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## **Supplementary Materials for:**

# Method development for speciation analysis of silver nanoparticles and silver ions in green algae and surface waters at environmentally relevant concentrations using single particle ICP-MS

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Table 1S. Instrumental parameters of ICP-MS for determination of Ag(I) and AgNPs

| Parameter              | ICP-MS                                | spICP-MS                              |  |  |
|------------------------|---------------------------------------|---------------------------------------|--|--|
| RF power               | 1:                                    | 550 W                                 |  |  |
| Plasma gas flow        | 15 L min <sup>-1</sup>                |                                       |  |  |
| Auxillary gas flow     | 1 L min <sup>-1</sup>                 |                                       |  |  |
| Carrier gas flow       | 1.05 L min <sup>-1</sup>              |                                       |  |  |
| Sample inlet flow      | 0.35 mL min <sup>-1</sup>             |                                       |  |  |
| Scan type              | Single Quad                           |                                       |  |  |
| Cell gas               | No gas mode, He mode                  | No gas mode                           |  |  |
| Monitored isotopes     | $^{107}$ Ag, $^{109}$ Ag              | $^{107}\mathrm{Ag}$                   |  |  |
| Dwell time             | 0.3 s                                 | 3 ms                                  |  |  |
| Total acquisition time |                                       | 60 s                                  |  |  |
| Internal standard      | $^{115}$ In                           | none                                  |  |  |
| Calibration solutions  | $0.1$ - $5.0 \ \mu g \ L^{-1} \ Ag^+$ | $1 \ \mu g \ L^{-1} \ Ag^+$ standard, |  |  |
|                        | standards                             | 50 ng L <sup>-1</sup> 75 nm PVP-AgNPs |  |  |
|                        |                                       | (RM 8017)                             |  |  |

### Calibration graphs for determination of size detection limit:



Fig. 1S. Calibration in 0.1% Triton X-100



Fig. 2S. Calibration in 0.1% Triton X-100 + 0.1% TMAH

#### Equation 1S. Calculation of background equivalent diameter (BED)

BED,  $d_{bkgnd}$  (nm), was calculated as:

$$d_{bkgnd} = \sqrt[3]{\frac{6}{\pi} \times \frac{m_{bkgnd}}{10^{15} \times \rho_p}} \times 10^7$$

 $m_{bkgnd}$  - background equivalent mass (fg)

 $\rho_p$  - particle density (g/cm<sup>3</sup>)

#### Equation 2S. Calculation of response factor (RF)

 $RF = (I_{ion} - I_{blk}) / C_{Ion}$ 

 $I_{ion}$  - signal of ionic standard solution (cps),  $I_{blk}$  - signal of ionic blank solution (cps),  $C_{Ion}$  - concentration of ionic standard solution (µg L<sup>-1</sup>)

 Table 2S. Sizes of particles extracted with 10% TMAH from spiked control algal cells

 determined by spICP-MS method with different calibration media

|  | Mean Size (nm) | Median Size(nm) | Most Freq. Size (nm) |  |  |  |
|--|----------------|-----------------|----------------------|--|--|--|
| Calibration in 0.1% Triton X-100 (Procedure A)             |                |                 |                      |  |  |  |
| 75 nm AgNPs (RM)   | $74.5\pm0.7$   | $75.0\pm0.0$    | $77.0\pm1.4$         |  |  |  |
| 60 nm AgNPs  | $62.8\pm1.0$   | $61.3\pm0.5$    | $59.0\pm2.0$         |  |  |  |
| Calibration in 0.1% TMAH + 0.1% Triton X-100 (Procedure B) |                |                 |                      |  |  |  |
| 75 nm AgNPs (RM)   | $73.5\pm0.7$   | $74.5\pm0.7$    | $75.0 \pm 1.4$       |  |  |  |

| 60 nm AgNPs   | $62.0\pm1.6$ | $61.8\pm1.3$ | $63.0\pm2.0$ |  |  |  |
|---|--------------|--------------|--------------|--|--|--|
| Calibration in cell lysate diluted with 0.1% Triton X-100 (Procedure C) |              |              |              |  |  |  |
| 75 nm AgNPs (RM)  | $74.5\pm0.7$ | $75.0\pm0.0$ | $77.0\pm1.4$ |  |  |  |
| 60 nm AgNPs   | $62.5\pm0.6$ | $61.0\pm0.8$ | $59.0\pm2.0$ |  |  |  |

## Studies of spectral interferences for Ag determination in biological samples

Polyatomic interferences are derived from plasma gas, sample matrix, atmospheric gas or solvent solution and imply the generation of polyatomic species that coincide at mass-charge ratio with the analyte. In this study, a high level of background (600 cps) was registered for algae cells disrupted by ultrasounds. Incorrect background subtraction leads to an underestimation of the number of peaks detected and may affect the results. Because spectral interferences generate a higher background signal and behave in the same way as a dissolved element measured by spICP-MS [1] we searched for polyatomic ions that could affect accurate determination of <sup>107</sup>Ag. The polyatomic interferences can be a result of formation of <sup>67</sup>Zn<sup>40</sup>Ar<sup>+</sup> and <sup>91</sup>Zr<sup>16</sup>O<sup>+</sup> ions from algae contaminated by the incubation medium such as BBW or SW. However, since the algae cells were rinsed with MQ water before the wall disruption so this reason can be ignored. Another possible source of interference may be the intrinsic Zn content in the algae. To eliminate Zn-derived interferences, collision-reaction cell (ORS<sup>3</sup>) technology in MS/MS mode was used.

Disrupted algae, used as control samples, were spiked with 1 and 10 mg L<sup>-1</sup> Zn and measured in no gas and helium modes. Addition of 1 mg L<sup>-1</sup> of Zn resulted in an increase of background signal from 600 to 1024 counts, while in the presence of 10 mg L<sup>-1</sup> of Zn the background slightly increased to 1173 counts. Using He as a collision gas with a flow rate of 3 mL/min the signal in the control sample decreased to 320 counts, and was almost constant in the presence of both Zn concentrations (340 and 342 counts). However, the background signal was not fully eliminated.

[1] M. Loula, A. Kaňa, O. Mestek, *Talanta*, 2019, 202, 565-571