Particle size determination of metal oxides and metallic (nano-)particles in consumer products by DLS, AF4-MALLS-ICP-MS and SP-ICP-MS

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Abstract

Nanoparticles (NPs) have been recently used in consumer products mainly as anticaking agents, white pigments, UV filters and antimicrobial agents. The European Commission has established that the word “nano” should be included in the label of the product if NPs are present at 50 % or more in the size range of 1-100 nm. For the moment, in food products the presence of calcium carbonate (E170) and vegetable carbon (E153) NPs is allowed. In the following years (2015-2018), other additives that could be added in nano-form will be evaluated (including TiO_2 (E171), iron oxides and hydroxides (E172), Ag (E174), Au (E175), SiO_2 (E551), calcium silicate (E552), magnesium silicate (E553a) and talc (E553b)). Therefore, in order to accomplish these regulations, characterization of NMs becomes now necessary in daily products. Nevertheless, so far, there is no standardized analytical method to evaluate the presence and the size of NPs in these samples.

In this work, we develop a methodology for the evaluation of the presence of NPs in different consumer products including foods, drinks and personal care products. Several techniques have been compared such as Dynamic Light Scattering (DLS), Asymmetrical Flow Field-Flow Fractionation coupled to Multiangle Laser Light Scattering and Inductively-coupled Plasma Mass Spectrometry (AF4-MALLS-ICP-MS) and Single Particle Inductively-coupled Plasma Mass Spectrometry (SP-ICP-MS). A suitable sample preparation has been applied for the different consumer products: defatting with hexane and resuspension in water (sunscreens and toothpaste), extraction in water (sugar coated chocolate candies, chewing gum, pastry decoration pearls), suspension in water (cappuccino powder) and filtration (energetic drinks, wines, beer, fruit juices, coffee, hot chocolate).

Firstly, the analytical methodology has been validated using NPs reference materials of diverse nature, metallic and non metallic (*e.g.* polystyrene nanospheres, Au, SiO_2 and TiO_2). The size detection limits by SP-ICP-MS were 18 nm (Au), 20 nm (Ag), 32 nm (TiO_2) and 200 nm (SiO_2). The limits of detection in concentration were in the order of ng/L (SP-ICP-MS), µg/L (AF4-MALLS-ICP-MS) and mg/L (DLS). Results achieved for personal care products showed the presence of TiO_2 particles in sunscreens labeled as “nano”, and more than 50 % of the particles have a size in the nm range, being the Ti concentration of 13 mg/g and the particle size 86 ± 5 and 80± 10 nm achieved by AF4-MALLS-ICP-MS and SP-ICP-MS, respectively. Furthermore, TiO_2 particles were also found in toothpaste (50 - 125 nm). In the same way, TiO_2 particles (80 - 200 nm) were also detected in chocolate candies and chewing gum. The analysis of extracts of the covering of pearl decoration pastries shows the presence of Ag NPs. Finally, in the case of drinks, the particle size obtained by DLS was in the range of 10 - 300 nm that could correspond to metallic NPs, polysaccharides, micelles or biopolymers. Concretely, in some wine samples, Cu NPs were observed but in a very low concentration. For cappuccino powder and multifruit juice, some particles of Ti and Al can appear. Moreover, for hot chocolate, Al and organic particles were observed.

To conclude, this work shows the complementarities of several techniques for NPs size analysis. DLS gives only information of the hydrodynamic diameter of the particles. However, the use of AF4-MALLS-ICP-MS and SP-ICP-MS allows obtaining simultaneously information of the particle size and composition of the particles. SP-ICP-MS is a very fast technique, which will be in future years selected as NP screening technique.

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