Migration of nanoparticles from nano-silver food containers.

Yolanda Echegoyen, Cristina Nerín

I3A, Department of Analytical Chemistry, University of Zaragoza, C/ María de Luna 3, 50018, Zaragoza, Spain

cnerin@unizar.es

The applications of nanotechnology in the food sector are predicted to grow rapidly in the coming years. Many of the world's largest food companies are reported to have been actively exploring the potential of nanotechnology for its use in food or food packaging [1].

Polymer nanocomposites incorporating metal or metal oxide nanoparticles have been developed for antimicrobial "active" packaging, abrasion resistance, UV absorption and/or strength. The metal and metal oxide nanomaterials commonly used are silver, gold, zinc oxide, silica, titania, alumina and iron oxides.

Based on the antimicrobial action of nano-silver, a number of "active" FCMs have been developed that are claimed to extend the shelf-life of food by inhibiting the growth of microorganisms. As commercialization of nano-silver grows, the public and the governments become more concerned about the safety and environmental effects of the widespread use of products containing nano-silver [2]. Several studies have been carried out and they demonstrated the toxicity of nano-silver, which is proved to be hazardous to different kind of cells and edible plants [3-5].

The ubiquitous use of commercial products containing nano-silver may potentially compromise the health of many organisms, because food contact materials containing nano-silver may release silver nanoparticles into foods and the environment. It is important to study the migration of nano-silver from commercial products to foods. However, it is ignored whether nano-silver can migrate into food from nanomaterials and the potential hazard after nano-silver migrated into food. It is also important to be able to differentiate if silver migrates as dissolved form or as nanoparticles.

This work investigates the migration of nano-silver from three commercially available food containers (FresherLonger ™ Plastic Storage bags, Oso Fresh Food Storage container and Kinetic Go Green Basic Nanosilver Food Storage container) into food simulant solutions, as well as the quantity and the morphology of the migrated nano-silver. The amount of nano-silver in the plastic containers was quantified before carrying out the experimental work of migration.

The migration of silver nano-particles has been tested using two simulants (ethanol 50% v/v and acetic acid 3% v/v) at two assay conditions (40ºC for 10 days and 70ºC for 2 hours) according with the EU normative for migrations from plastic materials (Regulation 10/2011/EU). Prior to the migration assays, simulants were filtered through a 220nm Millipore filter.

The migration solutions were analyzed by inductively coupled plasma with mass spectrometry ICP-MS (Agilent 7500) both in spectrum and time resolved analysis mode to be able to differentiate between the total dissolved Ag and Ag nanoparticles. Samples were also studied by scanning electron microscopy (FE-SEM, Merlin, Zeiss) coupled to energy dispersive X-Ray spectroscopy (EDX).

Silver migration is observed for all samples and conditions studied, with the total silver migration values ranging between 1.66 and 31.46 ng/cm^2. Migration values are higher for the longer assays (40ºC for 10 days) and when acetic acid 3% v/v is used as simulant. Between the different commercialized products studied Kinetic Go Green was the sample with a higher Ag migration and Fresherlonger the sample with the lowest Ag migration.

Working on single particle mode, the ICP is able to differentiate between a silver nanoparticle solution, dissolved silver or a mixture of both [6]. When one particle is introduced into the ICP, the atoms of the analyte produce a flash of gaseous ions in the plasma, which are measured as a single pulse by the detector. For very diluted nanoparticle suspensions only a small fraction of aerosol droplets contains nanoparticles and is detected by the spectrometer as a single pulse of event, as shown in Figure 1. Dissolved silver is homogeneously distributed in the aerosol droplets so a constant number of atoms are ionized and detected as a function of time and the time scan just shows fluctuations due to the different sources of noise. In this way nanoparticles have been observed in all solutions studied.

The presence of silver in the form of nanoparticles is further confirmed by electron microscopy. One hundred and fifty microliters of each sample were deposited by drop casting on a Si chip. SEM imaging shows the presence of nanoparticles of different sizes. The bigger ones probably come from partial dissolving of the polymer. The smallest nanoparticles (around 15-20 nm) are more brilliant (marked with a circle in the image) and correspond to Ag nanoparticles, as the EDX analysis confirms (Figure 2).

References

[1] Cientifica Report. 2006. “Nanotechnologies in the Food Industry”. www.cientifica.com.
[2] Morris J, Willis J. U.S. Environmental Protection Agency Nanotechnology White Paper; U.S. Environmental Protection Agency: Washington, D.C., 2007.
[3] Hussain S, Hess K, Gearhart J, Geiss K, Schlager J. Toxicology in Vitro, **19** (2005) 975.
[4] Burd A, Kwok CH, Hung SC et al. Wound Repair and Regeneration, **15** (2007) 94.
[5] Rico CM, Majumdar S, Duarte-Gardea M, Peralta-Videa J, Gardea-Torresdey JL, Journal of Agricultural and Food Chemistry, **59** (2011) 3485.
[6] Laborda F, Jiménez-Lamana J, Bolea E, Castillo JR, Journal of Analytical Atomic Spectrometry, **26** (2011) 1362.

Figures

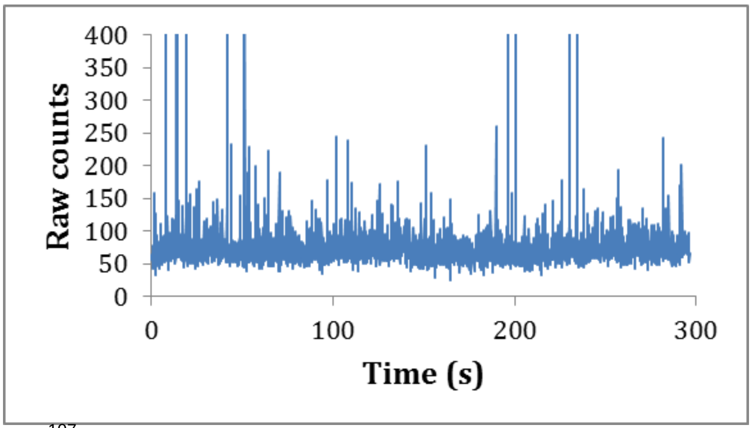

Figure 1: Time scans of ^{107}Ag for the Fresherlonger bag sample (assay conditions: 3% HAc, 10 days, 40ºC).

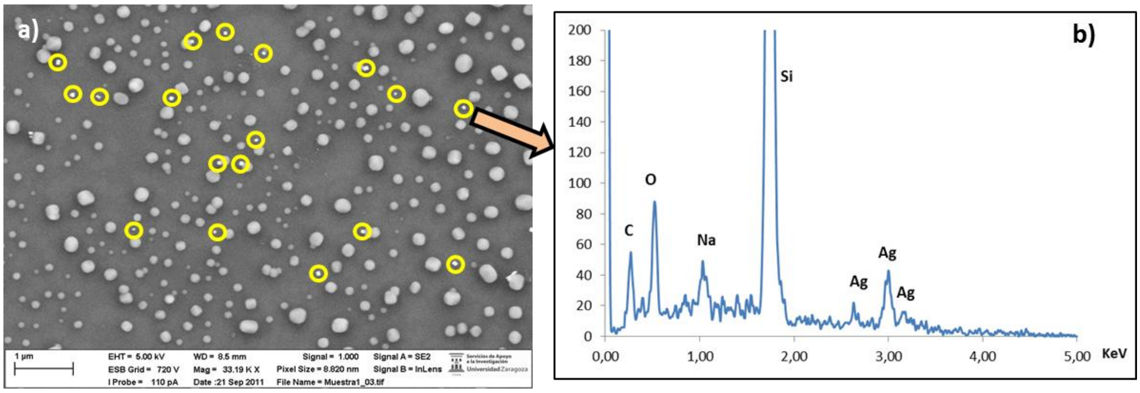

Figure 2: SEM examination of Kinetic Go Green sample (assay conditions: 3% HAc, 10 days, 40ºC). a) Overview image at 32000x. b) EDX analysis of the indicated area.