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## Изучение высвобождения наночастиц TiO2 из текстильных тканей с помощью ICP-MS

В текстильной промышленности использование наночастиц диоксида титана (TiO2) нашло широкое применение благодаря их способности обеспечить защиту от ультрафиолета, улучшения гидрофильности тканей, и обеспечения бактерицидных характеристик, а также нейтрализации запахов.

Поскольку использование наночастиц TiO2 возрастает в последние годы, возникает вопрос о том, как сильно наночастицы TiO2 внедряются в ткани и насколько легко они высвобождаются, из-за потенциального воздействия на людей, носящих одежду. А также насколько наночастицы TiO2 вымываются при стирке и что с ними происходит, когда ткани, содержащие их, в конце концов, выбрасываются.

В настоящее время высвобождение наночастиц TiO2 из тканей еще не тщательно изучено. Исследования, касающиеся высвобождения наночастиц, чаще всего используют обычные методы, такие как микроскопия (SEM, TEM, AFM), динамическое рассеяние света, рентгеновские методы (фотоэлектронная спектроскопия, дифракция), фракционирование потока поля, и УФспектроскопия. Тем не менее, все эти методы достаточно ограничены, вследствие неспособности выявлять наночастицы на уровнях ниже ppb, низкой пропускной способности или отсутствия информации об отдельных наночастицах.

С развитием метода (SP-ICP-MS), эти ограничения были преодолены. Быстрое измерение отдельных частиц позволяет измерять большое количество частиц за короткий промежуток времени и предоставляет информацию об отдельных наночастицах, включая их распределение по размеру частиц, количество частиц и концентрацию частиц. Кроме того, SP-ICP-MS может различать растворенные (ионные) и дисперсные формы металлов. SP-ICP-MS уже показала свою способность измерять содержание наночастиц TiO2 в солнцезащитных кремах.

В данной работе изучается высвобождение наночастиц TiO2 из различных коммерческих текстильных изделий.

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https://www.perkinelmer.com/lab-solutions/resources/docs/app\_013846\_01\_nexion\_sp-icpms\_tio2\_nps\_in\_fabric.pdf



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### **ICP** - Mass Spectrometry

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# Characterization of TiO<sub>2</sub> Nanoparticle Release from Fabrics by Single Particle ICP-MS

#### Introduction

In the textile industry, the use of titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) is increasing due to their ability

to provide UV protection, increase the hydrophilic nature of fabrics, provide antibacterial characteristics, and reduce odors.<sup>1</sup> As TiO<sub>2</sub> use has increased, questions have arisen about how strongly the TiO<sub>2</sub> NPs are bound to the fabrics and how easily they are released, due to potential impacts on people wearing TiO<sub>2</sub>-infused clothes and the environment, as TiO<sub>2</sub>-containing textiles are laundered and, eventually, discarded.

Currently, TiO<sub>2</sub> 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.<sup>2</sup> 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<sup>3,4</sup>: 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<sub>2</sub> NPs in sunscreens.<sup>5</sup>



This work studies the release of  ${\rm TiO_2}$  NPs from various commercial textile products which do not advertise that  ${\rm TiO_2}$  NPs have been added. A more detailed study of the work presented here is available.<sup>6</sup>

#### **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<sup>TM</sup> (Houston, Texas, USA). To aid in NP dispersion, Triton X-100 (Sigma-Aldrich<sup>TM</sup>, 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<sub>3</sub>BrO<sub>3</sub> (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  ${\rm TiO_2}$  NP release from fabric, a 400 cm² 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  ${\rm \mu g/L}$   ${\rm TiO_2}$  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  ${\rm TiO_2}$  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  ${\rm TiO_2}$  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 TiO₂ NP analysis. The transport efficiency was determined using 60 nm Au NPs (PerkinElmer, Shelton, CT USA). All TiO₂ 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 ⁴⁴Ca:⁴8Ca (11:1), any contributions to the ⁴8Ti 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  $\mu$ g/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.

| Co | ode | Product          | Composition                            | Ecolabel      | Color         |
|----|-----|------------------|--|---------------|---------------|
|    | А   | Baby Bodysuit    | 100% Cotton                            | Nordic        | White         |
|    | В   | Baby Bodysuit    | 48% Wool<br>47% Cotton<br>5% Polyamide | EU            | Natural White |
|    | C   | Table Placemat   | 100% linen                             | Not Available | Beige         |
|    | D   | Wet Wipes        | Polyester, Viscose<br>(With Lotion)    | Nordic        | White         |
|    | Е   | Microfiber Coths | 80% polyester<br>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             | <sup>48</sup> Ti, <sup>44</sup> 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                    |

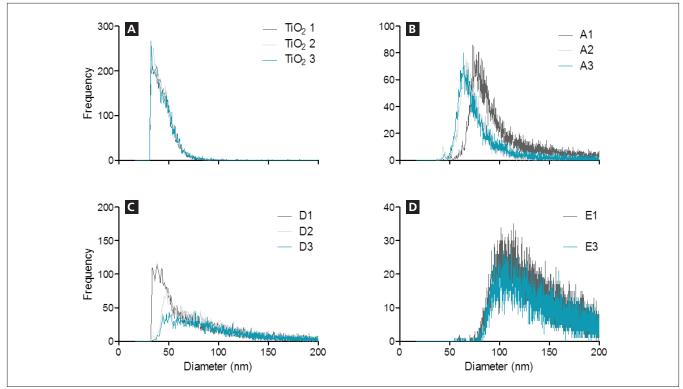


Figure 1. Measured TiO, NP control size distributions for (A) TiO, NP control (B) baby bodysuit (100% cotton) (C) wet wipes (D) microfiber cloths.

Table 4. TiO<sub>2</sub> NP Size and Concentrations in the Textile Samples.

| Sample                      | Size<br>(nm) | Particle Conc.<br>(10³ Particles/mL) | Particle Conc.<br>(Particles/cm²) |
|-----------------------------|--------------|--------------------------------------|-----------------------------------|
| TiO <sub>2</sub> 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

- 1. Kohler, A.R., Som, C. Technovation 34 (8), 2014, 420-430.
- 2. Laborda, F., Bolea, E., Cepria, G., et. al. *Analytica Chimica Acta*, 904, 2016, 1220-1232.
- 3. Stephan, C., Neubauer, K. "Single Particle Inductively Coupled Plasma Mass Spectrometry: Understanding How and Why", PerkinElmer, 2014.
- 4. Hineman, A., Stephan, C. *J. Anal. At. Spectrom.* 29, 2014, 1252-1257.
- Dan, Y., Shi, H, Liang, X, Stephan, C. "Measurement of Titanium Dioxide Nanoparticles in Sunscreen using Single Particle ICP-MS", PerkinElmer, 2015.
- Mackevica, A., Olsson, M.E., Hansen, S.F., 2018. "Quantitative characterization of TiO<sub>2</sub> nanoparticle release from textiles by conventional and single particle ICP-MS." Journal of Nanoparticle Research, 20(1), p.1-11. DOI: 10.1007/s11051-017-4113-2.

#### **Consumables Used**

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

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