APPLICATION NOTE

ICP - Mass Spectrometry

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Measurement of Titanium Dioxide Nanoparticles in Sunscreen using Single Particle ICP-MS

Introduction

Titanium dioxide (TiO_2) nanoparticles are commonly used in sunscreens as part of the formulation to block the sun's harmful UV rays. As the use of nanoparticles in consumer products has increased, concern has risen as to the health and environmental effects of nanoparticles. Since sunscreens contact skin and wash off in water, the TiO_2 nanoparticles can find their way into biological and environmental systems. As a result, there is a need to measure both the size and size distribution of these nanoparticles in sunscreens so as to assess their impact on human health and the environment.

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Traditionally, nanoparticle size characteristics have been determined by several methods, including field flow fractionation (FFF), dynamic light scattering, and microscopy, among others. Recently, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has been gaining attention as a way to both measure and characterize nanoparticles. Advantages of SP-ICP-MS include speed and the amount of information which can be gained from the analysis.

This work will focus on characterizing TiO_2 nanoparticles in sunscreens using SP-ICP-MS with a simple sample preparation.

Experimental

Sample Preparation

Sunscreen products were purchased at a local store and had the label information shown in Table 1. For each sample, 15 mL of sunscreen was added to a 50 mL container and mixed for three minutes to create a homogeneous sample. Next, 0.2 g of each homogenized sample was transferred to another container, followed by addition of 200 mL 1% Triton-X solution. These solutions were sonicated until all aggregates appeared to be broken up (5-10 minutes). After sonication, serial dilutions were performed on the samples with deionized water to produce particle concentrations of 100,000 – 200,000 particles/mL (as measured during analysis).

Transport efficiency determination was performed with gold nanoparticles (50, 80, 100 nm, nanoComposix, San Diego, California, U.S.A.) which were prepared by dilution in deionized water to a final nominal concentration of 100,000 particles/mL. All standards were sonicated for five minutes prior to analysis to ensure that any agglomerated particles were dispersed. Forty nanometer TiO_2 (US Research Nanomaterials Houston, Texas, U.S.A.) spikes were added to various samples to verify the accuracy of the TiO_2 size measurements.

Calibration standards for titanium consisted of 2, 5, and 10 ppb standards prepared in deionized water from a 1000 mg/L titanium standard (PerkinElmer, Shelton, Connecticut, U.S.A.).

Table 1. Label Information for Sunscreen Products.

Sunscreen	SPF	TiO_2 Content (%)
1	60+	4.9
2	50	6
3	45	0
4	50	6
5	45+	5.1

Instrument Conditions

All analyses were performed on a PerkinElmer NexION® 350D ICP-MS using the Syngistix™ Nano Application Software Module. Tables 2 and 3 show the instrumental and method parameters, respectively. When using the Syngistix Nano Application Module, the quadrupole settling time is automatically eliminated, thus ensuring that no particles are missed. The combination of elimination of quadrupole settling time and short dwell time results in the collection of multiple data points for each particle.

Table 2. NexION 350D ICP-MS Instrument Parameters.

Parameter	Value
Nebulizer	Glass concentric
Spray chamber	Glass cyclonic
Sample uptake rate	0.26-0.28 mL/min
RF power	1600W
Analysis mode	Standard
Quadrupole settling time	0 µs

Table 3. Method Parameters.

Parameter	Value
Analyte	Ti48
Dwell time	100 µs
Data acquisition time	100 sec
Density	4.23 g/cm^3
Ti mass fraction	60%

Results and Discussion

To characterize the Ti background of the system and reagents, a blank solution consisting of only the reagents (i.e. Triton X-100 in deionized water) was analyzed, with the resulting signal shown in Figure 1. While a few signal spikes are seen, the majority of the Ti background is below two counts, which demonstrates the cleanliness of the system.

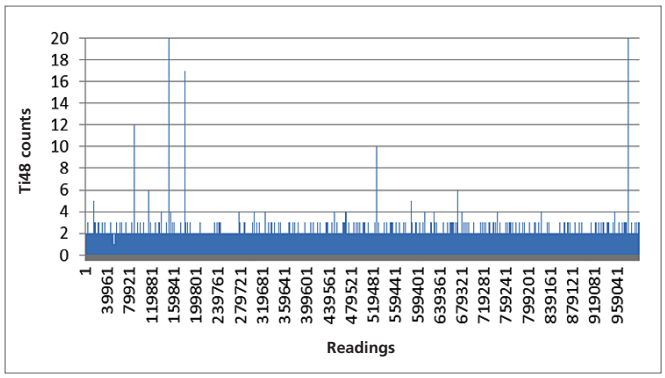

Figure 1. Ti background signal for blank.

To determine the ability to see TiO_2 particles in a sunscreen matrix, the sunscreen without any TiO_2 particles was analyzed. Figure 2A shows the TiO_2 particle signal from a sunscreen which does not contain TiO_2 (according to its label). Aside from a few spikes, the background is equivalent to the blank (Figure 1).

Next, this sunscreen solution was spiked with 40 nm TiO_2 particles at a concentration of 6.65 µg/L; the resulting signal is shown in Figure 2B. Since each spike represents a particle, it is evident that TiO_2 particles can easily be seen in a sunscreen matrix.

Furthermore, the most frequent size particle was 37.7 µm, demonstrating the accuracy of the measurement.

Figure 3 shows the TiO_2 particle size distribution for a 20,000 times-diluted sunscreen (Sunscreen 5).

With the ability to accurately measure TiO_2 particles in sunscreen established, other sunscreen samples were analyzed three times; the results are shown in Table 4.

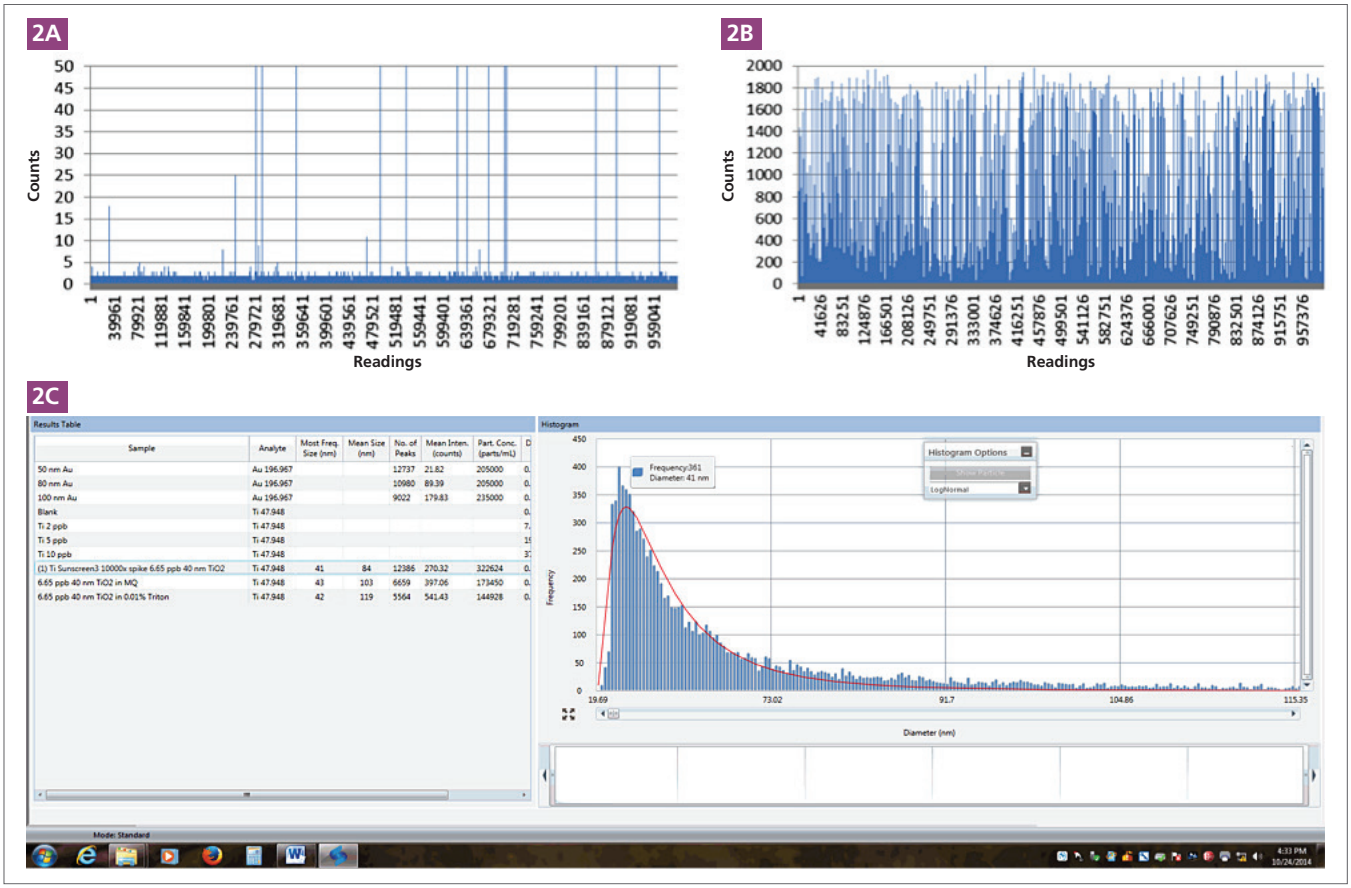

Figure 2. TiO_2 signals from a sunscreen which does not contain TiO_2 (2A), and spiked with 40 nm TiO_2 (2B) particles. The screen shot shows the processed data of spiking 40 nm TiO_2 into a sunscreen which does not contain any TiO_2 nanoparticles (2C).

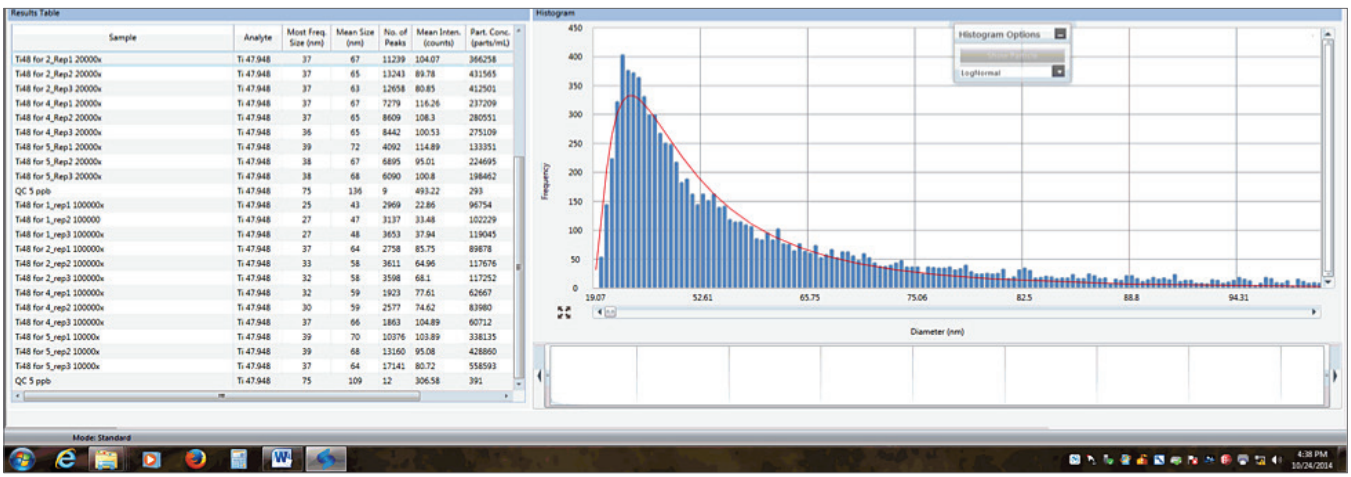

Figure 3. Processed data for 20,000 times-diluted sunscreen which contains TiO_2 nanoparticles.

Table 4. TiO_2 Nanoparticle Analysis in Commercial Sunscreens.

Sunscreen	Dilution Factor	Most Frequent Size (nm)	Particle Size Distribution (nm)	Particle Concentration (particles/mL)
1	100,000	32	24 – 58	102,229
2	100,000	34	24 – 64	117,252
3*	100,000	-	-	-
4	100,000	33	24 – 61	63,000
5	20,000	42	28 – 67	198,462

*This sunscreen contains no nanoparticles, as shown in Table 1.

These results indicate that the sunscreens had TiO_2 nanoparticles ranging from 24 – 67 nm, with similar size distributions in each. However, Sunscreen 5 is clearly different from the others: the smaller dilution factor required to obtain less than 200,000 particles/mL indicates that fewer TiO_2 particles are present in this sample than the others.

Conclusion

This work has demonstrated the ability to measure TiO_2 nanoparticles in commercial sunscreen samples. Using both the NexION 350 ICP-MS and the Syngistix Nano Application Software Module, the analysis is simple and rapid, yet can clearly differentiate the TiO_2 content among different samples.

Consumables Used

Component	Description	Part Number
Titanium standard	1000 ppm, 125 mL	N9303806
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

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