APPLICATION NOTE

ICP - Mass Spectrometry

Authors:

A. Mackevica

M.E. Olsson

S.F. Hansen

Technical University of Denmark
Department of Environmental Engineering
Kgs. Lyngby, Denmark

Characterization of TiO_2 Nanoparticle Release from Fabrics by Single Particle ICP-MS

Introduction

In the textile industry, the use of titanium dioxide (TiO_2) nanoparticles (NPs) is increasing due to their ability to provide UV protection, increase the hydrophilic nature of fabrics, provide antibacterial characteristics, and reduce odors.[1] As TiO_2 use has increased, questions have arisen about how strongly the TiO_2 NPs are bound to the fabrics and how easily they are released, due to potential impacts on people wearing TiO_2-infused clothes and the environment, as TiO_2-containing textiles are laundered and, eventually, discarded.

Currently, TiO_2 NP release from fabrics has not been studied extensively. Studies addressing NP release commonly use conventional techniques, such as microscopy (SEM, TEM, AFM), dynamic light scattering, X-ray techniques (photoelectron spectroscopy, diffraction), field flow fractionation, and UV spectroscopy.[2] However, all of these techniques suffer from limitations, the main ones being inability to analyze NPs at sub-ppb levels, low throughput, or lack of information on individual particles.

With the development of Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICP-MS), these limitations have been overcome[3,4]: rapid measurement of individual particles, allowing a large number of particles to be measured in a short time period and providing information on individual particles, including particle-size distribution, particle number, and particle concentration. In addition, SP-ICP-MS can distinguish dissolved (ionic) and particulate forms of the metal being measured. SP-ICP-MS has already shown its ability to measure TiO_2 NPs in sunscreens.[5]

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This work studies the release of TiO_2 NPs from various commercial textile products which do not advertise that TiO_2 NPs have been added. A more detailed study of the work presented here is available.[6]

Experimental

Samples and Sample Preparation

The five textile samples used for this evaluation were purchased in local stores and are described in Table 1. A suspension of 40% TiO_2 NPs (30-50 nm) was purchased from US Research Nanomaterials™ (Houston, Texas, USA). To aid in NP dispersion, Triton X-100 (Sigma-Aldrich™, St. Louis, Missouri, USA) was added to all solutions at a final concentration of 0.0001%.

For total Ti determination, 0.25 g of each textile sample was cut in small pieces and digested in a microwave, along with 5 mL of concentrated (65%) nitric acid and 1 mL of concentrated (49%) hydrofluoric acid. Post digestion, 6 mL of 10% H_3BrO_3 (v/v) was added to each sample to complex the HF during a 15-minute cycle in the microwave. The samples were then brought to a final volume of 50 mL with deionized water and analyzed by conventional ICP-MS.

To examine TiO_2 NP release from fabric, a 400 cm^2 piece of each sample was removed and immersed in 200 mL of deionized water. The container was sonicated for 15 minutes and then placed on a shaking table (150 movements/minute) for 24 hours. The containers were sonicated a second time before an aliquot of liquid was removed for analysis. A deionized (DI) water blank spiked with 2.7 µg/L TiO_2 NPs was used as a control. Samples were diluted further with DI water, if necessary, and sonicated between dilutions to minimize NP agglomeration.

For determination of total titanium released by the fabrics, a 150 mL aliquot of each sample was removed and evaporated to dryness. The resulting solid was then microwave digested in acid for total Ti analysis.

To aid in TiO_2 NP washout, a rinsing solution was composed of 100 mg/L EDTA, 10 mg/L Triton X-100 in 100 mM ammonium hydroxide solution was used. Experimentally it was found that a rinse time of 180s was required to make sure all TiO_2 NPs were out of the system prior to the analysis of the next sample.

Instrumental Conditions

All analyses were performed on PerkinElmer's NexION® ICP-MS running Syngistix™ for ICP-MS software. For nanoparticle analysis, the Syngisitix Nano Application Module was used for data collection and processing. Table 2 shows the NexION operating conditions for TiO_2 NP analysis. The transport efficiency was determined using 60 nm Au NPs (PerkinElmer, Shelton, CT USA). All TiO_2 NP measurements were made on Ti at m/z 48 since it is the most abundant Ti isotope. However, because a minor isotope of Ca also exists at m/z 48 (0.187%), all samples were measured a second time monitoring Ca at m/z 44 (2.056% abundance). Based on the isotopic ratio of ^{44}Ca:^{48}Ca (11:1), any contributions to the ^{48}Ti signal were removed.

Results and Discussion

First, all of the textile samples were measured for total Ti. It was found that Ti was present in all samples, as shown in Table 3, with concentrations ranging from 2.63 to 1448 µg/g.

Next, the samples were analyzed for TiO_2 NPs. Figure 1 shows signals from the TiO_2 NPs (i.e. control), and three of the samples. These plots clearly show differences between the samples: while the TiO_2 NP control shows a repeatable, uniform size distribution, the NP size distributions are much larger with the samples – up to 200 nm. In addition, there are variations from sample to sample within a sample type, as seen for Samples A and D. Table 4 shows the average NP size and particle concentration for each sample, where Samples B and C did not contain notable amounts of TiO_2 NPs.

Table 1. Description of Textiles.

Code	Product	Composition	Ecolabel	Color
A	Baby Bodysuit	100% Cotton	Nordic	White
B	Baby Bodysuit	48% Wool 47% Cotton 5% Polyamide	EU	Natural White
C	Table Placemat	100% linen	Not Available	Beige
D	Wet Wipes	Polyester, Viscose (With Lotion)	Nordic	White
E	Microfiber Coths	80% polyester 20% nylon	Nordic	Natural White

Table 2. NexION Operating Conditions for SP-ICP-MS Analysis.

Parameter	Value
Dwell Time	100 µs
Measurement Time	100 – 300 s
RPq	0.5
Analytes	^{48}Ti, ^{44}Ca
Transport Efficiency	6.5-7.5%
Sample Uptake Rate	0.288-0.298 mL/min

Table 3. Total Ti Content of the Samples.

Sample	Total Ti Content (µg/g)
A - Baby Bodysuit	2.63
B - Baby Bodysuit	57.3
C - Table Placemat	3.36
D - Wet Wipes	720
E - Microfiber Cloths	1448

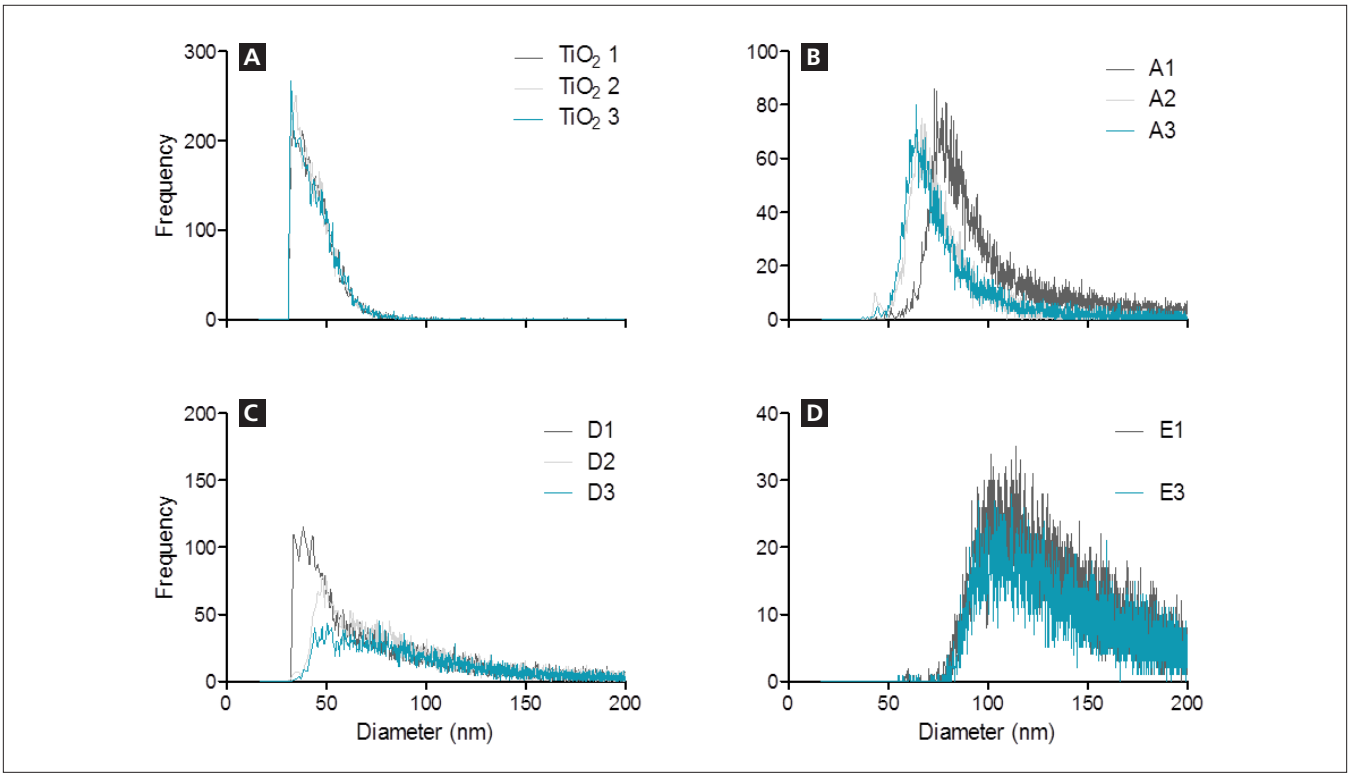

Figure 1. Measured TiO_2 NP control size distributions for (A) TiO_2 NP control (B) baby bodysuit (100% cotton) (C) wet wipes (D) microfiber cloths.

Table 4. TiO_2 NP Size and Concentrations in the Textile Samples.

Sample	Size (nm)	Particle Conc. (10^3 Particles/mL)	Particle Conc. (Particles/cm^2)
TiO_2 NP Control	34.8	12 655	---
A - Baby Bodysuit	76.7	187	468
B - Baby Bodysuit	N/A	< 3.5	N/A
C - Table Placemat	N/A	< 3.5	N/A
D - Wet Wipes	49.3	2788	8201
E - Microfiber Cloths	75.8	1655	4137

Conclusion

This work has demonstrated the ability of SP-ICP-MS to both detect and measure TiO_2 nanoparticles released from textiles. The use of SP-ICP-MS allows a large number of particles to be rapidly analyzed and provides information on individual particles, overcoming limitations of conventional techniques for NP analysis. The results of this study showed that a variety of textile products contain TiO_2 NPs of various sizes and concentrations.

References

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Consumables Used

Component	Description	Part Number
Sample Uptake Tubing	0.38 mm id (Green/Orange), Flared, 2-stop	N0777042
Drain Tubing	1.30 mm id (Gray/Gray), Santoprene, 2-stop	N0777444

PerkinElmer, Inc.
940 Winter Street
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P: (800) 762-4000 or
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