Analysis of Silicon Dioxide Food Additives

Sadia Afrin Khan[1], Monique E. Johnson[2], Matthew S. Kalan[1], Antonio R. Montoro Bustos[2], Savelas A. Rabb[2], Ingo H. Strenge[2], Karen E. Murphy[2] and Timothy R. Croley[1]

1. Center for Food Safety and Applied Nutrition (CFSAN), U.S. Food and Drug Administration, 5001 Campus Drive, College Park, MD 20740
2. Chemical Science Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

Amorphous silicon dioxide is an approved food additive (21 CFR 172.480) in the U.S., mainly used as an anticaking agent in powdered food products and as a stabilizer in beer production. Despite the ubiquity of amorphous silicon dioxide in food applications, there is limited data on the particle size distribution of commercially available amorphous silicon dioxide sold for this food additive use. This work describes the characterization of six commercially available food-grade SiO2 powders prepared for analysis using four different sample preparation procedures (shaking, sonication, shaking+filtration, and sonication+filtration). In this work, dynamic light scattering is used to measure particle size distribution, electron microscopy for imaging, and single-particle inductively coupled plasma mass spectrometry (sp-ICP-MS) for measuring the presence of nanosized materials in silicon dioxide sold for food additive uses. These results will enable the US FDA to address current knowledge gaps on the presence of nanosized particles in this commercial food additive and such as particle size and morphology.

FDA Mission Relevance

The objective of this project is to gain a greater understanding of the occurrence of nanoscale particles in silicon dioxide food additive which is an FDA regulated product.

Introduction

The amorphous form of silicon dioxide, an FDA regulated product, has a long history of use as a food additive. The fine white metal oxide powder is used as an anti-caking agent in spices, non-dairy coffee creamers, and other powdered food products. Amorphous silica can be manufactured through a variety of methods, including precipitation and fuming. These manufacturing processes have the potential to produce nanosize silica (particles with at least one dimension in the range of 1-100 nm). While amorphous silica is widely used in the food industry, there are limited data available on the particle size distribution of commercially available silica food additives. In order to investigate the possible presence of nanomaterials in metal oxide food additives, we analyzed the particle size distribution of several commercially available silica food additives using Dynamic Light Scattering assay, Transmission Electron Microscopy, Scanning Electron Microscopy and single-particle inductively coupled plasma mass spectrometry (sp-ICP-MS).

Materials and Methods

- ✓ Six commercially available silicon dioxide food additives were chosen and assigned a name (A, B, C1, C2, D1, and D2).
- ✓ Dispersions were prepared at a concentration of 0.100% (w/v) using ultrapure water (18 MΩ).
- ✓ Shaken samples were prepared using a Thermo MaxQ 6000 shaker at 250 rpm for 10 minutes. Sonicated samples were prepared using a QSONICA Q500 sonicator at 55% amplification for 10 minutes in pulse mode in an ice water bath.
- ✓ Shaken and sonicated samples were filtered using Stericup 0.22 µm and 0.80 µm vacuum driven filters.
- ✓ Samples were characterized using a JEOL JEM-1400 Transmission Electron Microscope (TEM).
- ✓ TEM grids were prepared using 8-10 µL of suspension and formvar/carbon grids.
- ✓ Samples were characterized using a TESCAN Mira3 Field Effect-Scanning Electron Microscope (FE-SEM).
- ✓ Samples were dusted on carbon tape for SEM imaging.
- ✓ Particle size distribution of filtered samples was analyzed by DLS using 1000 µL of suspension in a Malvern Zetasizer Nano ZEN3600.
- ✓ A PerkinElmer NexION 350D inductively coupled plasma mass spectrometer was used for the spICP-MS measurements.

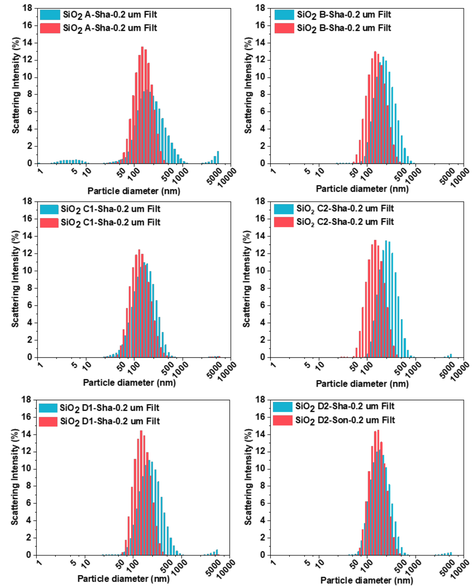

Figure 1. Particle size distribution of silicon dioxide food additives (A, B, C1, C2, D1, and D2), showing a comparison of two sample preparation methods: shaking and sonication.

Results and Discussion

- ✓ The particle size distribution graphs in figure 1 show a distinct difference between the shaken and sonicated samples of most of the food additives analyzed.
- ✓ In table 1, the Z-average shows the mean hydrodynamic size of a sample in nanometers. Also shown is the polydispersity index (PDI), a calculated parameter where higher values represent a wider range of hydrodynamic sizes present in the sample. Analysis of sonicated samples showed a smaller average particle size and lower polydispersity index for all six silica food additives tested.
- ✓ The FE-SEM images in figure 2 show the morphology of dry silicon dioxide additives. The TEM images in figure 3 confirm the presence of nanoparticles in both sonicated filtrate and shaken filtrate samples.
- ✓ Table 5 presents the results for spICP-MS characterization of SiO2 food additive A through D2 that underwent four sample preparation procedure.

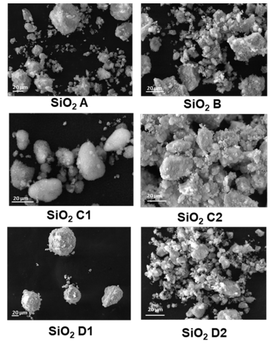

Figure 2. FE-SEM images of SiO_2 food additive powders.

Table 1. Comparison of Z-average and PdI between filtered shaken and sonicated SiO_2 food additive dispersion.

Sample Name	Z-Avg (d,nm)	PdI
SiO_2 A-Shk-0.2 µm Filt	233.5	0.362
SiO_2 A-Son-0.2 µm Filt	139.7	0.212
SiO_2 B-Shk-0.2 µm Filt	217.9	0.212
SiO_2 B-Son-0.2 µm Filt	138.3	0.153
SiO_2 C1-Shk-0.2 µm Filt	144.2	0.219
SiO_2 C1-Son-0.2 µm Filt	117.9	0.167
SiO_2 C2-Shk-0.2 µm Filt	256.0	0.179
SiO_2 C2-Son-0.2 µm Filt	131.7	0.136
SiO_2 D1-Shk-0.2 µm Filt	213.9	0.232
SiO_2 D1-Son-0.2 µm Filt	139.3	0.129
SiO_2 D2-Shk-0.2 µm Filt	178.1	0.175
SiO_2 D2-Son-0.2 µm Filt	149.4	0.123

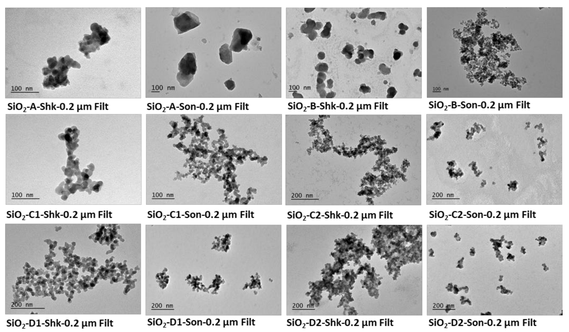

Figure 3. TEM images of SiO_2 food additive dispersions.

Table 2. Results for spICP-MS characterization of SiO_2 food additive

Sample	Sample Preparation[a]	Mean Diameter ± Width (nm)[c]	Dilution Factor	Modal Diameter (nm)	Median Diameter (nm)
SiO_2 A	**Shk**	368 ± 135	800	324	**335**
	Shk + Filt*	-	6	-	-
	Son	**328 ± 93**	**30,000**	**291**	**311**
	Son + Filt	278 ± 57	1,400	239	272
SiO_2 B	**Shk**	**336 ± 108**	**1,800**	**291**	**318**
	Shk + Filt	435 ± 294	5	316	342
	Son	**310 ± 86**	**180,000**	**303**	**298**
	Son + Filt	279 ± 57	3,000	263	277
SiO_2 C1	**Shk**	**309 ± 66**	**9,000**	**293.0**	**305**
	Shk + Filt*	-	145	-	-
	Son*	**-**	**58,000**	**-**	**-**
	Son + Filt*	-	500	-	-
SiO_2 C2	**Shk**	**333 ± 1091**	**3,600**	**269**	**317**
	Shk + Filt	314 ± 89	60	313	315
	Son	**334 ± 94**	**170,000**	**272**	**325**
	Son + Filt[b]	279 ± 58	5,000	270	275
SiO_2 D1	**Shk**	**313 ± 89**	**1,800**	**284**	**305**
	Shk + Filt	287 ± 87	160,000	289	289
	Son	**298 ± 76**	**9,000**	**270**	**289**
	Son + Filt	280 ± 60	7,000	268	277
SiO_2 D2	**Shk**	**333 ± 103**	**500,000**	**286**	**320**
	Shk + Filt	284 ± 66	25,000	284	282
	Son	**301 ± 80**	**260,000**	**269**	**293**
	Son + Filt	282 ± 59	1,000,000	293	279

[a] Sample preparation designation: Shk: shaken, Shk + Filt: shaken+0.8 µm filtered, Son: sonicated, Son+Filt: sonicated+ 0.8 µm filtered.
[b] Less than 1,000 particle events observed.
[c] The width of the diameter was calculated as the difference between the first and third quartile range of the diameters for the measured particles.
* Sample information with a (*) designation did not contain particle events above the background signal. This does not mean that the sample did not contain SiO2 particles, but it could indicate that the particles were below the detection limit of 170 nm for our instrumental conditions

Conclusion

We demonstrated a comprehensive physicochemical characterization of commercially available SiO2 food additive, with a specific focus on identifying the presence of nano-sized particles using various analytical methods. Our analysis has confirmed that SiO2 food additive contains both nanosized primary particles as well as larger agglomerates and aggregates, ranging from submicron to micron. These data serve as a foundation for determining the presence of nanoparticles in SiO2 food additive that are subject to regulation and will assist the FDA in addressing current challenges in the analysis of nanosized particles in commercial food additives.

Acknowledgements

The authors would like to acknowledge the FDA Advanced Characterization Facility for instrument use and technical assistance.