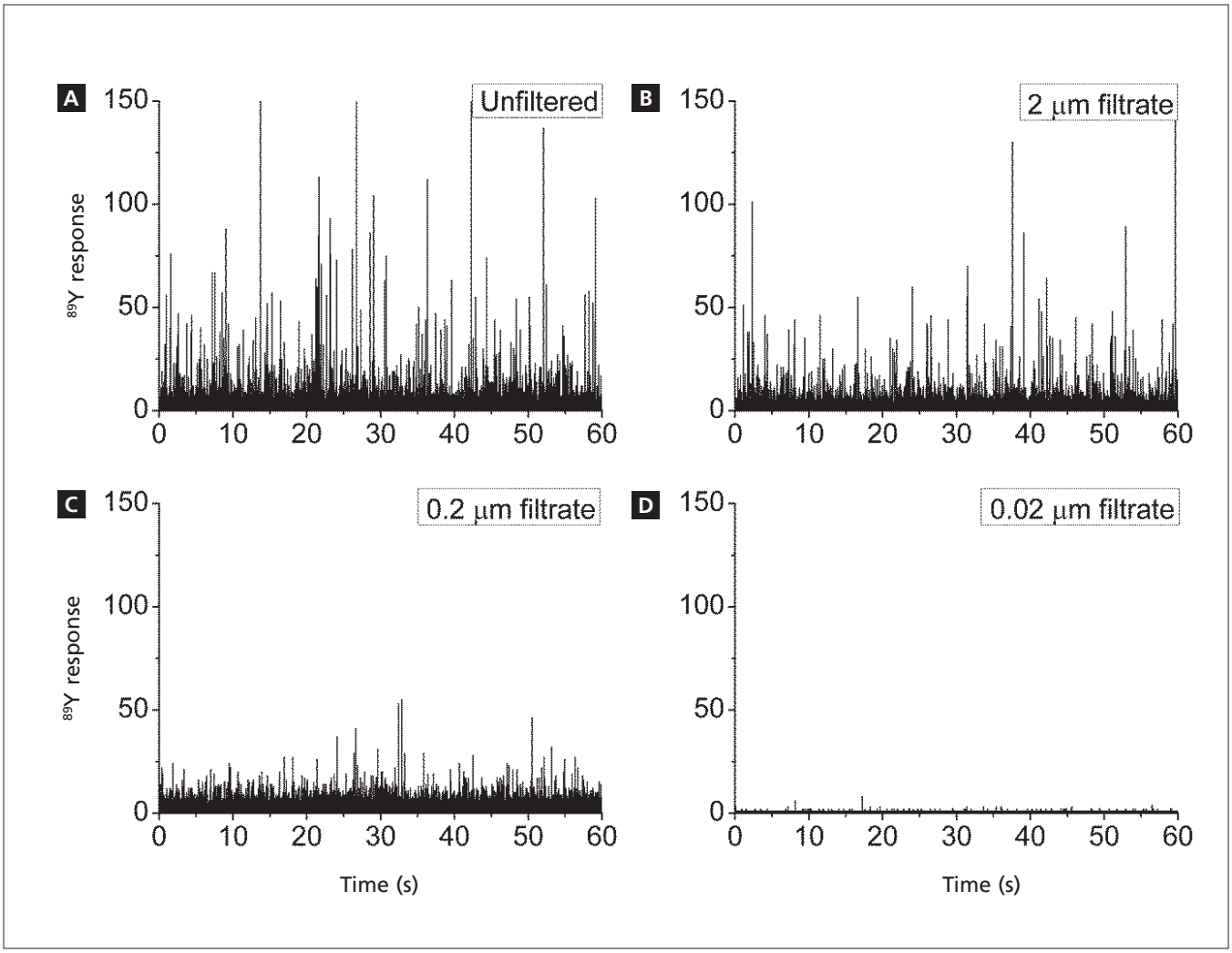

Figure 2. SP-ICP-MS signals for Y associated with CNTs. a) unfiltered; filtered through b) 2 µm pores; c) 0.2 µm pores; d) 0.02 µm pores (Wang, et al, 2016).

In this study, solutions containing 43.5 µg/L SWCNT were prepared. One of these solutions was acid digested, and the other was directly analyzed by SP-ICP-MS. The resulting SP-ICP-MS signals are shown in Figures 3a (digested) and 3b (undigested suspension). The absence of peaks from the digestion indicates that all CNTs were dissolved, while the presence of many peaks in Figure 3b shows numerous Y-containing NPs are being detected. The digested solution had a Y concentration of 2.18 µg/L, while the SP-ICP-MS analysis yielded a Y concentration of 2.15 µg/L, confirming the accuracy of the SP-ICP-MS results for undigested suspensions. These results also indicate that the CNTs contained about 5% Y.

Summary

SP-ICP-MS provides a means to quantify the metal-content of SWCNTs. The use of metal impurities allows determination of SWCNT number concentrations, with possible applications to complex media. Furthermore, if metal content is known, SWCNT concentrations in unknown samples can be determined. The significance of this work is that metallic contaminants in CNTs can be accurately quantified without the need to digest the CNTs, a long, difficult process.

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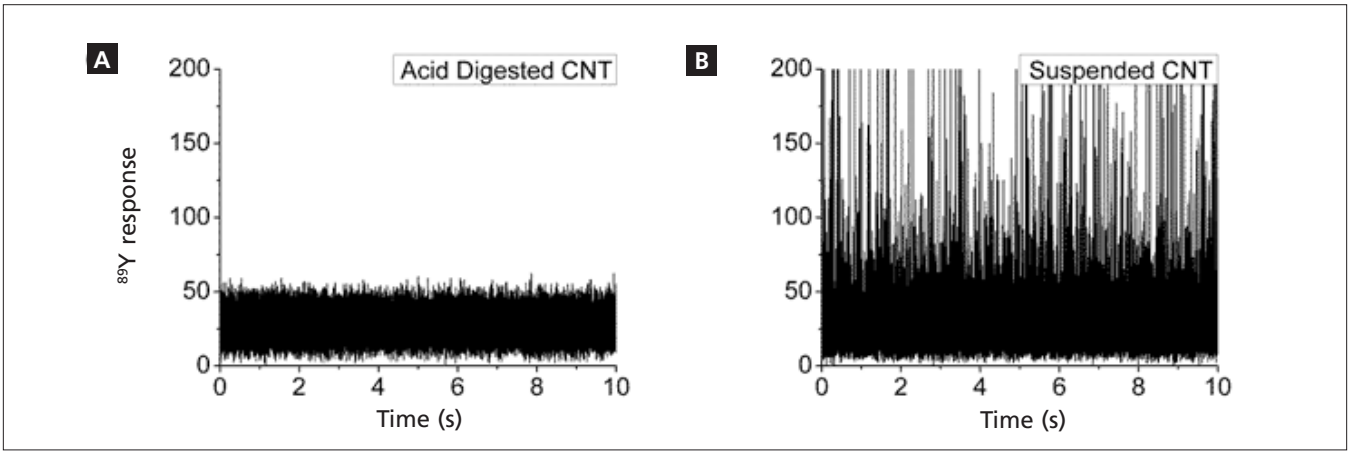

Figure 3. Analysis of Y in a.) acid digested, and b.) undigested 43.5 µg/L CNT solutions.

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