A systematic comparison between millisecond and microsecond dwell time SP-ICPMS for the selective discrimination of silver nanoparticles from ionic silver as required for biomedical applications

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OVERVIEW

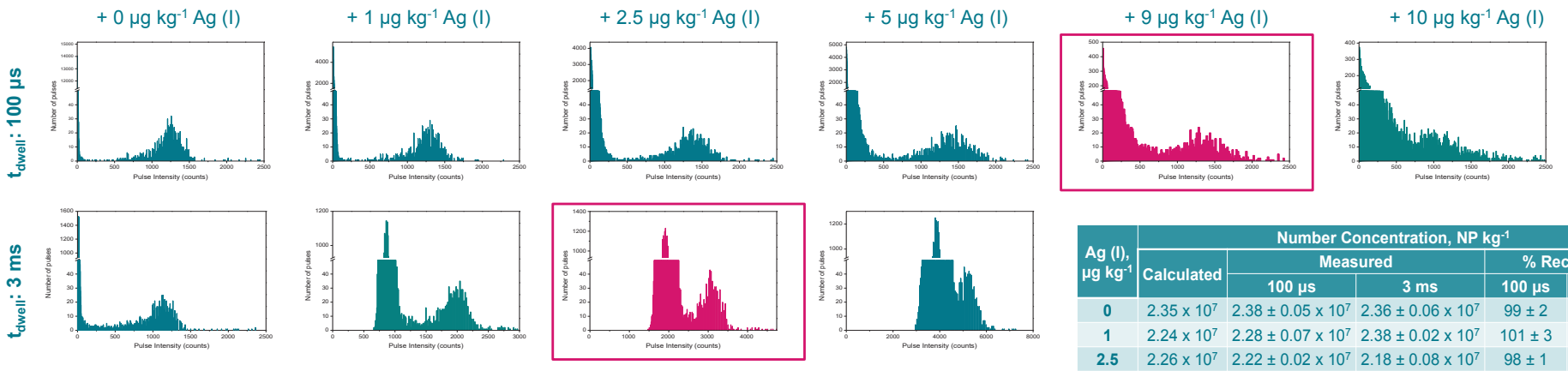
- **The antimicrobial properties of the silver-based nanomaterials have made them attractive for use in biomedical applications. In this area, information about silver release cannot be limited to the determination of total silver concentration, but information about particulate and dissolved silver is rather required for a better understanding of the toxicological effects of these nano-devices.**
- **Single Particle Inductively Coupled Plasma Mass Spectrometry (SP-ICPMS) allows to differentiate between dissolved and particulate forms of the element in a sample at ultratrace levels. The feasibility of SP-ICPMS is compromised by the achievable size detection limits, which are critically affected by the presence of a high background signal usually from procedural blanks and/or the dissolved fraction.**
- **This work presents a systematic comparison of single Ag nanoparticle detection (AgNP) using ms and µs dwell times in the presence of different AgNP-to-ionic Ag ratios by SP-ICPMS. This is achieved in a tetramethylammonium hydroxide (TMAH)-Triton complex matrix, which was proven not to affect the NP stability after AgNP quantitative extraction from blood.**

SELECTIVE DISCRIMINATION OF AgNPs FROM IONIC SILVER: EFFECTS OF SIZE AND DWELL TIME

Agilent 8900 ICP-QQQ-MS

AgNPs 75 nm (NIST 8017) in 2.5% TMAH, 0.1% Triton X-100

AgNPs 75 nm 2.5x10^7 NP kg^{-1}



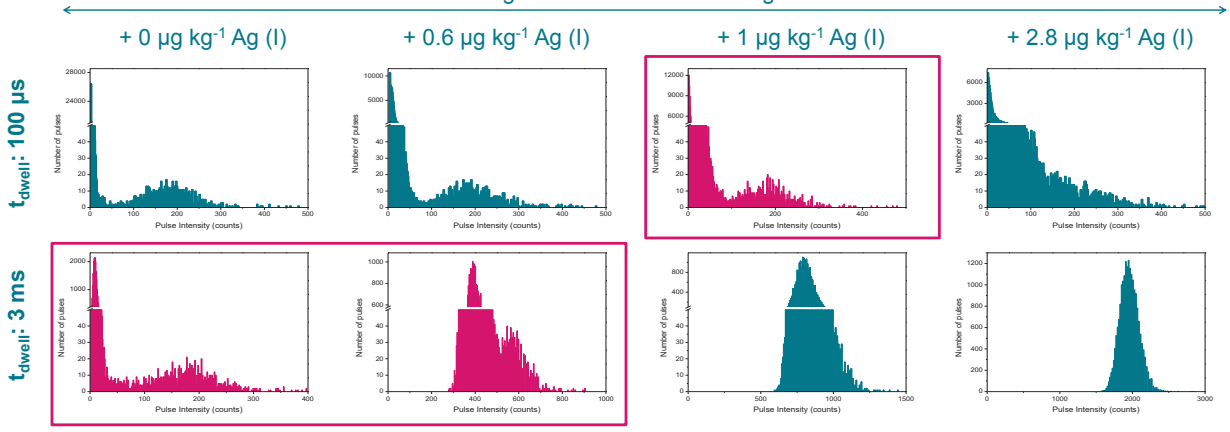
Ag (I), µg kg^{-1}	Number Concentration, NP kg^{-1}				
	Calculated	Measured		% Recovery	
		100 µs	3 ms	100 µs	3 ms
0	2.35 x 10^7	2.38 ± 0.05 x 10^7	2.36 ± 0.06 x 10^7	99 ± 2	100 ± 3
1	2.24 x 10^7	2.28 ± 0.07 x 10^7	2.38 ± 0.02 x 10^7	101 ± 3	106 ± 1
2.5	2.26 x 10^7	2.22 ± 0.02 x 10^7	2.18 ± 0.08 x 10^7	98 ± 1	96 ± 4
5	2.32 x 10^7	2.38 ± 0.12 x 10^7	3.47 ± 0.10 x 10^7	103 ± 5	150 ± 4
9	2.24 x 10^7	2.39 ± 0.10 x 10^7		107 ± 4	
10	2.32 x 10^7	3.15 ± 0.13 x 10^7		136 ± 6	

$\bar{x} \pm s\ (n = 3)$

The optimal dissolved Ag ions to AgNP ratios [Ag(I)/AgNPs] for the selective detection of 75 nm were found at 175 and 48, when working at dwell times of 100 µs and 3 ms, respectively

AgNPs 40 nm (Nanocomposix) in 2.5% TMAH, 0.1% Triton X-100

AgNPs 40 nm 3.5x10^7 NP kg^{-1}



Ag (I), µg kg^{-1}	Number Concentration, NP kg^{-1}				
	Calculated	Measured		% Recovery	
		100 µs	3 ms	100 µs	3 ms
0	3.60 x 10^7	2.69 ± 0.05 x 10^7	2.62 ± 0.17 x 10^7	**75 ± 1**	**73 ± 5**
0.6	3.54 x 10^7	2.83 ± 0.17 x 10^7	2.33 ± 0.17 x 10^7	80 ± 5	66 ± 5
1	3.57 x 10^7	2.56 ± 0.05 x 10^7	8.33 ± 2.6 x 10^7	72 ± 1	234 ± 72
2.8	3.57 x 10^7	3.81 ± 0.26 x 10^7		107 ± 7	

$\bar{x} \pm s\ (n = 3)$

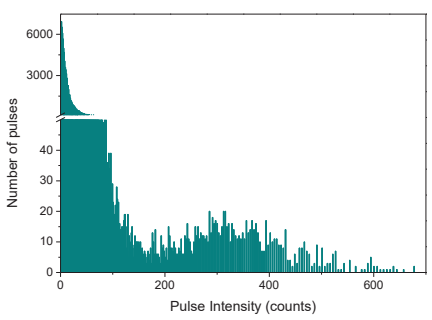
% Recovery and signal distribution histograms showed AgNPs 40 nm, with no Ag (I) added, were initially partially dissolved

The optimal dissolved Ag ions to AgNP ratios [Ag(I)/AgNPs] for the selective detection of 40 nm were found to be approximately 113-fold and <56-fold, when working at dwell times of 100 µs and 3 ms, respectively

BLOOD SAMPLE

Blood sample digested with TMAH-Triton and spiked with AgNPs 40 nm 4.5 x 10^7 NP kg^{-1} + 1.5 µg kg^{-1} Ag (I)

Isotope: ^{107}Ag η_{neb}: 11%
t_{dwell}: 100 µs t_i: 60 s



% Recovery AgNP
93 ± 1
% Recovery Ag (I)
110 ± 2

For a ratio Ag(I)/AgNPs = 82 in a real blood matrix, quantitative recoveries were achieved using a dwell time of 100 µs

CONCLUSIONS

- ✓ **Working at µs dwell times allows a better discrimination of AgNP from Ag (I).**
- ✓ **NP size affects discrimination of AgNPs from Ag (I). The smallest, the hardest.**
- ✓ **For 40 nm AgNP, SP-ICPMS is able to distinguish AgNPs from Ag (I) even if the ionic silver concentration is 113-fold the AgNP concentration for a dwell time of 100 µs.**
- ✓ **SP-ICPMS with 100 µs dwell time allowed to simultaneously determine both particulate and ionic silver in a digested blood sample with spiked recoveries of 93% and 110%, respectively.**

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