



Multimethod approach for the detection and characterisation of food-grade synthetic amorphous silica nanoparticles



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ARTICLE INFO

Article history:

Received 18 August 2015

Received in revised form

16 December 2015

Accepted 20 December 2015

Available online 23 December 2015

Keywords:

Silica nanoparticle

AF4

ICP-MS

DLS

TEM

Food-grade

ABSTRACT

Synthetic amorphous silica (SAS) has been used as food additive under the code E551 for decades and the agrifood sector is considered a main exposure vector for humans and environment. However, there is still a lack of detailed methodologies for the determination of SAS' particle size and concentration. This work presents the detection and characterization of NPs in eleven different food-grade SAS samples, following a reasoned and detailed sequential methodology. Dynamic Light Scattering (DLS), Multiangle Light Scattering (MALS), Asymmetric Flow-Field Flow Fractionation (AF4), Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Transmission Electron Microscopy (TEM) were used. The suitability and limitations, information derived from each type of analytical technique and implications related to current EC Regulation 1169/2011 on the provision of food information to consumers are deeply discussed. In general the z-average, AF4 hydrodynamic diameters and root mean square (rms) radii measured were in good agreement. AF4-ICPMS coupling and pre channel calibration with silica NPs standards allowed the reliable detection of NPs below 100 nm for ten of eleven samples (AF4 diameters between 20.6 and 39.8 nm) and to quantify the mass concentration in seven different samples (at mg L^{-1} concentration level). TEM characterisation included the determination of the minimum detectable size and subsequent measurement of the equivalent circle diameter (ECD) of primary particles and small aggregates, which were between 10.3 and 20.3 nm. Because of the dynamic size application range is limited by the minimum detectable size, all the techniques in this work can be used only as positive tests.

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1. Introduction

Silica, and specifically synthetic amorphous silica (SAS), has been used in the food industry sector as food additive under the code E551 for decades. The most frequent functions of SAS as E551 usually are anticaking agent, antifoaming agent or flow aid in powdered food, but it is also used for other applications during the food processing such as clarifying/fining agent in the juice, oil and brewery sector or as flavour/aroma carrier [1]. This widespread use increases the possibility of the occurrence of anthropogenic silica nanoparticles (NPs) in various environmental compartments [2,3] and the agrifood sector has been identified as one of the main exposure vectors for both humans and environment [4].

SAS is produced synthetically by either a vapour-phase process yielding pyrogenic (or fumed) SAS, or by a wet process yielding precipitated silica or silica gel. Related to this, although composition

and purity criteria for food additives are described in the European Commission Directive 2008/84/EC, applying also to E551, there is no mention of size or dimensional requirements [5]. In this regard, recent Regulation 1169/2011 on the provision of food information to consumers [6], which came into force on December 14th 2014, includes a specific definition of engineered nanomaterial (ENM). Such a definition, in contrast to the EC Recommendation on the definition of nanomaterial 2011/696, does not include any established threshold in the number of particles (neither in mass nor number) with at least one dimension below 100 nm [7]. Hence, currently according to a strict interpretation of the Regulation 1169/2011 on the provision of food information to consumers an ingredient should be considered ENM if NPs are detected, independently of its number fraction. With regard to the case of SAS, producers of food-grade SAS often provide information about the particle size and describe the material as agglomerates formed from aggregates of covalently bound primary particles. Although some authors have reported on the detection and characterisation of silica (SiO_2)-NPs in food [8–11], in general there is still a lack of detailed methodologies for the detection, and characterisation

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of SAS' particle size. In this regard, dynamic light scattering (DLS) is a valuable sizing technique present in many laboratories and often used to characterise and evaluate suspensions of nanoparticles due to the simplicity of handling and operation, as well as potentially good repeatability for monomodal samples [12]. For instance, it has been used as measuring technique in validation and interlaboratory studies [13,14] and in the development of size reference materials [15]. However, DLS is less suitable for multimodal samples or for broad size distributions. Furthermore, DLS is not a selective technique and, on the contrary, provides an overall size for all the particulate in suspension. Therefore, depending on particular needs, DLS is considered as a complementary technique to be used together with others. Field-Flow Fractionation (FFF) techniques, such as Sedimentation Field-Flow Fractionation (SdFFF) and Asymmetric Flow Field-Flow Fractionation (AF4), are powerful separation techniques well suited for the characterization of NPs in complex matrixes [16–18], including food and environmental samples [19–23]. Changing the separation settings, the dynamic size range of application can be modified. If appropriate calibration of the channel is performed, it is also possible to obtain accurate information on the size of the eluting particles [24]. Moreover, depending on the detector coupled to the AF4 instrument, it is possible to collect additional information of particle size and concentration. Related to this, Multi Angle Light Scattering (MALS) is often coupled to AF4 and used as detector, as it can provide independent information about the NPs' size [25]. AF4 separation can be also coupled to inductively coupled plasma mass spectrometry (ICPMS), thus combining the advantage of AF4's ability to separate NPs according to their hydrodynamic diameter with the excellent sensitivity and selectivity of ICPMS detection [26]. Each measuring technique exhibits its own advantages and limitations, and derived information should be interpreted carefully [27]. A combined use of all of them following a multimethod approach has been sometimes proposed since the information from each individual method is usually complementary [28–30].

In the present work a systematic sequential evaluation scheme that involves the use of different techniques is proposed for the assessment on the presence of NPs in food-grade SAS. Different samples received from some of the main producers of food-grade SAS have been characterised in their dispersed form in water, in the framework of the Regulation on the provision of food information to consumers. The use of DLS, AF4-MALS and AF4-ICPMS has been proposed as they are commonly applied to the characterisation of nanomaterials. Last, but not least, Transmission Electron Microscopy (TEM) analysis was also applied for particle size characterisation and to compare the results obtained by previous techniques. The suitability and type of information derived from every type of analysis has been discussed.

2. Materials and methods

2.1. Chemicals

The following chemicals were obtained from Sigma–Aldrich (Sigma–Aldrich Corp., St. Louis, USA): ammonium carbonate (product code 379999), nitric acid (product code 84385), silicon standards for ICPMS (code 08729). Water used in all the experiments was Milli-Q® ultrapure grade water.

2.2. Nanoparticles standards

SiO₂-NPs (NanoSilica™ Size Standards) with 20, 40, 60, 80, 100 and 150 nm nominal diameters, respectively, were purchased from MSP Corporation (Shoreview, MN, USA). SiO₂-NPs with 0.49 μm (8000 Series Silica Particle Size Standards) were obtained from

Thermo (ThermoFischer Scientific, Waltham, MA, USA). SiO₂-NPs standards were used for AF4 calibration.

Stock suspensions were stored in dark and following the supplier's recommendations. Dilutions and working suspensions from the stock materials were freshly prepared each week.

2.3. Dispersion and filtration of food-grade synthetic amorphous silica samples

All SAS samples under study were voluntarily donated from suppliers after request. Eleven different types of SAS were received and subsequently subjected to characterisation. SASs in the form of powder were exactly weighted (approximate 300 mg) in a 50 mL polypropylene tube and 25 mL of ultrapure water added. The tube was vortex-stirred for 10 s and sonicated for 10 min using a 130 Watt Ultrasonic Processor equipped with a 6 mm probe from Sonics, (Sonics & Materials, Inc., Newtown, CT, USA), which operated at 50% amplitude (theoretical input to sonicator was 8000 J). A 2 mL aliquot of the original suspensions was filtered through 0.45 μm membrane filters (Millex®-HV, i.d. 25 mm, PVDF) using a vacuum manifold operating at 16 inc Hg.

2.4. Dynamic light scattering

A Zetasizer Nano-ZS, (Malvern, England) was used to perform dynamic light scattering (DLS) measurements. Measurements of the just-prepared stock suspensions were performed in triplicate immediately after preparation, using 1 mL disposable sizing cuvettes at 25 °C. DLS settings included automatic optimisation of the measurement position and automatic selection of attenuator. All samples were stored in their respective sizing cuvettes for 24 h and measurements were repeated under identical settings without stirring or shaking the suspensions. The analyses of the filtered samples were performed with identical settings after the immersion of the filtrates in an ultrasound bath for ten minutes.

2.5. Characterisation of synthetic amorphous silica samples by transmission electron microscopy

TEM (JEOL JEM 2100, Japan) at an accelerating voltage of 200 kV was used to visualize the nanoparticles. Ultrathin Formvar-coated 200-mesh copper grids (Tedpella Inc.) were previously functionalized by placing the carbon-coated side on a drop of about 20 μL of Alcian blue (2 % in water) placed on a parafilm and incubating for 10 min. The grid was then washed by transferring it to 5 drops of water placed on a parafilm and the excess fluid was removed by blotting its edge on a strip of paper tissue, leaving a trace of humidity. Finally the grid was placed on a 20 μL drop of the corresponding dispersion, incubated for 10 min and excess of fluid removed again with a paper tissue. Digital images were analyzed with the ImageJ software and a custom macro without background subtraction, smoothing nor separation of touching particles, using manual global threshold settings and varying the minimal size provided by ImageJ. No circularity filter was used to exclude agglomerates. The macro can be downloaded from <http://code.google.com/p/psa-macro> For each sample, the size of at least 200 particles was measured to obtain the average and the size distribution.

2.6. Elemental analysis of silica nanoparticles by ICPMS

The elemental analysis was performed using a PerkinElmer Nexion 300D quadrupole ICPMS, equipped with a SC Fast peristaltic pump, a Meinhard concentric nebulizer, a glass cyclonic spray chamber and a standard quartz torch (2.5 mm i.d). The system operated in standard mode monitoring isotopes *m/z* 28 and 29 for Si with

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