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Dermal transfer quantification of nanoparticles from nano-enabled surfaces

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Graphical abstract

Abstract

Engineered nanoparticles are used in various applications due to their unique properties, which has led to their widespread use in consumer products. Silver, titanium, and copper-based nanoparticles (NPs) are a few of the commonly used nanomaterials in surface coatings, mainly due to their biocidal, optical, or photocatalytical properties. The knowledge concerning potential dermal exposure to nanoparticles from nanoparticle-enabled surfaces is currently lacking, partly due to analytical challenges. The aim of this study is to perform dermal wiping tests on nano-enabled surfaces and characterize NP release from keyboard covers and freshly painted surfaces, in terms of mass and number concentration, as well as released particle size distribution through the use of spICP-MS. Three types of NPs were selected for method validation testing, Ag, TiO₂, and CuO; and, the particle extraction from wipes was found to be efficient for Ag and CuO, but not for TiO₂ particles. Thereafter, potential dermal transfer was tested by wipe sampling for two nanoAg-containing silicon keyboard covers, and wood painted with nanoCuO-containing paint. AgNP release was observed for one of the keyboard cover types, with around 5000 particles/cm² (corresponding to 0.002 ng/cm²) dislodged from the matrix after 3 wiping events. CuO NP release was 20000 particles/cm² (0.885 ng/cm²) from the freshly painted surface, and magnitudes higher after the paint

was subjected to wear, reaching 1.4million particles/cm² (2.5 ng/cm²). The dermal transfer testing by wipe sampling and analytical approach used in this study demonstrates that wipe testing in combination with spICP-MS analysis can provide both qualitative data in terms of mass and number-based NP release, as well as particle characterization in terms of NP size distribution. Obtaining nano-specific release data can aid in providing a better understanding of dermal exposure to NPs from nano-enabled surfaces.

Keywords

Dermal exposure; release; nano-enabled surfaces; consumer products; wipe testing

1 Introduction

The number of nano-enabled consumer products has been growing rapidly in recent years. There is still a high degree of uncertainty associated with the extent of exposure to nanoparticles (NPs) and the potential adverse effects exerted by NPs, which has led to an increased concern about both environmental and consumer safety (Hansen, 2017; Broomfield et al., 2017). There is a broad range of nano-enabled products available on the market, and many of them are likely to cause consumer exposure during normal use. According to the data presented in The Nanodatabase (2017), which holds an overview of what products that are marketed as “nano” are available on the EU market, when it comes to potential consumer exposure, dermal exposure is the most prominent route of exposure across most product categories (Hansen et al. 2016). Likelihood of consumer exposure to take place is attributed to both product properties and product use, the latter being highly dependent on how the user applies or uses the product.

Skin is the largest organ of the body and is a potential route of exposure through skin adsorption and subsequent inadvertent hand-to-mouth exposure. Nanoparticle penetration through skin has been shown to be dependent on skin integrity, as well as NP composition, shape and size, among other properties (Brouwer et al., 2016; Larese Filon et al., 2016; Oberdörster et al., 2005). A commentary by Larese Filon and coworkers based on the published literature with regard to NP penetration and penetration revealed that NPs smaller than 4 nm can penetrate and permeate intact skin, particles in sizes 4-20 nm can permeate both intact and damaged skin, 21-45 nm particles can penetrate and permeate only damaged skin, but NPs larger than 45 nm cannot penetrate nor permeate skin (Larese Filon et al., 2015).

Experimental studies dealing with dermal exposure to NPs are scarce, unless they are dealing with personal care products, such as sunscreens, which are widely known to contain different types of NPs (Lorenz et al., 2011). Much less attention has been drawn to assessing dermal exposure potential from nano-enabled coatings and paints, which are frequently in contact with human skin and may lead to inadvertent ingestion of NPs. Several experimental studies have investigated NP release from solid articles that may have potential for dermal exposure. Some of the examples include leaching from nano-enabled textiles either in wash water (e.g. Geranio et al. 2009; Lorenz et al. 2012; Impellitteri et al. 2009; Mitrano et al. 2014), or various types of artificial sweat (e.g. Geranio et al. 2009; von Goetz et al. 2013b), and the most commonly tested NP is Ag. Dermal transfer of NPs through simulated skin-surface contact has been addressed by a handful of studies (e.g. Platten et al., 2016; Quadros et al., 2013), which have used different wipes as a surrogate for human skin. Quadros et al. (2013) assessed potential dermal transfer from various baby products that were known to contain AgNPs, including plush toys, baby blankets, and disinfecting spray

deposited on a surface. Surface wiping experiments revealed that there is a considerable potential for Ag transfer from product surfaces to the skin, ranging from 0.3 to 23 $\mu\text{g Ag/m}^2$. Platten et al. (2016) investigated dermal exposure potential of copper particle pressure-treated lumber, also by using wipes as surrogate for skin exposure and found that around 1.5 mg Cu/m² was released per contact event. Studies like these provide relevant data for potential release from nano-enabled products that might result in dermal exposure, however, the dermal transfer is usually presented as the total amount of the chemical that is dislodged from the product, lacking nano/specific characterization for potential exposure to NPs.

As the nano-specific effects that might arise from NP exposure are not well known, characterization of the released particles is an essential part for understanding the total risks exerted by NPs. In this study, we aimed to perform dermal wiping tests on different nano-enabled surfaces and characterize NP release in terms of total mass concentration, particle number concentration, as well as released particle size distribution. We selected three types of NPs for testing – Ag, TiO₂, and CuO, based on the knowledge about their applications for surfaces that may come into contact with skin and are thus relevant for dermal exposure testing. All three of those NPs are commonly used substances and additives in surface coatings – Ag as an antibacterial coating for various food contact materials, textiles and personal care products, TiO₂ in self-cleaning coatings due to its photocatalytical abilities for glass and ceramics, and CuO as an active biocidal substance in antifouling paints (Poland et al., 2013). The method for dermal transfer testing was following the NIOSH guideline Elements on Wipes: Method 9102 (NIOSH, 2003) with minor adjustments, namely, instead of acid-digesting the whole wipe for total contaminant analysis, the wipes were kept intact and particles were extracted without destroying the wipe. Before conducting the wiping tests, we performed method validation tests to establish a procedure for extracting particles from the wipes without destroying the sample and maximally maintaining the information regarding particle number and size. The NP characterization was performed by single particle inductively coupled plasma mass spectrometry (spICP-MS). Thereafter, several NP-containing consumer products that are likely to come into contact with skin and therefore cause dermal exposure were selected for the execution of wiping tests, such as silicon keyboard covers coated with Ag NPs, and wooden blocks painted with antifouling paint containing CuO NPs.

2 Materials and methods

2.1 Nanoparticle suspensions and chemicals

Three types of NP suspensions were used for method validation purposes in this study – citrate coated 30 nm Ag NP suspension (Cline, Sweden), 30-50nm TiO₂ NP suspension (US Research Nanomaterials Houston, Texas, USA) and 30-50 nm CuO NP powder (PlasmaChem GmbH, Germany).

For the dermal transfer tests, artificial sweat was prepared according to ISO 105-E04 guideline (ISO, 2013) for alkaline sweat preparation. The composition of the artificial sweat was 0.5 g/L L-histidine monohydrochloride monohydrate (99.99%, Sigma Aldrich), 5 g/L sodium chloride (>99.0%, Sigma Aldrich), 5 g/L disodium hydrogen orthophosphate dodecahydrate (>99.0%, Sigma Aldrich), and 2.5 g/L disodium hydrogen orthophosphate dehydrate (99.9%, Merck). The final solution was adjusted to pH 8±0.2 with 0.1 mol/L sodium hydroxide solution.

2.2 Consumer articles

Several consumer articles with nano-enabled surfaces were selected for dermal transfer testing, namely two AgNP-enabled keyboard covers and one CuO NP-enabled acrylic paint on wood. Three types of commercially available silicon keyboard covers were purchased for testing of Ag NP transfer: two of those were advertising antimicrobial activity and claimed to contain AgNPs (referred to as Ag-1 and Ag-2), and one that was not advertising Ag content or antimicrobial activity was selected to be used as a Ag-free control (Ag-control). Products were purchased from online retailers (Amazon.de). The product information provided by the manufacturers and surface areas of the keyboard covers are noted in Table 1. The Ag concentration in the keyboard covers was analyzed by ICP-MS (PerkinElmer, NexION 350D), following microwave-assisted acid digestion (Multiwave 3000, Anton-Paar). Samples were prepared by weighing 0.25 g of shredded keyboard covers and adding 5 mL of HNO₃ (65%, Merck) and 1 mL of HF (40%, Merck). Thereafter, samples were microwave-digested at 1400 W for 15 min. After digestion, 6 mL of H₃BrO₃ (10%, Sigma Aldrich) were added for HF complexation, and samples were again microwaved at 600 W for 15 min. Finally, samples were diluted with deionized (DI) water (18.2 MΩ, Milli-Q, Merck KGaA) and analyzed using ICP-MS.

For testing of CuO NP transfer to the wipes, painted wooden blocks were used with sizes of 35 x 35 x 11 mm (provided by BASF, Germany). The blocks were covered with CuO-containing acrylic paint on all sides with final CuO content of approximately 1.5% in the dried paint (final concentration corresponding to 5.7 ±

0.2 mg CuO per wooden block) (samples henceforth referred to as CuO-paint). The CuO embedded in paint were spherical with pristine particle sizes of 30-50 nm, according to the information provided by the manufacturer. Blocks covered with the same type of CuO-free acrylic paint were used as control samples (CuO-control).

To obtain information regarding surface morphology and location, chemical identity and size of NPs in the products, the surfaces of the articles were analyzed by Scanning Electron Microscopy (SEM) (FEI, Quanta 200 ESEM FEG) imaging coupled with Energy-Dispersive X-Ray Spectroscopy (EDS) (Oxford Instruments 80 mm² X-Max silicon drift detector).

The AgNP-enabled keyboard cover samples (Ag-1 and Ag-2) were prepared by cutting square pieces of the covers (approx. 0.5 cm²) and mounting them onto aluminum SEM specimen holders (Agar Scientific) using double-coated carbon conductive tape. Samples were then analyzed by SEM operated in high vacuum mode at an accelerating voltage of 10 KeV. To confirm the presence of silver, qualitative EDS was performed and analyzed using Aztec Software (Oxford Instruments).

To analyze the surface morphology of the painted wood samples, specimens were prepared by cutting triangular pieces of approximately 1 cm width from the corner of the wooden block by using a fine hacksaw. Each specimen was fixed onto aluminum specimen holders (Agar scientific) with carbon adhesive and strips of aluminum tape. Before analysis the specimens were surface coated with carbon for 3 x 30 seconds using a Carbon coater (Cressington, model 208).

The painted wood specimens were analyzed in low or high vacuum mode with acceleration voltages between 3 – 15 KeV. To confirm the presence of copper, qualitative EDS analysis was performed on selected specimens.

Table 1: Description of the products used for wiping tests.

	Surface area (cm ²)	Area used for wiping (cm ²)	Mass per unit area (g/cm ²)	Product information*	Concentration (µg/cm ²)
Silicon keyboard covers					
Ag-1	371	247	0.051	Contains nano-Ag	0.22
Ag-2	314	209	0.067	Contains nano-Ag	0.14
Ag-control	285	190	0.049	n/a	<0.08
Wooden blocks					
CuO-paint	12	49	0.417	CuO added	9.5*
CuO-control	12	49	0.417	No CuO added	n/a*

*Information provided by the manufacturer.

2.3 Design and execution of wiping experiments

As noted above, three types of keyboard covers were selected, as well as two types of painted wooden blocks to execute wiping experiments. The testing procedure for dermal transfer from the coated surfaces was following the NIOSH guideline Elements on Wipes: Method 9102 (NIOSH, 2003). Briefly, textile wipes were used as a surrogate for skin to test for dermal transfer from solid surfaces through dermal contact. Stepwise procedure is schematically represented in Figure 1. Three types of wipes were used for the wipe testing – (i) 100% ecological cotton for Ag testing, (ii) eco-labelled blend of 48% wool, 47% cotton and 5% polyamide for CuO testing, and (iii) 100% linen for TiO₂ testing. More detailed information about these fabrics can be found elsewhere (referred to as samples A, B and C, respectively in Mackevica et al. 2018). The wipes were cut in 5x5 cm size, and each wipe was wetted with 0.5 mL of artificial sweat (pH 8±0.2) before executing the wiping test. Then, the surface of the article was wiped by hand, using two fingertips held together and applying firm pressure, using an overlapping “S” pattern covering the entire surface with horizontal strokes. Subsequently, the same wipe was used for wiping the same surface with overlapping “S” patterns with vertical strokes, and then once more with horizontal strokes. The wipe was then put in a polypropylene tube (Falcon® 50mL Conical Centrifuge Tubes) with 20 mL DI water, which was then sonicated in the sonicator bath (Retsch, UR 1) for 10 min and immediately analyzed by single particle ICP-MS (spICP-MS). Further throughout the paper, this procedure is referred to as one wiping event. This procedure was repeated three times (i.e. three wiping events) on each surface to test for potential dermal transfer after multiple uses. The wiping procedure was executed on a laboratory weighing scale, in order to ensure that similar pressure was exerted during all wiping events (approximately 500 g/cm², which is similar to the force exerted by a person sitting on a chair, according to Clausen et al. (2016)). Because of the size of the weighing scale, size of keyboard cover samples had to be adjusted to the confined area that could fit on the scale. As the provided wooden block samples were relatively small and did not provide sufficient surface area for wiping tests, four blocks were put together to make a composite sample, creating a larger surface area that can be used for performing wiping events. For each wiping event, a new pair of

gloves was used to avoid any carry-over and contamination. Three wipe samples were used as method blanks.

Figure 1: Schematic representation of execution of wiping tests, the procedure depicted here is referred to as one wiping event.

2.4 Simulated wear of wooden blocks

To simulate the wear of the CuO-paint coated wooden block samples, they were sanded by hand with 180 grit sand paper three times after the final wipe sampling event. While standardized sanding procedures usually include a Taber abrasion apparatus (e.g. ASTM, 2013; ASTM, 2014), we chose a simplified non-standardized approach, namely sanding by hand, to simulate accelerated wear and tear of the surface. The sanding was done by applying the same procedure as for the wiping tests – by applying the sand paper with overlapping “S” patterns three times on the same surface. The pressure applied during sanding was the same as during wiping events, i.e. around 500 g/cm^2 , which falls within typical pressure levels applied through Taber abrasion to mimic normal stress (15-500 kPa) applied to surfaces in a domestic setting, e.g. handling various furnishings (Shandilya et al. 2015). After sanding, the surface was subjected to the same wiping procedure as described above.

2.5 Characterization of nanoparticles

The released NP content was measured by spICP-MS. Samples were diluted with DI water, if necessary, and Triton X-100 (0.0001%) was added to the TiO₂-containing samples. The instrument settings for spICP-MS measurements are presented in Table 2. The particle size was calculated based on the dissolved calibration curve, which was matrix-matched with the experimental samples (i.e. having the same content of artificial sweat). The transport efficiency was calculated using 60 nm Au particles (Perkin Elmer, USA), and the measurements were conducted in the same matrix as experimental samples. To evaluate the linear range of particle number concentration measurements, serial dilutions of NP suspensions were prepared to acquire the maximum particle number count for reliable and quantifiable measurements. The nanoparticle suspensions were sonicated by using a bath sonicator between every dilution step and also prior to the analysis by spICP-MS.

Table 2: spICP-MS operating parameters.

	Ag	TiO ₂	CuO
Gas flow (mL/min)	No gas	No gas	5.7 (He)
Measurement time (s)	100	100	100
Dwell time (μs)	100	100	100
Analytes	¹⁰⁷ Ag	⁴⁸ Ti, ⁴⁴ Ca	⁶³ Cu
Mass fraction	1.00	0.60	0.80
Density (g/cm ³)	10.49	4.23	6.31
Transport efficiency (%)	8.89	7.59	8.74
Sample uptake rate (mL/min)	0.304	0.303	0.307
LOD _{size} (nm)	21	30	28

The lower size limit of detection (LOD_{size}) for spICP-MS is defined as the lowest detectable particle diameter. It can usually be calculated by using the average background intensity (blank sample) and adding a value of three standard deviations and calculating the corresponding particle size (Pace et al., 2011). In this study, the LOD_{size} was calculated based on the average of reported mean particle size for blank samples and adding three standard deviations.

As mentioned earlier, bigger particles might not be able to reach the plasma or be fully ionized in the plasma and thus result in inaccurate size calculation. Bigger particles and agglomerates also greatly contribute to the total mass calculations as well as shifting the mean particle size and introducing a higher degree of uncertainty for nanoparticle content in the sample. To obtain more robust results and set the focus on nanoscale measurements, only the particles up to 200 nm in size were counted as particle events. Particles and agglomerates above 200 nm were not included in particle number calculations as well as total particle mass fraction calculations.

Transmission Electron Microscopy (TEM) was used for imaging of the particles released from the wipe samples. Approximately 4 μL of the sample was transferred to a copper (for Ag-containing samples) or nickel (for Cu-containing samples) grid covered with holey carbon film (Agar Scientific, UK) and dried. TEM (FEI, Tecnai G2) was operated at 200 keV accelerating voltage and the chemical identity of the particles was investigated by EDS. There was one replicate taken from each sample type.

2.6 Recovery of nanoparticle extraction from wipes

The nanoparticle extraction from the wipes is not a standardized procedure and to verify the applicability of the method to dermal transfer testing, particle recovery analysis was performed before executing the wiping tests. Monodisperse NP suspensions (the aforementioned 30nm Ag, 30-50nm TiO_2 and 30-50nm CuO NP suspensions) were used to spike the wipes, and then the particles were extracted in the exact same manner as in the wiping tests (described in 2.3 Design and execution of wiping experiments).

The schematic illustration of the recovery testing setup is shown in Figure 2. A 5x5 cm wipe was wetted with 0.5 mL of artificial sweat, and then 0.25 mL of NP suspension was added (referred to as Sample). Then, the wipe was immersed into 20 mL deionized water in a polypropylene Falcon® conical centrifuge tube, which was then sonicated for 10 min in a sonicator bath with added ice (to prevent particle dissolution). The suspension was then immediately analyzed by spICP-MS, details of the analysis are provided in Table 1. To examine the quantity of NPs that can be extracted from the wipes, the same amount of NP suspension and artificial sweat was added to 20 mL of DI water and treated the same way (NP-control). To check for the background created by the wipe itself, wipes were wetted with 0.5 mL of artificial sweat and immersed in 20 mL DI water (Control). The mixture of DI water and artificial sweat was used as a blank sample (Blank). The method validation was then based on the differences between the recovered NP amounts from the different samples. All samples were prepared in triplicates.

Figure 2: Schematic representation of the setup used for testing of NP extraction efficiency from the wipes. From left to right: Sample, Control, NP-control, Blank.

3 Results and discussion

3.1 Method validation for NP extraction from the wipes

Before executing the wiping tests, method validation tests were performed to evaluate the applicability of the particle extraction process for the actual wiping experiments. Three types of NPs were selected for testing, namely Ag, TiO₂ and CuO, and the method validation was done by spiking the wipes with NP suspensions and simulating the wiping test conditions. Amongst the three NP types, Ag and CuO exhibited relatively high recoveries in terms of NP size and particle number that can be extracted from the wipes. For particle number concentration, 81% of Ag NPs could be extracted by this method, and 84% of CuO NPs, while TiO₂ had a recovery of only 6%, indicating that particles likely remain on the textile fibers and ultrasonication is not able to dislodge them from the textile matrix. In terms of mass concentration recovery of NPs, Ag recovery was 82%, while for CuO and TiO₂ it was 109% and 36%, respectively. For CuO the extracted NP mass concentration was demonstrated to be slightly overestimated, indicating that the wipe could contribute to the increase in CuO background (Figure S1, Supplementary Information), and some CuO particles could be aggregating or agglomerating, leading to larger particle size (Table 3) and fewer particle events, thus lowering particle number concentration. CuO data for the blank (DI water and artificial sweat) showed relatively high particle counts, but this did not contribute significantly to the total mass of CuO recovered. It might be an indication for counting “false positives”, i.e. smaller particles that likely are part of the background signal rather than represent actual CuO particles.

Considering particle size measurements, it can be observed that the extraction process had minor effect on Ag and CuO particle sizes. As depicted in Table 3, AgNP sizes were very close to the nominal particle size indicated by the manufacturer, and both mean and mode sizes remained almost entirely unchanged after extraction from the wipes. Similarly, CuO did not exhibit large deviations from pristine particle size, however, nearly 20% increase was observed for both mean and mode sizes of NPs after extraction process. The dissolved fraction for all NP types was below the limit of detection (<0.5 µg/L).

For method validation of TiO₂ NPs, the extraction process was unsuccessful. Pristine particles in diluted artificial sweat medium resulted in slightly higher particle size measurements than the nominal size of the particles (60 nm instead of 30-50 nm range). The reason might be TiO₂ interactions with the artificial sweat components present in the medium, or the agglomeration of the particles. It has been shown before that stability and the size of TiO₂ particles in suspension are highly dependent on the pH and ionic strength of the medium (Cupi et al., 2016). In low pH and lower ionic strength media TiO₂ NPs are able to form stable aggregates of fewer particles, whereas increased ionic strength, in this case as a result of the relatively high NaCl content in the artificial sweat medium, facilitates formation of larger aggregates.

Table 3: spICP-MS size measurements for method validation of NP extraction from the wipes. Average size $\pm$ standard deviation is presented for the measured data, $n=3$. NP-control – DI water and artificial sweat medium spiked with NPs; Sample – NPs extracted in DI water from wipe wetted with artificial sweat and spiked with NPs.

	Nominal size (nm)	Measured mean size (nm)		Measured mode size (nm)	
		NP-control	Sample	NP-control	Sample
Ag	30	31 $\pm$ 0	31 $\pm$ 1	29 $\pm$ 0	28 $\pm$ 1
TiO ₂	30-50	72 $\pm$ 1	178 $\pm$ 4	60 $\pm$ 1	132 $\pm$ 3
CuO	30-50	53 $\pm$ 2	62 $\pm$ 1	41 $\pm$ 1	49 $\pm$ 1

Based on the data from method validation testing, it was concluded that this type of NP extraction method works well for AgNPs and is valid for quantification of dermal transfer of AgNPs from surfaces to wipes. For CuO extraction the method can be used for quantitative measurements, but the results have to be interpreted with caution, taking into account the slight overestimation in particle size and mass recovery after the extraction procedure. TiO₂ measurements indicated that this setup is not suited for testing dermal transfer of TiO₂ NPs, due to the very poor particle extraction efficacy. Other extraction methods might be more suited to determine the quantity of NPs transferred to the wipes, for instance, methods that would allow degradation of the wipe matrix without interfering with the size distribution and number concentration of NPs. It has already been done with other types of NPs in different organic matrices, such as using enzymatic digestion to separate AgNPs from chicken meat (Loeschner et al., 2015), or employing solvent extraction for Ag- and AuNP in *Daphnia magna* (Gray et al., 2013) and TiO₂ in sunscreens (Nischwitz et al., 2012). For NPs that are insoluble in acids, which includes TiO₂, acid digestion with e.g. nitric acid could be applicable for matrix degradation (Laborda et al., 2016), and it has been successfully utilized for determination of SiO₂ in tomato soup (Wagner et al., 2015) and biological matrices (Tadjiki et al., 2009). Moreover, different sampling methods may be more suited for TiO₂ transfer testing, such as tape stripping, patch sampling, or hand washing, provided that study allows the use of volunteers (Schneider et al., 2000).

3.2. Characterization of the articles

Consumer products that were selected for wiping tests were wooden blocks coated with CuO-containing paint, and two types of keyboard covers that claimed to contain AgNPs. The total NP content for CuO in the wooden blocks was provided by the manufacturer and corresponded to $9.5 \mu\text{g}/\text{cm}^2$, whereas Ag content in the keyboard covers was experimentally determined by microwave-assisted acid digestion and ICP-MS analysis and resulted in 0.22 and $0.14 \mu\text{g}/\text{cm}^2$ for Ag-1 and Ag-2, respectively (Table 1).

Surface characterization, including both surface morphology and elemental analysis with EDS, was performed on samples of Ag-1 and Ag-2, and CuO-paint using SEM. Ag-1 exhibited an amorphous landscape with very few pronounced defects and almost no discernible particles not labelled as silicon with EDS, making individual nanoparticle recognition extremely difficult (Figure 3a, 3b). Although, when a region of approx. $400 \mu\text{m}^2$ was analysed with EDS, a small signal of Ag was detected, corresponding to $< 0.1\%$ Ag (Figure S2, Supplementary Information). Ag-2, on the other hand, displayed a highly patterned morphology with many waves and ridges creating a uniform texture throughout consisting of primarily silicon (Figure 3c, 3d). Again, as was the case with Ag-1, when a region of approx. $400 \mu\text{m}^2$ was analysed with EDS, a small signal of Ag was detected, corresponding to $< 0.1\%$ Ag (Figure S3, Supplementary Information). These Ag quantities in Ag-1 and Ag-2, however, are not surprising given the extremely low amount of Ag detected with ICP-MS.

CuO-paint samples were analysed by SEM-EDS before and after performing the sanding procedure. The surface of unused and unmodified samples (Figure 4a and 4b) had a grainy structure and larger agglomerates forming the surface, where the EDS analysis confirmed the presence of copper and titanium on the surface of the unused specimen (Figure S4, Supplementary Information). Copper only seems to be present in very low amounts, with EDS signal corresponding to $< 0.1\%$, whereas titanium signals were detected in relatively high amounts. Titanium is used as a pigment for the paint, and the abundance of Ti particles on the painted surface was making it more difficult to detect individual CuO particles that might be present on the surface. The low magnification SEM images confirmed the influence of sanding treatment on the surface morphology (Figure 4b and 4c), having scratches on the surface that are exposing deeper layers of paint, which may facilitate particle release and further surface degradation.

Figure 3: SEM images of keyboard covers in various magnifications. A and B: Ag-1 sample, C and D: Ag-2 sample.

Figure 4: SEM images of wooden blocks painted with CuO-containing paint before and after sanding procedure. A and B: CuO-paint sample, C and D: CuO-paint sample after sanding.

3.2 Silver nanoparticle transfer from keyboard covers

From the three types of commercial keyboard covers tested, only one of the types (Ag-2) showed Ag NP release that was notably different from the control keyboard covers (Ag-control) (Figure 5). For all three sample types the AgNP transfer could be considered rather negligible, as the total mass release is in sub-ng per cm^2 range and very close to the limit of detection. Furthermore, no AgNPs were identified by TEM-EDS due to the very low NP concentrations in the test suspensions. As analyzed by spICP-MS, the wiping test for Ag-2 keyboard resulted in a maximum nanoparticle transfer of 0.001 ng/cm^2 , corresponding to around 2000 particles/ cm^2 . The mean size for particles released from Ag-2 keyboard covers was 28 nm, and for Ag-1 and Ag-control keyboard covers the mean released particle sizes were 27 and 25 nm, respectively (Table S1, size distributions presented in Figure S6, Supplementary Information). The dermal loading from these articles may be considered negligible, as the magnitude of Ag released is low, also in comparison with other items that have been tested for dermal transfer potential. For example, dermal wiping study by Quadros et al. (2013) addressed surface transfer from such commercial Ag NP-enabled items as baby blanket, plush toy, dried disinfecting spray, dry surface wipes and kitchen scrubber. Their tests resulted in silver transfer of 0.03 ng/cm^2 for kitchen scrubber, and the highest transfer of 2.3 ng/cm^2 measured for baby blanket. Even for the highest observed releases, the authors concluded that the amounts of Ag released are below the threshold that could cause damage even to one of the most sensitive populations at risk, such as children. However, it must be noted that only the total Ag release was reported and the characterization of Ag NP release was lacking.

Figure 5: Ag NP transfer from keyboard covers to wipes. Left – transfer in number of particles per cm^2 , Right – mass transfer in ng/cm^2 . Error bars represent standard error of mean, $n=3$.

A general trend can be observed that AgNP transfer is decreasing with the subsequent wiping events, indicating that most likely with increasing frequency of use the Ag NPs would detach from the surface until

no more transfer is possible. Several studies have reported that surface-bound NPs have a tendency to show high initial release, and then slower subsequent release rates with each following use of the same article. For example, several food contact materials with Ag NPs in the inner lining have shown declining release after multiple uses (Echegoyen and Nerín, 2013; von Goetz et al., 2013a). Silver NP coatings for textiles have also shown the same pattern, where most Ag was released after already two washing events (e.g. Limpiteeprakan et al. 2016). Generally, desorption of NPs is assumed to be dependent on several important factors, such as how strongly the particle is bound to the matrix of the article, as well as how the product itself is treated by the consumer. Release of NPs through desorption is more likely when NPs are loosely bound to the surface of the product, which is the case for e.g. spray-on coatings. If NPs are embedded in the matrix, the NP release is dependent on how the product is treated, i.e. if matrix degradation can be induced which would allow liberation of particles from the solid (Duncan and Pillai, 2015). In the case of Ag-enabled keyboard covers, it can be assumed that fraction of the particles are present as surface coating, but there might be AgNPs that are also relatively strongly bound to or embedded in the silicon matrix, as there is continuous release observed by wiping tests.

3.3 Copper oxide nanoparticle transfer from painted wooden blocks

Dermal transfer testing for the painted wooden blocks showed that the CuO NP release from painted and sanded wooden blocks was markedly different from blocks with untreated paint. Sanding by hand was used to simulate accelerated wear and tear of the painted surface, to depict potential dermal exposure from older paint. While this type of sanding procedure arguably provides less reproducibility than standardized Taber abrasion methods, the applied pressure used in this study is similar to normal stress levels applied to surfaces in a domestic setting, as described in section 2.4.

In terms of released particle counts, there was nearly no CuO NP release from the CuO-containing paint matrix for the paint that had not been subjected to any weathering or external impacts, and the observed release was not significantly different from CuO-control samples (Figure 6). However, after sanding of the paint surface, the CuO release was substantially increasing and the released Cu concentrations were magnitudes higher. Various types of natural and artificial weathering and aging of paints are known to have an effect on NP release, e.g. UV exposure increasing TiO₂ release from painted surfaces (Olabarrieta et al., 2012), milling and aging facilitating SiO₂ release from paints (Al-Kattan et al., 2015), or accelerated aging by sanding resulting in elevated amounts of micronized Cu dislodging from treated wood (Platten et al., 2016).

In the current study, particle count was markedly increased when wiping the sanded wooden blocks, resulting in potential dermal transfer of up to $5 \cdot 10^5$ particles per cm², compared to around $2 \cdot 10^5$ particles

per cm^2 for non-sanded paint (observed in the 2nd wiping event for Cu-paint samples, see Figure 6). The mean sizes of the released particles were 84 nm and 79 nm for CuO-paint without and with sanding, respectively, and the mode sizes were 61 nm and 54 nm without and with sanding, respectively (Table S1, size distributions presented in Figure S7, Supplementary Information). The total mass of CuO released after three wiping events was 0.9 and 2.5 ng/cm^2 for non-sanded and sanded paint, respectively, which is less than 0.01% of the CuO amount originally present in the painted surface per cm^2 .

The sizes of the released NPs are similar to the size of the pristine CuO particles (presented in Table 3), that were used for painting the wooden blocks, according to the manufacturer. This might indicate that high amount of un-altered particles can be released from the paint matrix, especially after some initial wear-and-tear, weathering or long-term normal use. TEM imaging, however, revealed that bigger agglomerates are also released by wiping, in sizes up to 200 nm (Figure 7). Freely occurring single particles were not found by TEM imaging, but that may also be because of drying artifacts during sample preparation for TEM analysis, e.g. drying. Even if larger agglomerates are observed by TEM, it may be that they are broken up and dispersed as single particles or smaller agglomerates during ultrasonication allowing spICP-MS to detect suspended individual particles.

Figure 6: CuO NP transfer from painted wooden blocks to wipes. Left – transfer in number of particles per cm^2 , Right – mass transfer in ng/cm^2 . Error bars represent standard error of mean, $n=3$.

The potential dermal transfer from painted surfaces has not been extensively addressed in the literature so far. Only a handful of studies have addressed this, including a study regarding dermal transfer of Cu from pressure-treated lumber, which was focusing on micronized and ionic copper azole-treated wood (Platten et al., 2016). This study was applying a dermal wiping method developed by Consumer Product Safety Commission (Thomas et al., 2005), which involves, in brief, using a wiping apparatus that applies controlled pressure on a confined area. The total released Cu was extracted from the wipes by acid digestion followed by ICP-AAS analysis, and revealed no significant differences in total Cu release between timber that was

impregnated with micronized or ionized Cu. A total of 12 wiping events showed that there was higher initial release of Cu from micronized Cu-treated timber during the first three wiping events, whereafter the release was reaching a plateau. Additionally, the wood that was previously weathered exhibited considerably higher total Cu release quantities up to around 25 mg Cu/m² for the first wiping event after wood exposure to weathering. The release of other types of NPs, such as Cu₂O, TiO₂, and Ag, from painted surfaces has been investigated by several other studies (e.g. Adeleye et al., 2016; Kaegi et al., 2010, 2008; Olabarrieta et al., 2012), which have shown that weathering or abrasion are important factors for dislodging NPs from the paint matrix, and NP release can be magnitudes higher when the paint is not intact and unused.

Figure 7: TEM images from particles released from CuO-paint sample (2nd Wiping event).

Nano CuO is known to be more toxic than micronized CuO particles, and the assumed mechanism of toxicity is the release of Cu²⁺ ions that leads to intracellular reactive oxygen species (ROS) generation (Keller et al., 2017). Generally, dermal exposure to copper compounds is not known to be of concern apart from potential allergic reactions. However, also ingestion of copper has been shown to have toxic effects (Civardi et al., 2015; Platten et al., 2016). Hand-to-mouth exposure particularly might be of concern when it comes to Cu-treated surfaces that come into contact with skin. The study by Thomas et al. (2005) attempted to estimate what would be possible child exposure to wood preservatives. It was estimated that the area of treated lumber surfaces that a child might come into contact with during a typical visit to a playground is 1.29 m². Considering the highest CuO release observed in the present study (1st wiping event after sanding

of CuO-paint samples), it can be estimated that assuming this area for exposure, a child might have up to 0.15 mg CuO in total transferred to the hand.

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4 Conclusions

In this study, we investigated the potential for dermal transfer of nanoparticles from nano-enabled solid surfaces, namely two commercially available Ag NP-containing silicon keyboard covers, and industrially manufactured CuO NP-containing paint that was applied on wooden blocks. The dermal transfer of Ag and CuO particles was quantified by using spICP-MS, and additionally, released particles were characterized by TEM-EDS. Initial method validation for dermal transfer measurements was conducted for three nanomaterial types, Ag, TiO₂ and CuO, by spiking the wipes with the NPs and extracting them via ultrasonication. Results obtained by spICP-MS determined that ultrasonication of the wipes can extract around 81% of the Ag nanoparticles transferred to the wipes and 84% of the CuO NPs, with little or no changes in particle size due to the extraction process. It was concluded that this method is not applicable for TiO₂ particles, due to poor extraction efficiency (around 6%). For analysis of CuO and Ag NP dermal transfer from solid surfaces, the analytical approach presented in this paper provides a relatively quick procedure for NP extraction and analysis, which again provides both qualitative data in terms of mass and number-based release, as well as particle characterization in terms of NP size distribution. Additional measurements using other analytical techniques would be necessary to investigate potential transformation of the particles (e.g. complexation, oxidation, dissolution).

Sampling of transfer from the Ag keyboard covers demonstrated relatively low released amounts, both in terms of particle number and mass concentration. Only one of two types had a higher release compared to the control sample, with the total release resulting in only <0.1% of the initial Ag content. The analysis of CuO transfer from the painted surface to the wipes indicated that CuO NPs could indeed be dislodged from the painted surface, both when paint was intact or subjected to wear and tear. After simulated surface wear of the paint (i.e. sanding by hand), the observed release of CuO NPs was magnitudes higher in terms of particle counts, but after three consecutive wiping events less than 0.01% of the initial CuO was released.

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References

- Adeleye, A.S., Oranu, E.A., Tao, M., Keller, A.A., 2016. Release and detection of nanosized copper from a commercial antifouling paint. *Water Res.* 102, 374–382. doi:10.1016/j.watres.2016.06.056
- Al-Kattan, A., Wichser, A., Vonbank, R., Brunner, S., Ulrich, A., Zuin, S., Arroyo, Y., Golanski, L., Nowack, B., 2015. Characterization of materials released into water from paint containing nano-SiO₂. *Chemosphere* 119, 1314–1321. doi:10.1016/j.chemosphere.2014.02.005
- ASTM, 2013. Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion, ASTM D1044-13. ASTM International, West Conshohocken, PA.
- ASTM, 2014. Standard Test Method for Abrasion Resistance of Organic Coatings by the Taber Abraser, ASTM D4060-14. ASTM International, West Conshohocken, PA.
- Brouwer, D.H., Spaan, S., Roff, M., Sleenwenhoek, A., Tuinman, I., Goede, H., van Duuren-Stuurman, B., Filon, F.L., Bello, D., Cherrie, J.W., 2016. Occupational dermal exposure to nanoparticles and nano-enabled products: Part 2, exploration of exposure processes and methods of assessment. *Int. J. Hyg. Environ. Health* 219, 503–512. doi:10.1016/j.ijheh.2016.05.003
- Broomfield, M., Hansen, S.F., Pelsy, F. 2017. Support for 3rd regulatory review of nanomaterials – environmental legislation. Brussels: European Commission.
- Civardi, C., Schwarze, F.W.M.R., Wick, P., 2015. Micronized copper wood preservatives: An efficiency and potential health risk assessment for copper-based nanoparticles. *Environ. Pollut.* 200, 126–132. doi:10.1016/j.envpol.2015.02.018
- Clausen, P.A., Spaan, S., Brouwer, D.H., Marquart, H., le Feber, M., Engel, R., Geerts, L., Jensen, K.A., Kofoed-Sørensen, V., Hansen, B., De Brouwere, K., 2016. Experimental estimation of migration and transfer of organic substances from consumer articles to cotton wipes: Evaluation of underlying mechanisms. *J. Expo. Sci. Environ. Epidemiol.* 26, 104–112. doi:10.1038/jes.2015.35
- Cupi, D., Hartmann, N.B., Baun, A., 2016. Influence of pH and media composition on suspension stability of silver, zinc oxide, and titanium dioxide nanoparticles and immobilization of *Daphnia magna* under guideline testing conditions. *Ecotoxicol. Environ. Saf.* 127, 144–152. doi:10.1016/j.ecoenv.2015.12.028
- Duncan, T. V., Pillai, K., 2015. Release of Engineered Nanomaterials from Polymer Nanocomposites: Diffusion, Dissolution, and Desorption. *ACS Appl. Mater. Interfaces* 7, 2–19. doi:10.1021/am5062745
- Echegoyen, Y., Nerín, C., 2013. Nanoparticle release from nano-silver antimicrobial food containers. *Food Chem. Toxicol.* 62, 16–22. doi:10.1016/j.fct.2013.08.014
- Hansen, S.F., 2017. React now regarding nanomaterial regulation. *Nature nanotechnology*, 12, p.714.
- Hansen, S.F., Heggelund, L.R., Revilla Besora, P., Mackevica, A., Boldrin, A., Baun, A., 2016. Nanoproducts – what is actually available to European consumers? *Environ. Sci. Nano* 3, 169–180. doi:10.1039/C5EN00182J
- Geranio, L., Heuberger, M., Nowack, B., 2009. The behavior of silver nanotextiles during washing. *Environ. Sci. Technol.* 43, 8113–8118.
- Gray, E.P., Coleman, J.G., Bednar, A.J., Kennedy, A.J., Ranville, J.F., Higgins, C.P., 2013. Extraction and Analysis of Silver and Gold Nanoparticles from Biological Tissues Using Single Particle Inductively Coupled Plasma Mass Spectrometry. *Environ. Sci.*

Technol. 47, 14315–14323. doi:10.1021/es403558c

Impellitteri, C.A., Tolaymat, T.M., Scheckel, K.G., 2009. The Speciation of Silver Nanoparticles in Antimicrobial Fabric Before and After Exposure to a Hypochlorite/Detergent Solution. *J. Environ. Qual.* 38, 1528. doi:10.2134/jeq2008.0390

ISO, 2013. ISO 105-E04:2013 - Textiles: Tests for colour fastness. Part E04: Colour fastness to perspiration.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., Burkhardt, M., 2010. Release of silver nanoparticles from outdoor facades. *Environ. Pollut.* 158, 2900–2905. doi:10.1016/j.envpol.2010.06.009

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M., 2008. Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* 156, 233–239. doi:10.1016/j.envpol.2008.08.004

Keller, A.A., Adeleye, A.S., Conway, J.R., Garner, K.L., Zhao, L., Cherr, G.N., Hong, J., Gardea-Torresdey, J.L., Godwin, H.A., Hanna, S., Ji, Z., Kaweeteerawat, C., Lin, S., Lenihan, H.S., Miller, R.J., Nel, A.E., Peralta-Videa, J.R., Walker, S.L., Taylor, A.A., Torres-Duarte, C., Zink, J.I., Zuverza-Mena, N., 2017. Comparative environmental fate and toxicity of copper nanomaterials. *NanoImpact* 7, 28–40. doi:10.1016/j.impact.2017.05.003

Laborda, F., Bolea, E., Cepriá, G., Gómez, M.T., Jiménez, M.S., Pérez-Arantegui, J., Castillo, J.R., 2016. Detection, characterization and quantification of inorganic engineered nanomaterials: A review of techniques and methodological approaches for the analysis of complex samples. *Anal. Chim. Acta* 904, 10–32. doi:10.1016/j.aca.2015.11.008

Larese Filon, F., Bello, D., Cherrie, J.W., Sleuwhoeck, A., Spaan, S., Brouwer, D.H., 2016. Occupational dermal exposure to nanoparticles and nano-enabled products: Part I—Factors affecting skin absorption. *Int. J. Hyg. Environ. Health* 219, 536–544. doi:10.1016/j.ijheh.2016.05.009

Larese Filon, F., Mauro, M., Adami, G., Bovenzi, M., Crosera, M., 2015. Nanoparticles skin absorption: New aspects for a safety profile evaluation. *Regul. Toxicol. Pharmacol.* 72, 310–322. doi:10.1016/j.yrtph.2015.05.005

Limpitprakan, P., Babel, S., Lohwacharin, J., Takizawa, S., 2016. Release of silver nanoparticles from fabrics during the course of sequential washing. *Environ. Sci. Pollut. Res.* 1–9. doi:10.1007/s11356-016-7486-3

Loeschner, K., Navratilova, J., Grombe, R., Linsinger, T.P.J., Købler, C., Mølhave, K., Larsen, E.H., 2015. In-house validation of a method for determination of silver nanoparticles in chicken meat based on asymmetric flow field-flow fractionation and inductively coupled plasma mass spectrometric detection. *Food Chem.* 181, 78–84. doi:10.1016/j.foodchem.2015.02.033

Lorenz, C., Von Goetz, N., Scheringer, M., Wormuth, M., Hungerbühler, K., 2011. Potential exposure of German consumers to engineered nanoparticles in cosmetics and personal care products. *Nanotoxicology* 5, 12–29. doi:10.3109/17435390.2010.484554

Lorenz, C., Windler, L., Goetz, N., Von, Lehmann, R.P., Schuppler, M., Hungerbühler, K., Heuberger, M., Nowack, B., 2012. Chemosphere Characterization of silver release from commercially available functional (nano) textiles. *Chemosphere* 89, 817–824. doi:10.1016/j.chemosphere.2012.04.063

Mackevica, A., Olsson, M.E. and Hansen, S.F., 2018. Quantitative characterization of TiO₂ nanoparticle release from textiles by conventional and single particle ICP-MS. *Journal of Nanoparticle Research*, 20(1), p.6.

Mitrano, D., Rimmele, E., Wichser, A., Erni, R., Height, M., Nowack, B., 2014. Presence of nanoparticles in wash water from conventional silver and nano-silver textiles. *ACS Nano* 8, 7208–7219. doi:10.1021/nn502228w

- NIOSH, 2003. Elements on wipes: Method 9102, in: NIOSH Manual of Analytical Methods 4th Edition.
- Nischwitz, V., Goenaga-Infante, H., Bolea, E., Castillo, J.R., Scherrers, R., Ludwig, C., Ulrich, A., Rose, J., Bottero, J.-Y., Zazueta, C., Pedraza-Chaverri, J., Garcia-Cuellar, C.M., Chirino, Y.I., 2012. Improved sample preparation and quality control for the characterisation of titanium dioxide nanoparticles in sunscreens using flow field flow fractionation on-line with inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* 27, 1084. doi:10.1039/c2ja10387g
- Oberdörster, G., Maynard, A., Donaldson, K., Castranova, V., Fitzpatrick, J., Ausman, K., Carter, J., Karn, B., Kreyling, W., Lai, D., Olin, S., Monteiro-Riviere, N., Warheit, D., Yang, H., 2005. Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy. Part. *Fibre Toxicol.* 2, 8. doi:10.1186/1743-8977-2-8
- Olabarrieta, J., Zorita, S., Peña, I., Rioja, N., Monzón, O., Benguria, P., Scifo, L., 2012. Aging of photocatalytic coatings under a water flow: Long run performance and TiO₂ nanoparticles release. *Appl. Catal. B Environ.* 123, 182–192. doi:10.1016/j.apcatb.2012.04.027
- Pace, H.E., Rogers, N.J., Jarolimek, C., Coleman, V.A., Higgins, C.P., Ranville, J.F., 2011. Determining Transport Efficiency for the Purpose of Counting and Sizing Nanoparticles via Single Particle Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem.* 83, 9361–9369. doi:10.1021/ac201952t
- Platten, W.E., Sylvest, N., Warren, C., Arambewela, M., Harmon, S., Bradham, K., Rogers, K., Thomas, T., Luxton, T.P., 2016. Estimating dermal transfer of copper particles from the surfaces of pressure-treated lumber and implications for exposure. *Sci. Total Environ.* 548, 441–449. doi:10.1016/j.scitotenv.2015.12.108
- Poland, C.A., Read, S.A.K., Varet, J., Carse, G., Christensen, F.M., Hankin, S.M., 2013. Dermal Absorption of Nanomaterials. Part of the “Better control of nano” initiative 2012–2015, Environmental Project No. 1504, 2013. Copenhagen, Denmark.
- Quadros, M.E., Pierson, R., Tulve, N.S., Willis, R., Rogers, K., Thomas, T.A., Marr, L.C., 2013. Release of Silver from Nanotechnology-Based Consumer Products for Children. *Environ. Sci. Technol.* 47, 8894–8901. doi:10.1021/es4015844
- Schneider, T., Cherrie, J.W., Vermeulen, R., Kromhout, H., 2000. Dermal exposure assessment. *Ann. Occup. Hyg.* 44, 493–499. doi:10.1093/annhyg/44.7.493
- Shandilya, N., Le Bihan, O., Bressot, C. and Morgeneyer, M., 2015. Emission of titanium dioxide nanoparticles from building materials to the environment by wear and weather. *Environmental science & technology*, 49(4), pp.2163–2170. DOI: 10.1021/es504710p
- Tadjiki, S., Assemi, S., Deering, C.E., Veranth, J.M., Miller, J.D., 2009. Detection, separation, and quantification of unlabeled silica nanoparticles in biological media using sedimentation field-flow fractionation. *J. Nanoparticle Res.* 11, 981–988. doi:10.1007/s11051-008-9560-3
- The Nanodatabase, 2017. The Nanodatabase [WWW Document]. URL <http://nanodb.dk/> (accessed 3.1.17).
- Thomas, T.A., Levenson, M.S., Cobb, D.G., Midgett, J.D., Porter, W.K., Saltzman, L.E., Bittner, P.M., 2005. The Development of a Standard Hand Method and Correlated Surrogate Method for Sampling CCA (Pressure)-Treated Wood Surfaces for Chemical Residue. *J. Child. Heal.* 2, 181–196. doi:10.3109/15417060490930047
- von Goetz, N., Fabricius, L., Glaus, R., Weitbrecht, V., Günther, D., Hungerbühler, K., 2013a. Migration of silver from commercial plastic food containers and implications for consumer exposure assessment. *Food Addit. Contam. Part A* 30, 612–620.

von Goetz, N., Lorenz, C., Windler, L., Nowack, B., Heuberger, M., Hungerbühler, K., 2013b. Migration of Ag- and TiO₂-(Nano)particles from Textiles into Artificial Sweat under Physical Stress: Experiments and Exposure Modeling. *Environ. Sci. Technol.* 47, 9979–9987.

Wagner, S., Legros, S., Loeschner, K., Liu, J., Navratilova, J., Grombe, R., Linsinger, T.P.J., Larsen, E.H., von der Kammer, F., Hofmann, T., Solans, C., Lehner, A., Allmaier, G., 2015. First steps towards a generic sample preparation scheme for inorganic engineered nanoparticles in a complex matrix for detection, characterization, and quantification by asymmetric flow-field flow fractionation coupled to multi-angle light scattering and ICP-MS. *J. Anal. At. Spectrom.* 30, 1286–1296.
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Highlights

- Potential transfer from nano-enabled surfaces to hand was tested by wipe sampling.
- Ag and CuO nanoparticle transfer was measured by single particle ICP-MS.
- Wipe sampling allows rapid estimation for dermal exposure to nanoparticles.

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