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Behavior of silver nanoparticles and ions in food simulants and low fat cow milk under migration conditions

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ABSTRACT

Research on the potential migration of nanoparticles (NPs) from nano-based food contact materials (FCMs) has often reached inconsistency in previous studies. Conventional food simulants and traditional migration tests, which are established for small molecules, have been used for studying the potential migration of NPs from nano-based FCMs. The suitability of conventional food simulants and migration tests was investigated by studying the behavior of 40 nm polyethylene glycol (PEG) coated AgNPs and silver ions in food simulants (10% ethanol, 20% ethanol, 50% ethanol, 3% acetic acid, olive oil) under migration conditions. Particle mass and number concentrations, ionic concentration and particle size distributions were determined by single particle inductively coupled plasma-mass spectrometry (spICP-MS) before and after incubation for 4 h or 10 days at 40 °C. In agreement with similar studies, 50% ethanol preserved the AgNPs, while acetic acid induced dissolution of AgNPs. Dissolution of the PEG-AgNPs obeyed pseudo-first-order reaction kinetics. PEG-AgNPs showed similar behavior in low fat cow milk during storage at 4 °C for 5 days as in the corresponding food simulant, 50% ethanol. Addition of sodium chloride to ultrapure water led to enhanced dissolution. The potential reduction of silver ions to NPs in food simulants, low fat milk and in alkaline conditions in the presence of reducing agents was studied. Based on the obtained results, it is unlikely that AgNPs are formed from Ag ions at the low concentration which are typically observed for the migration of Ag from polymeric FCMs.

1. Introduction

Nanomaterials (NM) can be used to improve the functional properties of food packaging materials such as barrier, mechanical and thermal characteristics, and to provide antimicrobial activity. The application of NMs may lead to an increase of the shelf life of food products, improve food safety, reduce food waste and subsequently contribute positively to the global food security (Hannon et al., 2015a). On the other hand, the use of NMs in food contact materials (FCMs) poses challenges in terms of regulation and potential health risks, that should be considered. Studying the migration of nanoparticles (NPs) from nano-based FCMs is crucial due to potential health risks of the migrating NPs, which is related to their small size, different physicochemical properties and potentially higher bioavailability due to increased and faster permit thorough natural biological barriers (Noonan, Whelton, Carlander, & Duncan, 2014). According to the European Food Safety Authority's (EFSA) Scientific Opinion from 2009 (EFSA, 2009), the potential risk arising from nanoscience and nanotechnology in food and FCMs has to be clarified, and the toxicology of engineered NMs cannot fully be inferred by extrapolation from data on their equivalent non-nano forms.

The literature has shown inconsistency about the migration of NPs from nano-based FCMs. The open questions regarding the migration of NPs from nano-based FCMs has been reviewed in our previous study (Jokar, Pedersen, & Loeschner, 2016). One of the challenges relates to the suitability of conventional food simulants and migration tests conditions for nano-based FCMs, which was discussed extensively in question number 4 in our review paper. Standard food simulants are used in migration test to simplify food matrices and represent different categories of foods, such as hydrophilic, acidic, alcoholic and lipophilic foods. Standard food simulants were established for molecular substances for which the

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chemical and physical structure remains stable during migration testing and where different food simulants influence only the migration rates of the substance. In contrast, the physicochemical characteristics of NPs (which are critical from a safety point of view), such as shape, size, agglomeration state, surface charge and chemical composition, may vary in different food simulants. In contrast to molecules, NPs can undergo transformation processes, like dissolution, chemical (surface) modification, agglomeration, and aggregation which lead to changes of their chemical composition, shape, and size. These processes are influenced by migration conditions (temperature and time) and food simulants properties (pH, ionic strength, and chemical composition).

The migration of Ag nanoparticles (AgNPs) from polymer-based FCMs has been studied extensively in recent years which can be explained by the relatively frequent use of Ag (as antimicrobial agent) in FCMs and, on the other, with the fact that Ag can be relatively easily analyzed by spICP-MS and electron microscopy (Jokar et al., 2016). Several studies evidenced migration of AgNPs from FCMs into food simulants (von Goetz et al., 2013; Echegoyen & Nerín, 2013; Artiaga, Ramos, Ramos, Cámara, & Gómez-Gómez, 2015; Hannon et al., 2015b; Mackevica, Olsson, & Hansen, 2016; Ramos, Gómez-Gómez, Cámara, & Ramos, 2016). The secondary formation of AgNPs from migrated ions by chemical reduction has been postulated (Mackevica et al., 2016; Noonan et al., 2014).

AgNPs are very far from chemically inert, and once released, multiple chemical and physical transformations such as aggregation, oxidation, dissolution and sulfidation are expected to occur. Similar to environmental transformation of AgNPs, where chemical transformation influences their characteristics and alters their transport, fate and toxicity (Levard et al., 2012), transformation of NPs in food can influence the behavior and fate of AgNPs in the gastrointestinal tract (EFSA, 2009).

Inductively coupled plasma-mass spectrometry in single particle mode (spICP-MS) has proven to be a powerful technique for detection and characterization of aqueous solutions of metal containing NPs. This method is based on the generation of discrete signals of ions that arise from single particles continuously introduced into the ICP-MS (Montaño, Olesik, Barber, Challis, & Ranville, 2016). The major analytical challenges in the case of migrations studies are the typically low concentrations of migrating NPs and the likelihood of artefacts during sample preparation (Hassellöv, Readman, Ranville, & Tiede, 2008; Tiede et al., 2008). The advantages of spICP-MS for migration studies are: i) the great sensitivity that allows the detection of NPs at low mass concentrations (ng L^{-1} range), ii) the ability to quantify the ratio between ions and NPs of a certain element in migration solutions, and iii) the possibility of direct analysis without the need for sample preparation or after simple dilution with ultrapure water.

There is insufficient data in the literature about the behavior of migrating NPs in food and in food simulants during migration test. Ntim et al. studied the effects of aqueous food simulants (water, 10% ethanol, 3% acetic acid) during 4 h incubation at 100 °C on 60 nm AgNPs coated with polyvinylpyrrolidone (PVP) by asymmetric flow field-flow fractionation, ultrafiltration, electron microscopy and spICP-MS (Ntim, Thomas, & Noonan, 2016). The testing conditions were chosen to simulate the reheating of ready-prepared foods (in frozen and refrigerated storage) in the container at the time of the use. AgNPs were preserved in the presence of water and 10% ethanol but dissolved in 3% acetic acid. In migration studies of commercially available food storage containers, similar size distributions of AgNPs in ultrapure water and ethanol were observed by spICP-MS, but much larger particles were detected in 3% acetic acid (Mackevica et al., 2016). For one storage container, dissolution of AgNPs in acetic acid was described. It was concluded that acetic acid could cause both, aggregation and dissolution of AgNPs. So far, no study investigated the likelihood of NP formation from migrating ions in food/food simulants. The objective of this paper was to investigate the effects of ultrapure water with and without added sodium chloride, a wider range of food simulants (10% ethanol, 20% ethanol, 50% ethanol, 3% acetic acid, olive oil) and low fat cow milk, as an example of a complex food matrix, on AgNPs and silver ions at times (4 h and 10 days) and temperature (40 °C) relevant for migration testing.

2. Materials and methods

2.1. Materials

Ultrapure water was obtained from a Millipore Element apparatus (Millipore, Milford, MA, USA) and used throughout the work. NIST gold nanoparticle (AuNPs) reference material, RM 8013, nominal diameter 60 nm, was purchased from the NIST (Gaithersburg, MD, USA). The 1000 μg mL^{-1} standard solutions of silver (Ag), gold (Au), and rhodium (Rh) in 4% HNO_3 (ICP-MS grade) were purchased from SCP Science (Quebec, Canada). Plasma-pure acids of HCl (34–37%) and HNO_3(67–69%) were purchased from SCP Science (Quebec, Canada). Ethanol (96% v/v, 0.81 kg L^{-1}) was purchased from CCS Healthcare AB (Borlange, Sweden). Methanol (HPLC-grade) was purchased from Rathburn Chemicals Ltd (United Kingdom). Silver nitrate ($AgNO_3$) and polyvinylpyrrolidone (PVP) with a molecular weight of 10000 g/mol were purchased from Sigma Aldrich (USA). Sodium hydroxide (NaOH) pellets, sodium chloride (NaCl) with analytical grade, glacial acetic acid (CH_3COOH), and Triton X-100 were purchased from Merck (Darmstadt, Germany). Extra virgin olive oil was purchased in a Danish supermarket from San Felipe, Aceites Del Sur, S.L. (Madrid, Spain). Polyethylene glycol (PEG) stabilized silver NPs (PEG-AgNPs) and citrate stabilized silver NPs (Citrate-AgNPs) from the NanoXact product line were ordered from Nanocomposix Inc. (San Diego, CA, USA). The nominal size of both types of AgNPs was 40 nm and the nominal mass concentration was 20 mg L^{-1}. The detailed information about PEG-AgNPs and Citrate-AgNPs are presented in Supplementary Table A. Organic low fat milk (0.4% fat) was purchased in a Danish supermarket from Arla Foods amba (Viby J, Denmark).

2.2. Incubation of AgNPs in food simulants and milk

2.2.1. Aqueous food simulants

EU standard aqueous food simulants including 10% v/v ethanol (E10%), 20% v/v ethanol (E20%), 50% v/v ethanol (E50%), 3% v/v acetic acid (AA3%), and ultrapure water as control were spiked with PEG-AgNPs at a concentration of 20 μg L^{-1} in 15 mL conical based poly propylene (PP) tubes. Spiked samples were mixed by vortexing for 30 s. Afterwards, the closed sample tubes were incubated at 40 °C for 4 h or 10 days in the dark in an oven (Heraeus Instrument, Hanau, Germany). After cooling to room temperature all of the aqueous simulants were diluted 1000-times with ultrapure water to a final concentration of 20 ng L^{-1} and characterized directly by spICP-MS.

2.2.2. Food simulant olive oil

Extra virgin olive oil as a fatty food simulant was spiked with PEG-AgNPs (20 μg L^{-1}) and then incubated at 40 °C for 4 h or 10 days as described above. Spiked olive oil samples were introduced to the ICP-MS instrument as diluted emulsion (oil in water). The emulsion was prepared according to the procedure described in (Castillo, Jiménez, & Ebdon, 1999). A volume of 2 mL of oil and 2 mL of Triton X-100 surfactant were mixed by vortexing for 3 min using a (MS2 minishaker (IKA-Werke GmbH & Co, Germany) for 3 min to