ELECTRONIC SUPPLEMENTARY INFORMATION

Single Particle Inductively Coupled Plasma Mass Spectrometry with Nanosecond Time Resolution

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Theoretical Considerations on the Probability of the Number of Detector Events during Different Dwell Intervals

To estimate and compare the signal intensity distribution with the new data acquisition system with a dwell time of 4 ns (accurately: 4.167 ns), the probability density functions and the cumulated probabilities of a hypothetical signal intensity of 350 000 counts per second (which would correspond to a typical intensity of the $^{115}In^{+}$ analyte ion signal from the analysis of a solution containing 1 ppb dissolved indium) were calculated for 1 s, 5 µs, and 4.167 ns. For probability calculations, the dwell time of the nsDAQ was assumed to be 4.167 ns, which was rounded to 4 ns in the full text of the publication.
The expected mean value per dwell (y) was calculated from the exemplary signal intensity of 350 000 counts per second and the number of dwell intervals according to Equation 1 for the three different dwell times.

$$\lambda\,[counts] = \frac{350\,000\;counts\;per\;second}{\#\;dwell\;intervals\;per\;second} \tag{1}$$

Normal Distribution

To calculate the probability density function of the signal intensity with a dwell time of 1 s, Normal distribution with a typical relative standard deviation of 1% (3500 cps) was assumed. At high count rates and long dwell intervals, various factors contribute to the error of the signal intensity per dwell (plasma temperature fluctuations, sample liquid flow variations, gas flow variations, pressure variations, etc.). The standard deviation of the ICP-MS signal intensity is composed of the combined different directions and weights of those errors and leads to a signal intensity distribution that corresponds to Normal statistics. The probability density function was obtained from Equation 2 and the cumulated probability was calculated with Equation 3.

$$p(y,\lambda) = \frac{1}{\sqrt{2\pi\sigma^2}} \cdot e^{-\frac{1}{2}\left(\frac{y-\lambda}{\sigma}\right)^2} \tag{2}$$

$$P_k(y,\lambda) = \sum_{k=0}^{y} \frac{1}{\sqrt{2\pi\sigma^2}} \cdot e^{-\frac{1}{2}\left(\frac{k-\lambda}{\sigma}\right)^2} \tag{3}$$

Here, p is the probability for a particular number of events (y) to occur during one dwell, P is the cumulated probability, λ is the expected mean value per dwell, and σ is the standard deviation.

Poisson Distribution

To calculate the probability of a certain number of detector events (y) to occur during 5 µs and 4 ns, respectively, Poisson distribution was assumed. The probability density function was obtained from Equation 4 and the cumulated probability was calculated with Equation 5.

$$p(y,\lambda) = \frac{\lambda^y}{y!} \cdot e^{-y} \tag{4}$$

$$P_k(y,\lambda) = \sum_{k=0}^{y} \frac{\lambda^k}{k!} \cdot e^{-k} \tag{5}$$

Here, p is the probability for a particular number of events (y) to occur during one dwell, P is the cumulated probability, and λ is the expected mean value per dwell.

Table S1. Probabilities (*p*) and cumulated probabilities (*P*) for a certain number of detector events (*y*) to occur during one dwell interval of 5 µs or 4.167 ns.

5 µs dwell time, $\lambda = 1.75$			4.167 ns dwell time, $\lambda = 0.001458$		
y	$p(y,\lambda)$	$P_k(y,\lambda)$	y	$p(y,\lambda)$	$P_k(y,\lambda)$
0	0.1738	0.1738	0	0.9985	0.9985
1	0.3041	0.4779	1	$1.456 \cdot 10^{-3}$	1.000
2	0.2661	0.7440	2	$1.062 \cdot 10^{-6}$	1.000
3	0.1552	0.8992	3	$5.163 \cdot 10^{-10}$	1.000
4	$6.791 \cdot 10^{-2}$	0.9671	4	$1.882 \cdot 10^{-13}$	1.000
5	$2.377 \cdot 10^{-2}$	0.9909	5	$5.491 \cdot 10^{-17}$	1.000
6	$6.932 \cdot 10^{-3}$	0.9978	6	$1.335 \cdot 10^{-20}$	1.000
7	$1.733 \cdot 10^{-3}$	0.9995	7	$2.781 \cdot 10^{-24}$	1.000
8	$3.791 \cdot 10^{-4}$	0.9999	8	$5.070 \cdot 10^{-28}$	1.000
9	$7.372 \cdot 10^{-5}$	1.0000	9	$8.215 \cdot 10^{-32}$	1.000
10	$1.290 \cdot 10^{-5}$	1.0000	10	$1.198 \cdot 10^{-35}$	1.000

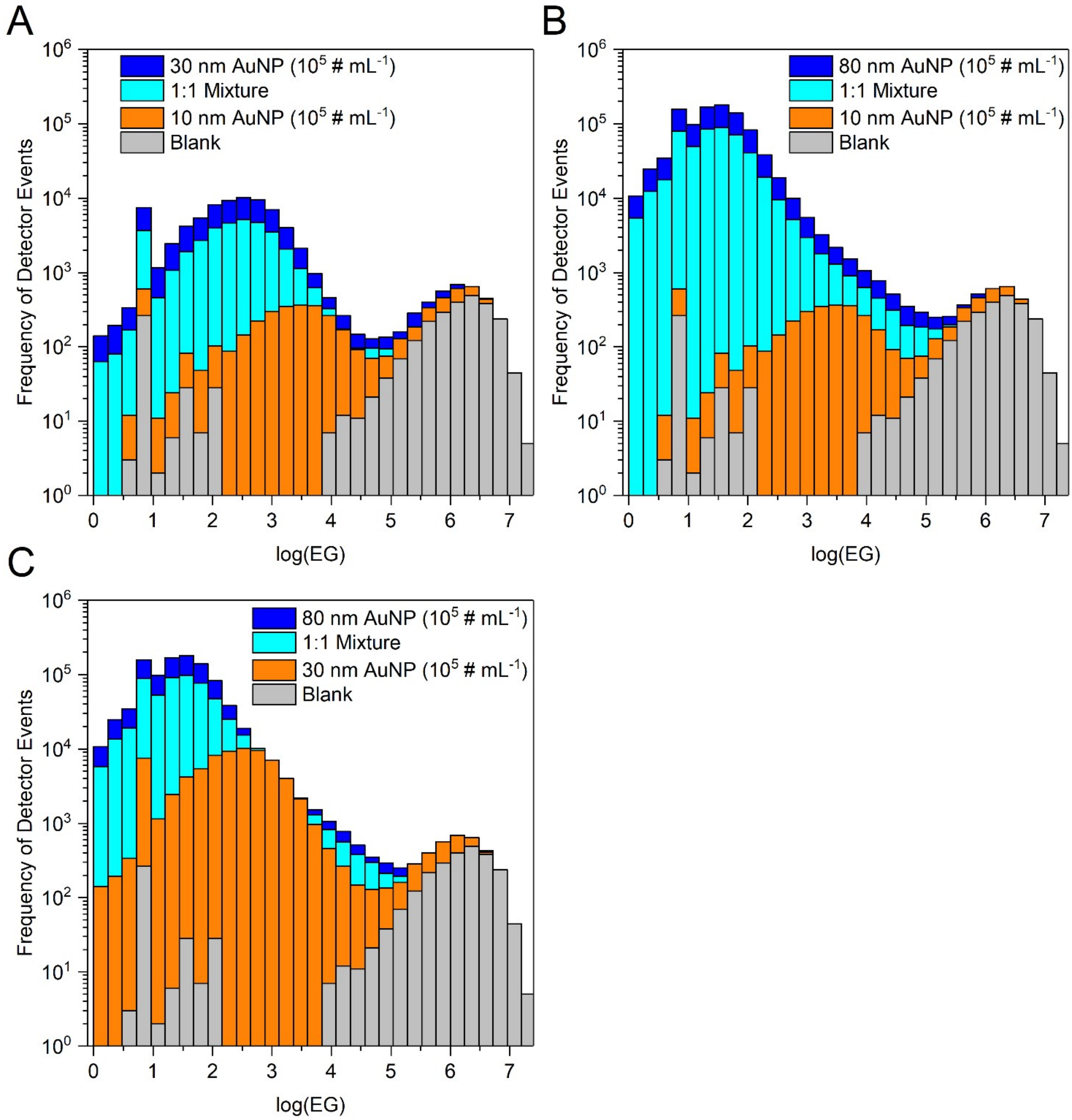

Figure S1. Frequency histograms of the logarithm of the event gap (log(EG)) of the individual measurements of AuNP with two different sizes and a PNC of 10^5 # mL^{-1}, a 1:1 mixture of the two respective samples, and a blank measurement. **A**. Measurements of a mixture of 10 and 30 nm AuNP, as well as individual size samples and a blank. **B**. Measurements of a mixture of 10 and 80 nm AuNP, as well as individual size samples and a blank. **C**. Measurements of a mixture of 30 and 80 nm AuNP, as well as individual size samples and a blank. The total number of ions from small nanoparticles is much lower than from larger nanoparticles. Therefore, the mean of the log(EG) distribution of a suspension with small particles has a lower y-axis value than from a suspension with larger particles. Consequently, the resulting distribution of a 1:1 mixture of small and large nanoparticles mostly resembles the distribution of the larger particles, except for the fact that the amplitude of the maximum is ca. half as high due to the dilution. It is not possible to recognize a third log(EG) maximum of a peak shoulder between the log(EG) of the larger particles and the blank distribution.