International Journal of Hygiene and Environmental Health 218 (2015) 345–357

Contents lists available at ScienceDirect

International Journal of Hygiene and Environmental Health

journal homepage: www.elsevier.com/locate/ijheh

Characterization of silver nanoparticles in selected consumer products and its relevance for predicting children's potential exposures

Nicolle S. Tulve[a,*], Aleksandr B. Stefaniak[b], Marina E. Vance[c], Kim Rogers[a], Samuel Mwilu[d], Ryan F. LeBouf[b], Diane Schwegler-Berry[b], Robert Willis[a], Treye A. Thomas[e], Linsey C. Marr[f]

[a] U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Research Triangle Park, NC, United States
[b] National Institute for Occupational Safety and Health, Morgantown, WV, United States
[c] Virginia Tech, Institute for Critical Technology and Applied Science, Center for Sustainable Nanotechnology, Blacksburg, VA, United States
[d] U.S. Environmental Protection Agency, Office of Research and Development, National Exposure Research Laboratory, Las Vegas, NV, United States
[e] U.S. Consumer Product Safety Commission, Bethesda, MD, United States
[f] Virginia Tech, Department of Civil and Environmental Engineering, Blacksburg, VA, United States

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 4 February 2015
Accepted 5 February 2015

Keywords:
Children
Nanosilver
Consumer products
Inventory
Exposure

ABSTRACT

Due to their antifungal, antibacterial, antiviral, and antimicrobial properties, silver nanoparticles (AgNPs) are used in consumer products intended for use by children or in the home. Children may be especially affected by the normal use of consumer products because of their physiological functions, developmental stage, and activities and behaviors. Despite much research to date, children's potential exposures to AgNPs are not well characterized. Our objectives were to characterize selected consumer products containing AgNPs and to use the data to estimate a child's potential non-dietary ingestion exposure. We identified and cataloged 165 consumer products claiming to contain AgNPs that may be used by or near children or found in the home. Nineteen products (textile, liquid, plastic) were selected for further analysis. We developed a tiered analytical approach to determine silver content, form (particulate or ionic), size, morphology, agglomeration state, and composition. Silver was detected in all products except one sippy cup body. Among products in a given category, silver mass contributions were highly variable and not always uniformly distributed within products, highlighting the need to sample multiple areas of a product. Electron microscopy confirmed the presence of AgNPs. Using this data, a child's potential non-dietary ingestion exposure to AgNPs when drinking milk formula from a sippy cup is 1.53 μg Ag/kg. Additional research is needed to understand the number and types of consumer products containing silver and the concentrations of silver in these products in order to more accurately predict children's potential aggregate and cumulative exposures to AgNPs.

Published by Elsevier GmbH.

Introduction

Silver nanoparticles (AgNP) are the most common nanomaterial found in consumer products because of their antifungal, antibacterial, antiviral, and antimicrobial properties. They are reportedly being used in many different types of consumer products intended for use by children and/or in the home, including baby bottles, pacifiers, plush toys, blankets, clothing, paints and coatings, and cleaning products (Benn et al., 2010; Klaine et al., 2008; Morones et al., 2005; Project on Emerging Nanotechnologies, 2014; Sun et al., 2005; Wijnhoven et al., 2009; Weir et al., 2008; Yoon et al., 2008).

Because many different types of consumer products contain AgNPs, it is important to understand their release from products, their potential for human exposure, and their environmental fate and effects. Few studies have evaluated the release of AgNPs from consumer products found in the residential environment to better understand their potential for human exposure. One set of leaching experiments by Quadros et al. (2013) reported that among 13 products selected for testing, fabrics, a plush toy, and cleaning products were most likely to release silver, resulting in the potential for human exposure.

Most studies reported in the literature have focused on release to the environment and ecological effects (Benn and Westerhoff,

* Corresponding author. Tel.: +1 919 541 1077; fax: +1 919 541 0905.
E-mail address: tulve.nicolle@epa.gov (N.S. Tulve).

http://dx.doi.org/10.1016/j.ijheh.2015.02.002
1438-4639/Published by Elsevier GmbH.

2008; Benn et al., 2010; Cleveland et al., 2012; Farkas et al., 2011; Hagendorfer et al., 2010; Quadros and Marr, 2011; Som et al., 2011). For example, Benn et al. (2010) evaluated the likelihood of several different consumer products (shirt, medical mask and cloth, toothpaste, shampoo, detergent, towel, teddy bear, two humidifiers) to release AgNPs into environmental media (air, water, soil) when washed with water. Silver was released in quantities up to 45 μg Ag/g product, and scanning electron microscopy confirmed the presence of AgNPs in most of the products evaluated, as well as the wash water. Earlier, Benn and Westerhoff (2008) evaluated the release of silver from socks and its fate in waste water treatment plants. Cleveland et al. (2012) evaluated the environmental impact of AgNP-containing consumer products (wound dressing, sock, teddy bear) on an estuarine mesocosm system. Numerous *in vitro* studies have shown that AgNPs are toxic to viruses (Xiang et al., 2011), bacteria (Choi and Hu, 2009), aquatic and soil organisms (Griffitt et al., 2008; Hayashi et al., 2012; Navarro et al., 2008; Roh et al., 2009), and mouse, rat, and human cells (Arora et al., 2009; Braydich-Stolle et al., 2005; Hussain et al., 2005; Mukherjee et al., 2012). A mini-review by de Lima et al. (2012) discussed the *in vivo* cytotoxicity and genotoxicity of AgNPs in different organisms, including Daphnia, fish, rats, and mice. Despite these research efforts, children's potential exposures to AgNPs are not well characterized.

Children may be especially affected by the normal use of consumer products designed specifically for them (e.g., milk bottles, pacifiers, toys) or used in home environments (e.g., cleaners, paints, coatings) due to their physiological functions, developmental stage, and activities and behaviors. All of these, as well as other factors, may influence their exposure to agents found in their environment (Cohen Hubal et al., 2000). The use of AgNPs in consumer products used in the home has resulted in the need to evaluate children's potential exposures to AgNPs through the dermal, ingestion, and inhalation routes of exposure.

In 2010, the U.S. Consumer Product Safety Commission (CPSC) entered into inter-agency agreements with the U.S. Environmental Protection Agency (EPA) and the U.S. National Institute for Occupational Safety and Health (NIOSH) in response to the Commission's interest in developing reliable methods for quantifying and characterizing the release of AgNPs from commercially available products within its jurisdiction. EPA, in turn, teamed with Virginia Tech and NIOSH researchers to perform the work reported in this manuscript.

The objectives of this research project were to develop tools, approaches, and protocols to characterize selected consumer products containing AgNPs and to use the data to estimate a child's potential non-dietary ingestion exposure to AgNPs. In this manuscript we describe the product inventory and a tiered analytical strategy to detect and characterize AgNPs in a variety of consumer products.

Materials and methods

Product inventory

Through a search of the Internet, peer-reviewed literature, direct marketing, and The Project on Emerging Nanotechnologies database (Project on Emerging Nanotechnologies, 2014), we identified and cataloged 165 consumer products claiming to contain AgNPs that may be used by or near children or found in the home. Each agency worked independently to create a database and then worked with CPSC to prioritize products within CPSC's jurisdiction that should be included for further testing. Once a product was selected and obtained, each agency independently used a tiered approach (illustrated in Fig. 1) to answer the following questions. For a given product, does it contain silver? If the answer was yes, we then asked whether the form was particulate or ionic. If the silver was particulate, we characterized it to determine the size, morphology, agglomeration state, and chemical composition. In our studies, we used multiple complementary and confirmatory techniques to characterize the silver content of textiles, liquids, and plastics, including inductively coupled plasma (ICP) spectroscopy (mass and atomic emission), electron microscopy (scanning (SEM)/transmission (TEM)), energy dispersive X-ray analysis (EDX), electron energy loss spectroscopy (EELS), high-angle annular dark-field microscopy (HAADF), UV–vis absorption spectroscopy, dynamic light scattering (DLS), and ion selective electrode (ISE) detection (Fig. 1).

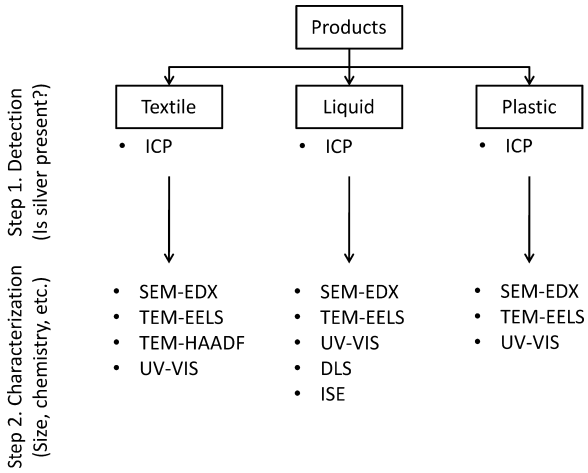

Fig. 1. Tiered approach for the analysis of consumer products for AgNPs.

We identified 165 consumer products as potentially containing AgNPs. In consultation with CPSC, we selected 19 products for further analysis. These products were classified as a children's toy (1), personal care product (1), textiles (8), storage containers (2), household cleaning products (5), dietary supplement (1), or control particles (1) for which characterization information was provided by the manufacturer. To report results from our analyses, the products were grouped by their physical matrix (textile, liquid, or plastic) rather than by their intended function. In addition, two products (t-shirt and toothbrush) that did not contain AgNPs were included in the analyses for quality control.

Chemical analysis for detection of total silver

Because no legislation in the United States regulates or requires labeling of products to disclose the presence of AgNPs, it is possible that some products claiming to be nano-enabled do not actually contain nanomaterials (and that other products not labeled nano-enabled could be nano-enabled). Thus, the first step was to verify the presence of silver in the selected consumer products. In this study, we selected inductively coupled plasma (ICP) spectroscopy to detect the presence of silver in products because it is a robust, sensitive, and relatively inexpensive detection method that is widely available. We used thermally assisted nitric acid sample digestion followed by quantification using ICP-MS (mass spectrometry) and ICP-AES (atomic emission spectroscopy). Details of the analytical techniques used to characterize the silver content for each matrix type are summarized in Table 1.

Electron microscopy methods

Silver particle size was measured using the freely available ImageJ software (http://rsbweb.nih.gov/ij/download.html).