

## **REPORT**

### **Identification & Quantification of Nanomaterials in Commercial Sunscreen Products**

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#### **Overview:**

We have completed testing four consumer sunscreen products selected by FOE for understanding the amount and form of nanomaterials in these products. All products are intended for use by children for broad spectrum skin protection. This report focuses on the characterization and quantification of engineered nanomaterials in the provided samples. This report includes detailed analytical protocols, raw and synthesized data from the analysis of nanoparticles in these products. We report that ZnO and/or TiO<sub>2</sub> nanoparticles (<100 nm) are consistently identified in the four sunscreen products. However, the information on the form and size of nanomaterials are not always clearly labeled or accurately disclosed by the manufacturer.

#### **Materials and methods:**

A total of four sunscreen products were purchased and received from FOE which potentially contain ZnO and/or TiO<sub>2</sub> nanoparticles. The complete list of products is shown in Table 1, including the commercial name, manufacturer info, potential nanomaterial inclusion, functionality, and the corresponding image.

Careful analyses were conducted for each of the received consumer product. Tiered approaches were used for the systematic detection, quantification, and characterization of nanomaterials in these products. Specifically, products were first subject to the analysis by an X-ray fluorescence (XRF) analyzer (Niton XL3t GOLDD+, Thermo Scientific) to detect the presence of titanium and zinc, which are reported as a weight percentage.

Prior to further characterization, TiO<sub>2</sub> and/or ZnO nanoparticles were extracted from sunscreen products. Briefly, the materials were extracted by dichloromethane (DCM) solvent through repeated sonication and centrifugation to remove organic constituents. The extracted pellets were then rinsed by ultrapure water to remove salts and surfactants. The extracted materials were finally resuspended in isopropanol and dropped onto TEM grids for analysis.

Transmission electron microscopy (TEM) was utilized to image the size, shape and morphology of nanomaterials extracted from product. Energy-dispersive X-ray spectroscopy (EDS) was used in couple with electron microscopy to confirm the chemical composition of nanomaterials. The number and dimensions of nanomaterials are reported along with these images.

Particle size analysis was performed using ImageJ, a free image processing program available from the National Institute of Health. The number of primary particles was noted and were sized. The scale bar was used to set the scale for calculating each particle's diameter. In the case of high aspect ratio structures both a width and length were measured. Error is reported as +/- 1 standard deviation.

**Table 1.** List of tested sunscreen products received from FOE

Product category	Commercial name	Company	Function	Nanomaterial inclusion (claim by manufacturer)	Image
Sunscreen cream	Sunscreen for kids SPF 50	Banana boat	sunscreen	TiO <sub>2</sub> (3.1%) ZnO (4.0%)	
Sunscreen face stick	Aveeno baby natural protection sunscreen SPF 50	Johnson & Johnson	broad spectrum protection; more natural alternative	TiO <sub>2</sub> (8.1%) ZnO (6.8%)	
Sunscreen cream	Kid's Safe Sunscreen SPF 50+	Thinksport	sunscreen	Non-nano ZnO (20%); average particle size >100 micron	
Sunscreen cream	Pure & free baby sunscreen, SPF 50	Neutrogena	broad spectrum protection	ZnO (21.6%) Helo technology	

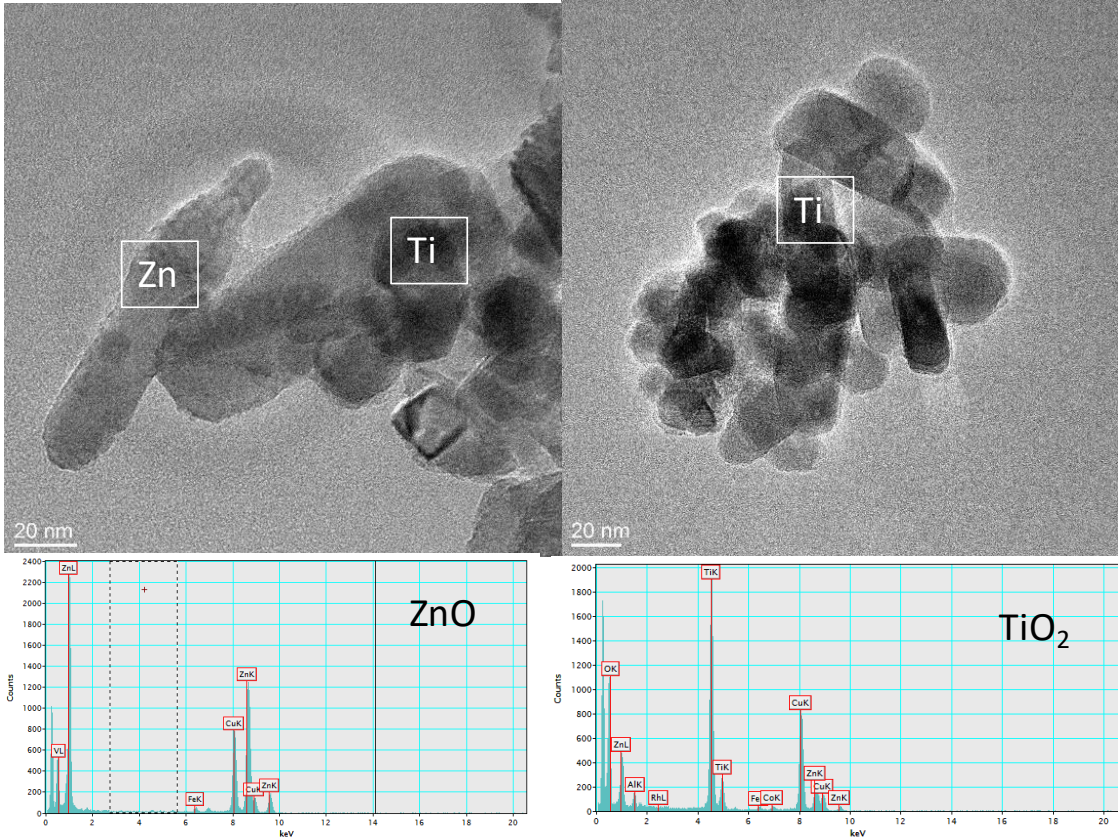
**Results:**

Using the tiered approaches, all four sunscreen products were tested for the presence, concentration, and characterization of engineered particles. Table 2 summarizes the results of the concentration, shape and size information of identified ZnO and TiO<sub>2</sub> particles. ZnO nanoparticles were identified in all four sunscreen products at concentrations generally greater than a few percentage of the total mass. In contrast, TiO<sub>2</sub> was only identified in two sunscreen products as shown in Table 1. By using XRF, we confirmed that ZnO and TiO<sub>2</sub> content generally agree with the active ingredient content on product label ( $\pm 4\%$  and  $\pm 2\%$ , respectively).

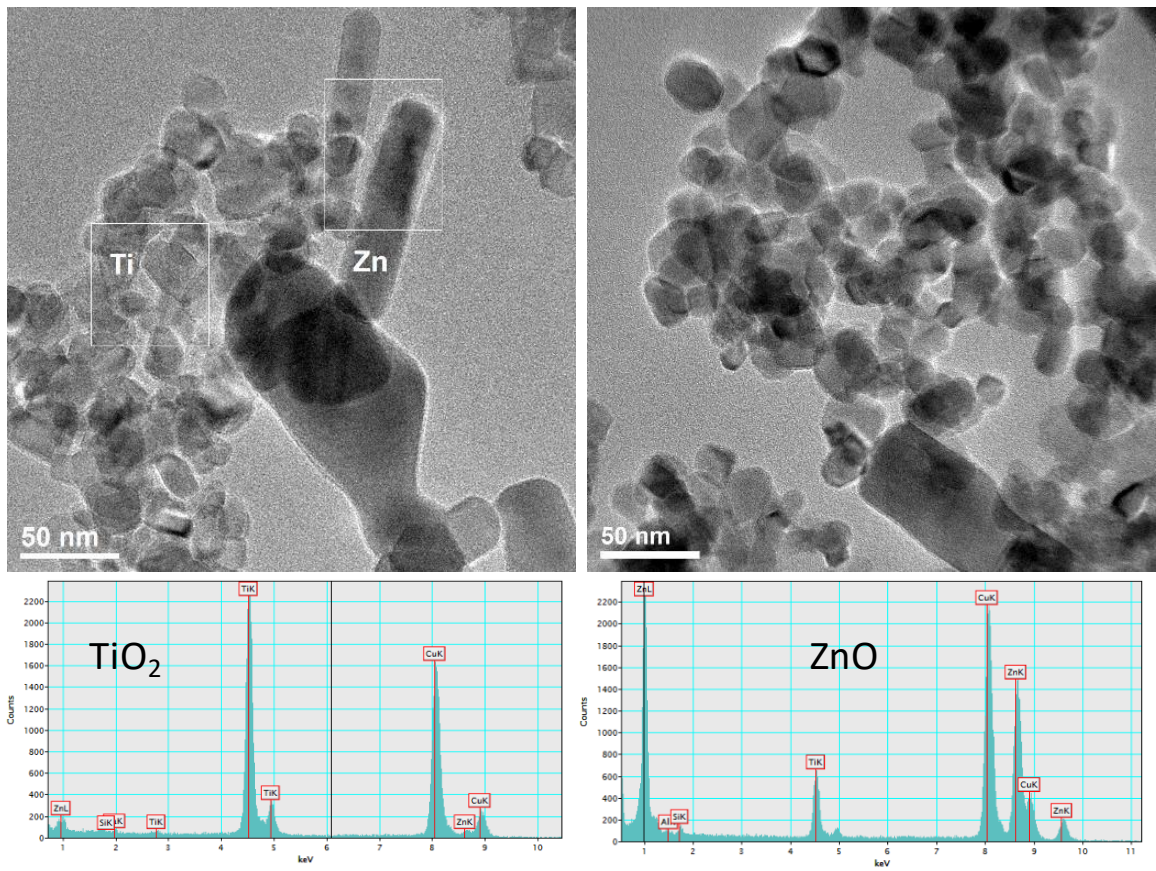
The size and shape of ZnO particles vary depending on the product manufacturer. In general, the size of ZnO particles in sunscreen is less than 100 nm in any dimension. The morphology of ZnO in sunscreen products is either rod or spherical. In contrast, the primary particle size of TiO<sub>2</sub> was determined to be 30 nm and 23 nm, respectively, in Banana boat sunscreen and Aveeno sunscreen stick. In both sunscreen, TiO<sub>2</sub> particles have spherical shape, which is generally uniform throughout the products. The TEM images and EDS analysis of particles extracted from the products are provided in Figure 1-4 for each sunscreen product.

**Table 2.** Summary of particle characteristics identified in in four sunscreen products received from FOE.

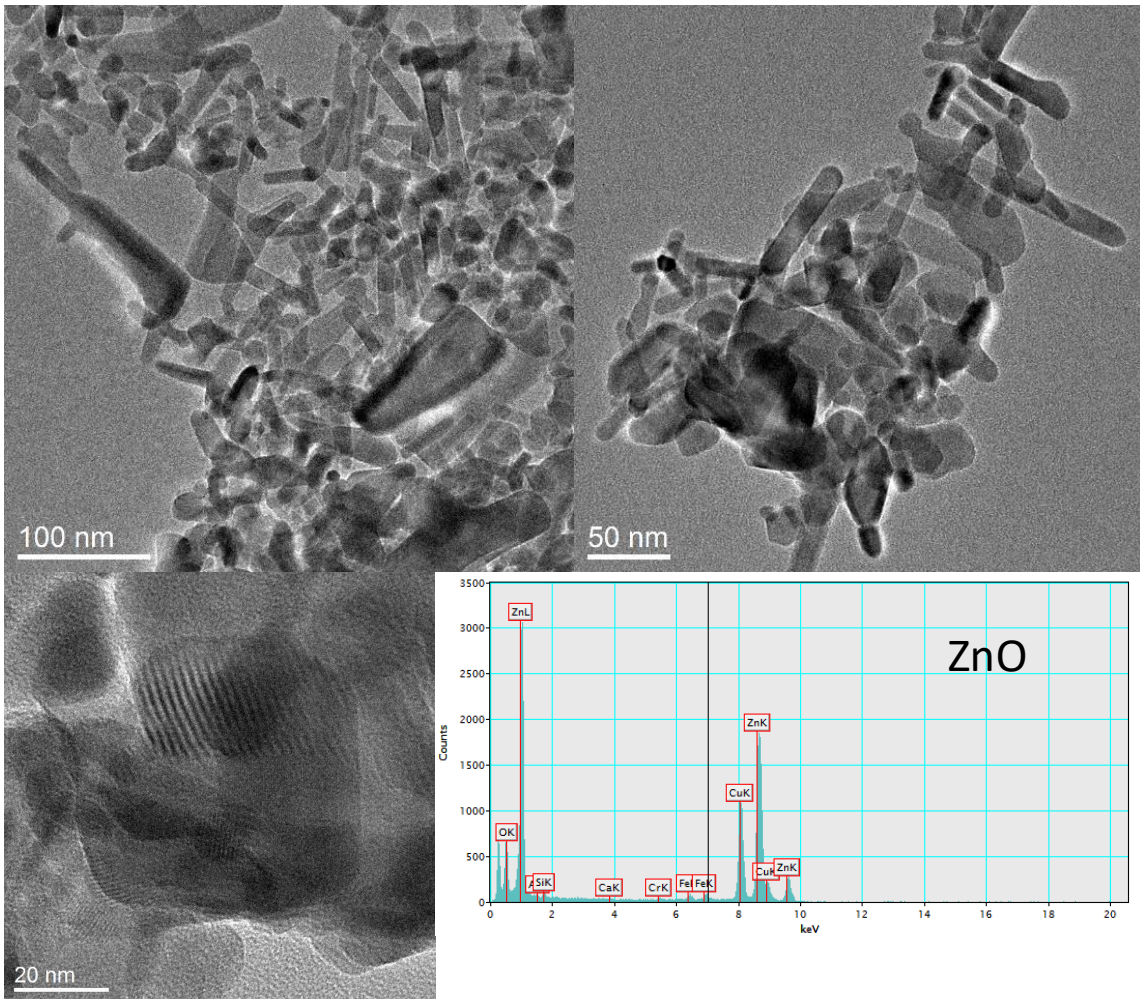
Product	Particles of interest	Shape	Size	Concentration (wt%)
Banana Boat for kids SPF 50	ZnO, TiO <sub>2</sub>	rod (ZnO) spherical	64.1 $\pm$ 13.9 nm 29.9 $\pm$ 6.1 nm	4.73 wt% (ZnO) 2.55 wt% (TiO <sub>2</sub> )
Aveeno baby natural protection SPF 50	ZnO, TiO <sub>2</sub>	rod (ZnO) spherical	117.7 $\pm$ 21.6 nm 22.8 $\pm$ 4.2 nm	7.61 wt% (ZnO) 7.21 wt% (TiO <sub>2</sub> )
Thinksport Kid's Safe SPF 50+	ZnO	rod	60.8 $\pm$ 19.1 nm	23.70 wt%
Neutrogena baby SPF 50	ZnO	spherical	29.2 $\pm$ 5.1 nm	17.10 wt%



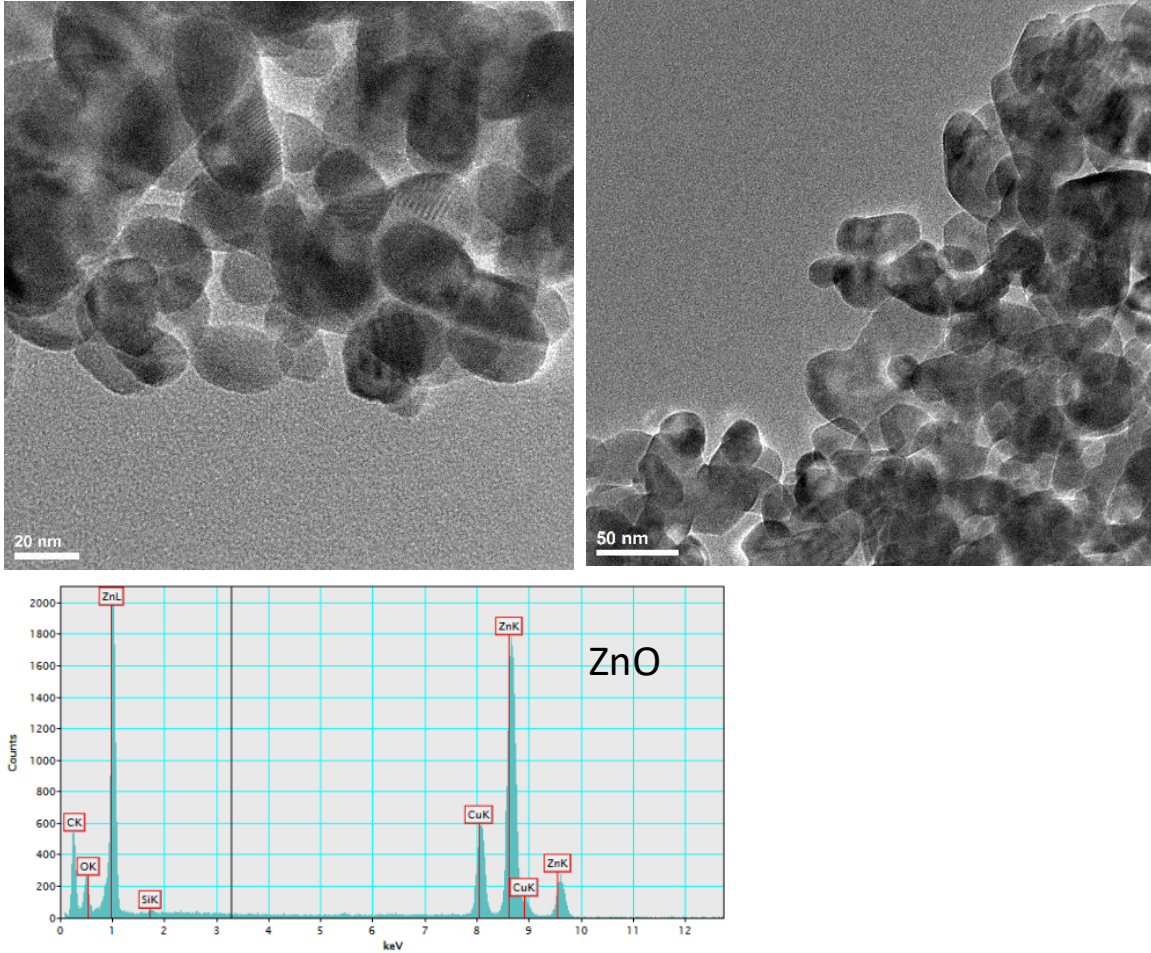
**Figure 1.** Representative TEM images of ZnO and TiO<sub>2</sub> particles extracted from Banana Boat for kids sunscreen cream. EDS spectra confirmed chemical composition of TiO<sub>2</sub> and ZnO.



**Figure 2.** Representative TEM images of ZnO and TiO<sub>2</sub> particles extracted from Aveeno baby sunscreen cream. EDS spectra confirmed chemical composition of TiO<sub>2</sub> and ZnO.



**Figure 3.** Representative TEM images of ZnO particles extracted from Thinksport Kid's sunscreen cream. EDS spectra confirmed chemical composition of ZnO.



**Figure 4.** Representative TEM images of ZnO particles extracted from Neutrogena baby sunscreen cream. EDS spectra confirmed chemical composition of ZnO.

### **Summary:**

Particles of interest were successfully identified, quantified, and characterized using appropriate extraction and analytical techniques. The concentration, shape, and size information of these particles are provided in this report for further evaluation by FOE. In general, the materials in use agree with manufacturer's claim with respect to particle size and concentration. However, exception also exists. The most notable example is the manufacturer of "ThinkSport Kid's Safe Sunscreen SPF 50+", who clearly claims to use Non-nano ZnO. Our results demonstrate that the average particle size in this product is  $60.8 \pm 19.1$  nm in length.