Challenges in the Identification of Engineered Nanomaterials in Foods

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INTRODUCTION

In food, nanomaterials (NMs) could be found as ingredient or additive but they might also appear as contaminants from the environment or from food contact materials. So far, analytical methods for the characterisation of isolated (mostly inorganic) NMs are available. These techniques are suitable for routine characterisation of isolated NM, and in some cases for NMs, which are dispersed in simple homogeneous media. However, significant problems arise when the nanoparticles are present in heterogeneous food matrices or in physiological media. Milk, a relative simple food matrix, was chosen here to illustrate the problems in detecting and characterising NMs in food materials. Furthermore colloidal SiO_2 was added to milk at various concentrations and considered as a model system for studying the problematic related with the detection of NMs in food.

MATERIALS & METHODS

Commercially available UHT-milk (skimmed 0.1 % fat and semi-skimmed 1.5 % fat) as well as a commercially available 50 %-colloidal alkaline stabilised amorphous silica formulation were used for particle size measurements. Particle size distributions and mean particle diameters were measured using SLS (Mastersizer 2000, Malvern Instruments Ltd., UK) and DLS (Malvern Zetasizer Nano ZS, Malvern Instruments Ltd., UK).

RESULTS & DISCUSSION

Particle size distributions can be described as volume, surface or number size distributions. One important characteristic value of particle size distributions is the median or D_{50} value. In contrast to the number distribution, the volume distribution rates larger particles more than smaller ones. Semi-skimmed milk showed a bimodal volume size distribution with a peak for the casein micelles and a smaller peak for the bigger fat globules when determined by SLS using a RI of 1.75 with an imaginary part of 0. The fat droplet peak disappeared completely in the number size distribution. To convert the scattered light intensity distribution into a size distribution, the optical properties (RI, RI_{imag}) of all components of the respective mixtures are needed. However, this approach is not feasible in practice. In general, only the RIs of the principal component of the mixture or a mean RI are used. Furthermore, nanoparticles in food may consist of different materials whose RIs might be unknown. In the case of milk the following RIs could be found in the literature: casein micelles: RI = 1.57, $RI_{imag} = 6*10^{-8}$; milk fat droplets: RI = 1.456, $RI_{imag} = 0$ resp. 0.01 [1-3]. Conversion of the scattered light intensity distribution into a size distribution using the two different sets of RIs did not have any significant effect on the calculated D_{50}-value. In addition, the effect of the imaginary part of RI on the volume size distribution of milk was investigated. Using $RI_{imag} = 0.01$ results in almost the same volume size distribution as for an absorptive value of 0. With $RI_{imag} = 0.1$ a

significant shift to larger particles was observed. This example demonstrates the need to use the correct RI in order to obtain reliable result. The dependence of the number size distribution on the real part of the RI of a colloidal silica dispersion measured by DLS did not show any effect on the number size distribution with RI of 1.456, 1.544 and 1.570.

A colloidal silica dispersion was mixed with skimmed milk in different concentrations and size distribution was determined by DLS. Increasing silica concentration from 0 to 2.5 %, results in a significant shift of the number size distribution to smaller sizes. Using the two different sets of RI of fat globules and casein micelles respectively, did not show significant differences in the calculated number size distributions. However, even with 2.5 % silica dispersed in milk no bimodal size distribution was observed. Thus, a clear identification of the silica nanoparticles in milk was not achieved. The number size distribution of a colloidal silica dispersion in water measured by SLS and DLS resulted in significant differences. The number size distribution obtained by DLS was shifted towards smaller particles compared to the distribution obtained by SLS. The D_{50} values were determined to be 38 nm (DLS) and 82 nm (SLS), respectively. This could be due to the different measurement principles of the two systems and the fact that SLS technique used does not allows size determinations below 20 nm, whereas the threshold for DLS was specified to be 0.3 nm.

CONCLUSION

Electron microscopy is still seen by some as the "gold standard", as it provides reassuringly direct visual images of the particles. In case of the described light scattering methods the quality of the results depends not only on sample preparation, but also on the knowledge of the properties of the sample to be analysed (RI, viscosity etc.) and instrument settings (selection of mathematical/analysis model). The particle size distribution of a defined NM added to a food matrix is furthermore dependent on its concentration and on the food matrix itself. In addition, some general questions need to be addressed. It is still unknown if the NMs we are identifying with our analytical tools are the same as the NMs we are exposed to. Furthermore, agreement upon the unit (e.g. mass, particle number) used for measurement is needed. In addition, it is almost impossible to distinguish natural from engineered NMs. Identification and characterisation of NMs in food is furthermore hampered by the low amount of nanoparticles present in a food, the presence of more than one type of NM, the necessity of determining a wide range of parameters (size, shape, composition, charge etc.) and the lack of standardised reference materials as well as standardised methods for sampling and measurement.

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