

## **ELECTRONIC SUPPLEMENTARY INFORMATION**

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Figure S.3: The effect of the cut-off on cumulate number distribution after mass-to-number conversion for a mixture of a AgNPs 20 60 100nm; the smaller the cut-off the greater the risk of erroneously considering void peak materials as small size particles

### S.1. Details on Determination of total silver in consumer products by batch ICP-MS

As a quality check, a number of silver-solutions of known concentration were run along with the samples on ICP-MS for the determination total silver. The average recovery obtained was 103%; NIST trace element in water declared to contain 0.963-1.109  $\mu\text{g}/\text{kg}$  was found to contain  $0.904 \pm 0.015 \mu\text{g}/\text{L}$  of silver. Limit of detection ( $3 \times$  standard deviation of 20 blanks+ average of 20 blanks\*dilution factor) and limit of quantification ( $10 \times$  standard deviation of 20 blanks+ average of 20 blanks\*dilution factor) of the method were found to be 0.029 and 0.084 mg/L for total silver respectively and therefore far below our expected analytical target (10-20 mg/L for consumer products).

**TableS.1: UV-VIS peak max found for the 6 analysed consumer products between 200 and 600 nm wavelengths**

Product code	SPR (max)
A	425
B	396
C	405
D	none
E	395
F	394

**Table S.2: Z-potential and pH determined for consumer products**

Product	pH <sup>^</sup>	Z-potential <sup>(</sup> ( mV)
A	6.9	-41.4 $\pm$ 3.38
B	6.6	-38.6 $\pm$ 0.24
C	7.6	-54 $\pm$ 0.81
D	7.4	NA
E	7.7	-49.8 $\pm$ 1.15
F	6.7	-44.3 $\pm$ 2.19

(<sup>^</sup>) average of 3 replicates; (<sup>(</sup>) average  $\pm$  standard error

### S.2. Determination of particulate silver by AF4-ICP-MS

For the quantification of particulate silver in consumer products, the ICP-MS was calibrated by pre-channel mass-calibration consisting of injection a known amount of AgNPs 20 nm 60nm and 100nm and analysis upon application of elution conditions. This approach has been previously addressed in (Geiss et al., 2013), showing that in contrast to post-channel mass-calibration with ionic silver, the pre-channel mass-calibration with particles takes into account possible material-losses in the channel or tubing and/or differences in recoveries. This is the reason why this type of pre-channel calibration was chosen in our approach instead of a standard calibration with ionic silver. For instance for 20 nm particles a median recovery of 85% was found on five replicates (Geiss et al., 2013). For quantification of the amount of particulate silver, the fractograms at the level of the ICP-MS were exported in Origin Pro 7.5 as counts rate 107/103 versus time in seconds. Count rate of consumer products was quantified versus the Ag 20 nm calibration curve, considering that this is the size of calibrant particles closer to consumer products. The results are displayed in table S.3. For this set of consumer products with unknown chemistry the recovery was estimated by injecting samples with and without cross-flow and comparing the different peak areas obtained on the UV-VIS. The recovery values ranged from 80% to 96%, with a low value of 70% for product A that shows a bimodal

distribution and has the lowest total silver concentration. These estimated values compared well to the 85-87% recovery rates for 10-20 nm citrate-stabilised silver nanoparticles as reported in Geiss et al. 2013. The zeta potential of the different products indicates that all of them are negatively charged, with values (table S.2.) comprised between -38.6mV and -54 mV that compare quite well with the value of -39.6 mV for the 20nm citrate stabilised silver nanoparticles standard. These considerations indicate that the eventual interaction with the channel membrane should be of a similar nature in the case of the products and the calibrant.

**TableS.3: Fitting data for ICP-MS detector data realised in OriginPro**

<b>Product</b>	<b>Model</b>	<b>R2</b>	<b>Peak Area (µg/L)</b>	<b>Error</b>
<b>A</b>	Gauss multipeak	0.957	(peak1) 83.68	0.98
			(peak2) 69.75	1.00
<b>B</b>	Gauss mod	0.953	468.07	3.69
<b>C</b>	Gauss mod	0.970	1260.55	8.33
<b>E</b>	Gauss mod	0.984	786.74	3.25
<b>F</b>	Gauss mod	0.977	414.95	2.32

**TableS.4: Quantification of total and particulate silver in consumer products**

<b>Product</b>	<b>AgNPs concentration (mg/L)</b>	<b>Total silver (mg/L)</b>	<b>Channel recovery</b>	<b>%AgNPs</b>
<b>A</b>	P1	0.08		
	P2	0.07		
		0.15	11.63	70%
<b>B</b>		5.14	9.26	88%
<b>C</b>		25.34	29.32	94%
<b>E</b>		13.14	25.57	96%
<b>F</b>		4.55	9.5	80%

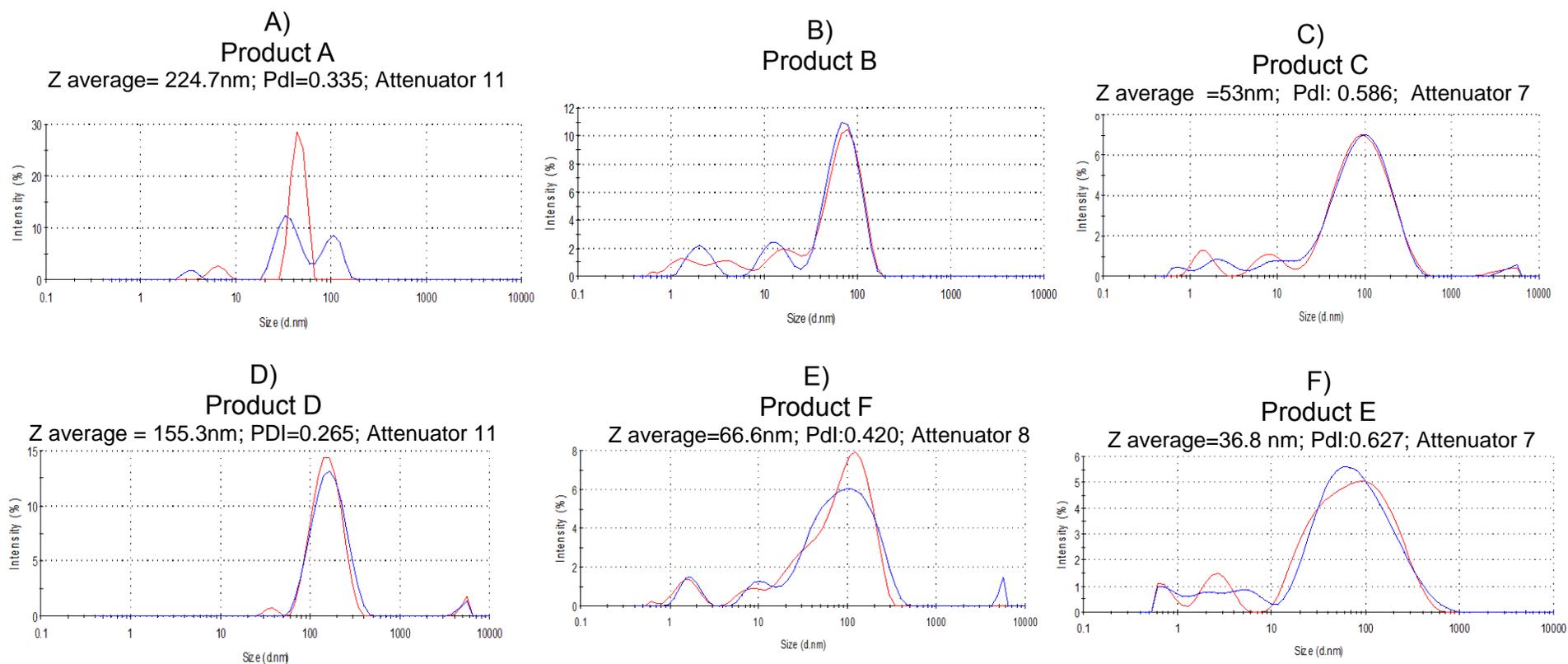
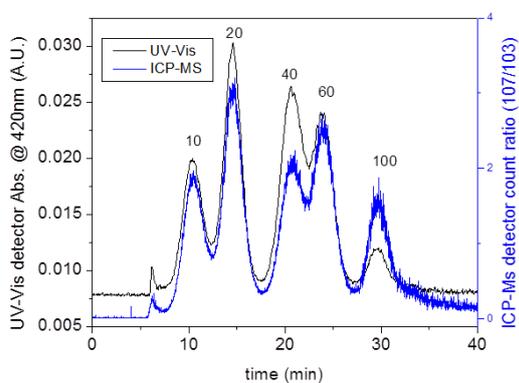


Fig.S.1: Batch DLS of pure consumer products. Blue and Red lines represent duplicate measurements. Z-averages and polydispersity index (PDI) and attenuator in the graph.

A)



B)

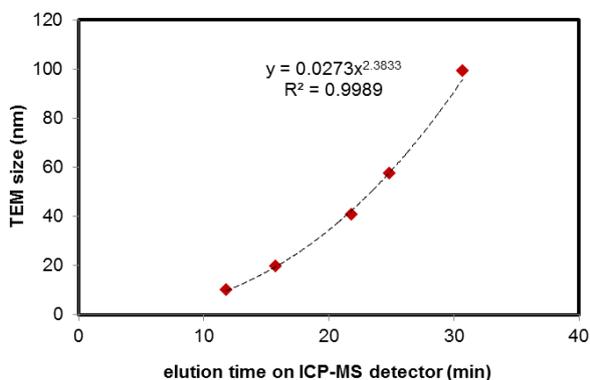


Fig.S.2: Sizing strategy applied to AF4 for channel calibration: A) elution of a mix of 10,20,40,60 and 100nm citrate coated AgNPs upon application of the developed AF4-UV-VIS-ICP-MS, B) example of relationship between size and retention time used for external size calibration

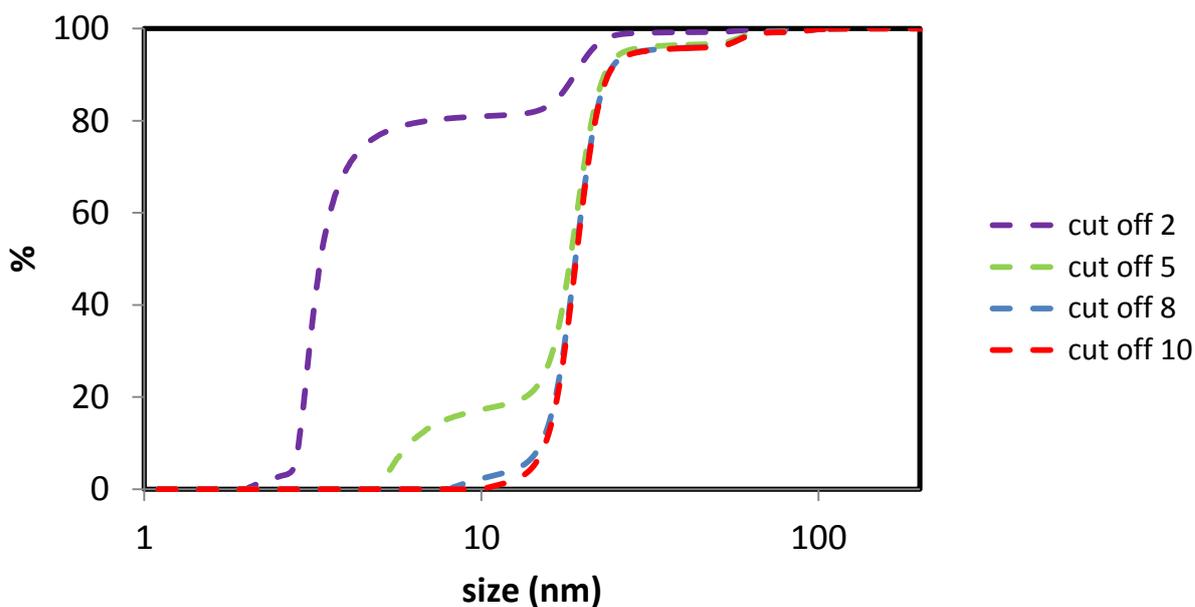


Figure S.3: The effect of the cut-off on cumulant-number distribution after mass-to-number conversion for a mixture of AgNPs 20 60 100 nm; the lower the cut-off value the greater is the risk that part of the void peak will be included in the calculation and erroneously considered as small particles