Analysis of nanoparticles in commercial sunscreen formulations

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Introduction

Nanosized particles have been employed in various applications in recent years. However, this gave rise to questioning and researching their potential safety issues, especially since they are frequently used in cosmetics staying in direct contact to the human body. So far, no acute toxic effects have been observed and especially TiO_2 and ZnO are widely used in sunscreens, but knowledge of their size is important for regulatory and health issues. In order to assess morphology and size of such nanoparticles, very expensive and time-consuming methods are needed, one of them being TEM. More cost-effective, quicker and simpler methods for assessment of nanoparticles in emulsion-like formulations would therefore pose a substantial benefit. Accordingly, the aim of the present study was to develop a method of analysis utilising laser diffraction.

Experimental Methods

Extraction procedure

About 3 g of an O/W emulsion were diluted with 10 ml of distilled water and stirred with a magnetic bar at 500 rpm until a homogenised state was accomplished. The suspension was extracted with n-hexane three times by shaking out to remove lipophilic components at least partially. The remaining hydrophilic phase was collected and centrifuged at 12500 rpm for 6 min. Subsequently, the floating, milky layer of emulsion residue was removed by means of a pipette and the sediment resuspended with fresh distilled water. Centrifugation and removal of emulsion residue was repeated until solely sediments were present after centrifugation. The supernatant was removed and the sediment resuspended with fresh water and shaken well until homogenisation before measurement. This method was developed using commercially available sunscreens containing TiO_2 or ZnO, respectively, which were kindly provided by the Austrian Agency for Health and Food Safety (AGES).

Laser diffraction

The Mastersizer 3000 (Malvern, UK) was employed using the Fraunhofer approximation to assess the size distribution of nanoparticles. In the present study, the stirrer speed of the measuring device was set to 1800 rpm to keep extracted particles suspended in the dispersant water. At least 3 measurements were taken for each sample and the size distribution of dispersed particles compared to the results of various particles in water.

Additionally, TEM images of TiO_2 nanoparticles suspended in water were taken to identify their tendency to form agglomerates in hydrophilic environment.

Results

Preliminary investigations analysing pure TiO_2 nanoparticles in water were performed to see their size distribution. Fig. 1 shows the strong tendency of TiO_2 nanoparticles to agglomerate. The single particles that can be seen are in the size range of 25 to 80 nm, but all particles were found in agglomerates with an average diameter of 1000 nm. Therefore, it is reasonable to conclude that suspended TiO_2 nanoparticles are clustered in the hydrophilic environment of O/W emulsions.

The Mastersizer 3000 displays the specific surface area of the measured sample as well as the percentage of particles found in 100 defined diameter ranges reaching from 0.01 to 3500 µm. For each sample, the surface area A was divided by the limits of the measured size ranges S to obtain the surface-size-ratio Q by the equation $Q = A/S$. Fig. 2 was created by plotting Q on a logarithmic scale against the percentage of particles in the various size ranges and shows data from various particles. In Fig. 3 there are the results already displayed in Fig. 2, but enhanced by results from commercial sunscreens to compare the size of extracted particles with the size of particles in water.

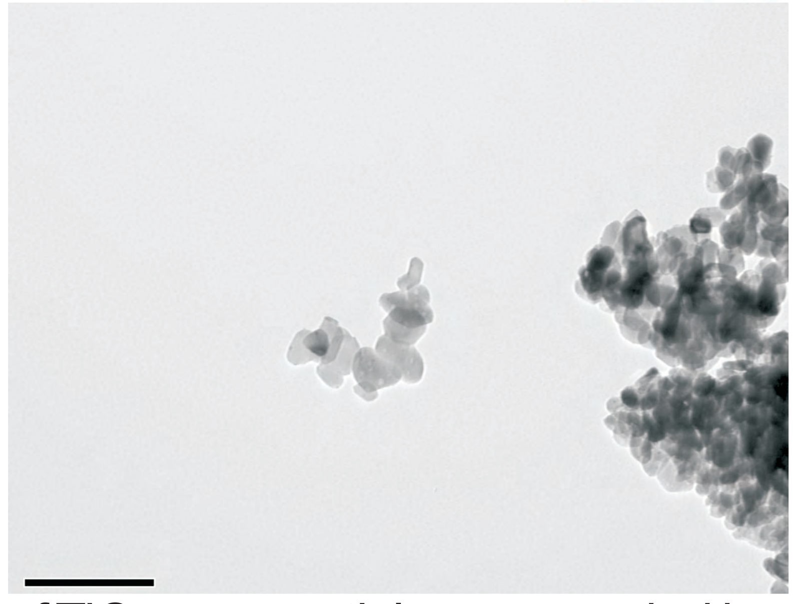

Fig. 1: TEM image of TiO_2 nanoparticles suspended in water. Bar corresponds to 200 nm.

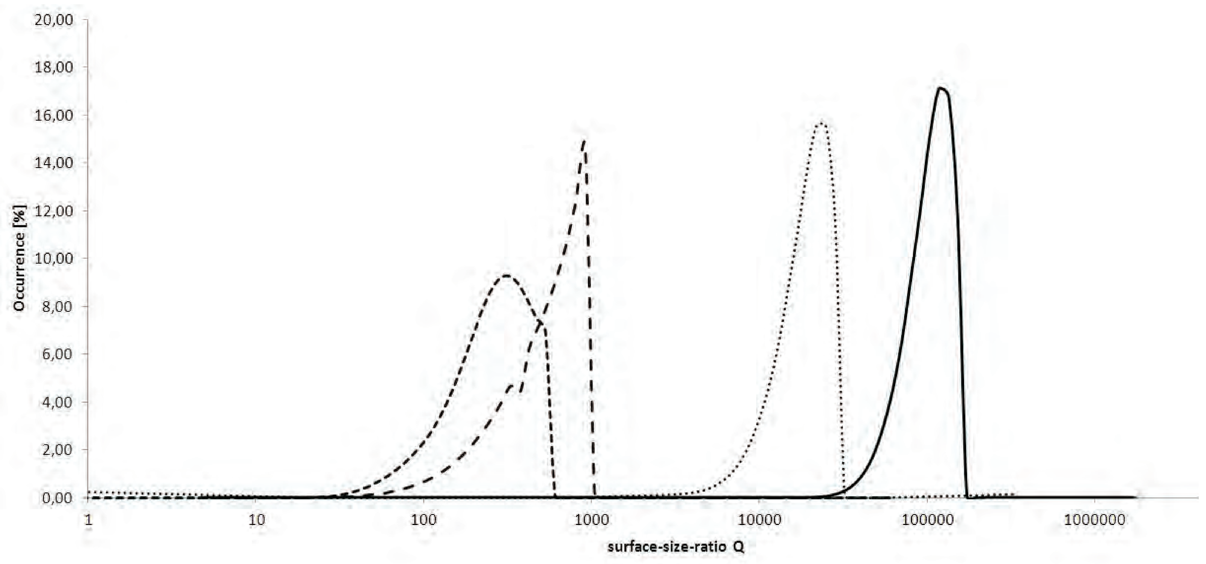

Fig. 2: Comparison of Q maxima of various particles: $MgCO_3$ (small dashed line), Talcum (dashed line), ZnO nanoparticles (dotted line), TiO_2 nanoparticles (solid line).

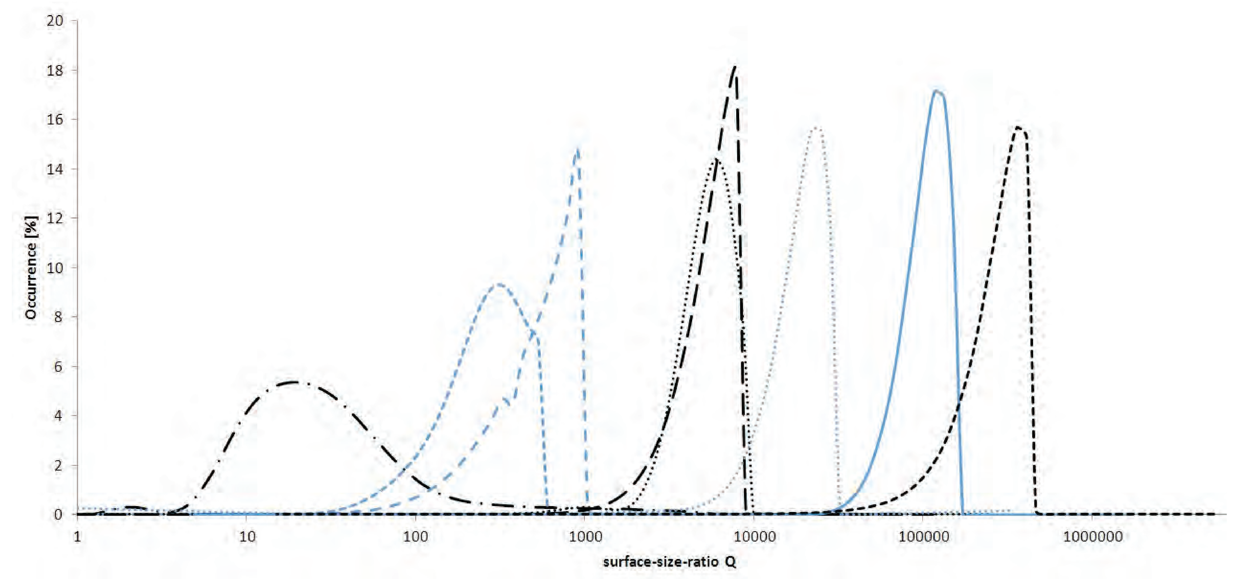

Fig. 3: Q maxima of various particles of Fig 2 (blue lines) and of particles extracted from O/W emulsions (in black from left to right): Sante SPF 15 (dash-dotted line), Sun Dance Dermo Kids (dotted line, containing nanoparticles), My Body SPF 50 (dashed line, containing nanoparticles), My Body SPF 15 (small dashed line, containing nanoparticles).

Conclusion

The presented method was suitable to remove emulsion components to a sufficient extent so that they did not interfere with the measurement of nanosized particles by Laser diffraction. Moreover, the combination of Laser diffraction and analysis via a basic equation offer a simple and cost-effective method of estimation of occurrence of nanoparticles in O/W emulsions. It is a useful tool to differentiate between agglomerates of small particles and single particles of the same diameter as the specific surface area is taken into account by the surface size ratio Q.

It has to be noted that agglomerates of nanoparticles might not possess all the properties of single nanoparticles, because although their surface area is apparently larger than for microsized particles, the diameter of agglomerates is exceptionally extended when compared to isolated nanoparticles. Therefore, the exact effects of agglomerated nanoparticles have yet to be thoroughly researched, but the presented method nevertheless provides a useful possibility of fast estimation whether nanoparticles are present in the tested formulations or not.

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