Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Capabilities of fast data acquisition with microsecond time resolution in inductively coupled plasma mass spectrometry and identification of signal artifacts from millisecond dwell times during detection of single gold nanoparticles

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Supplementary Information

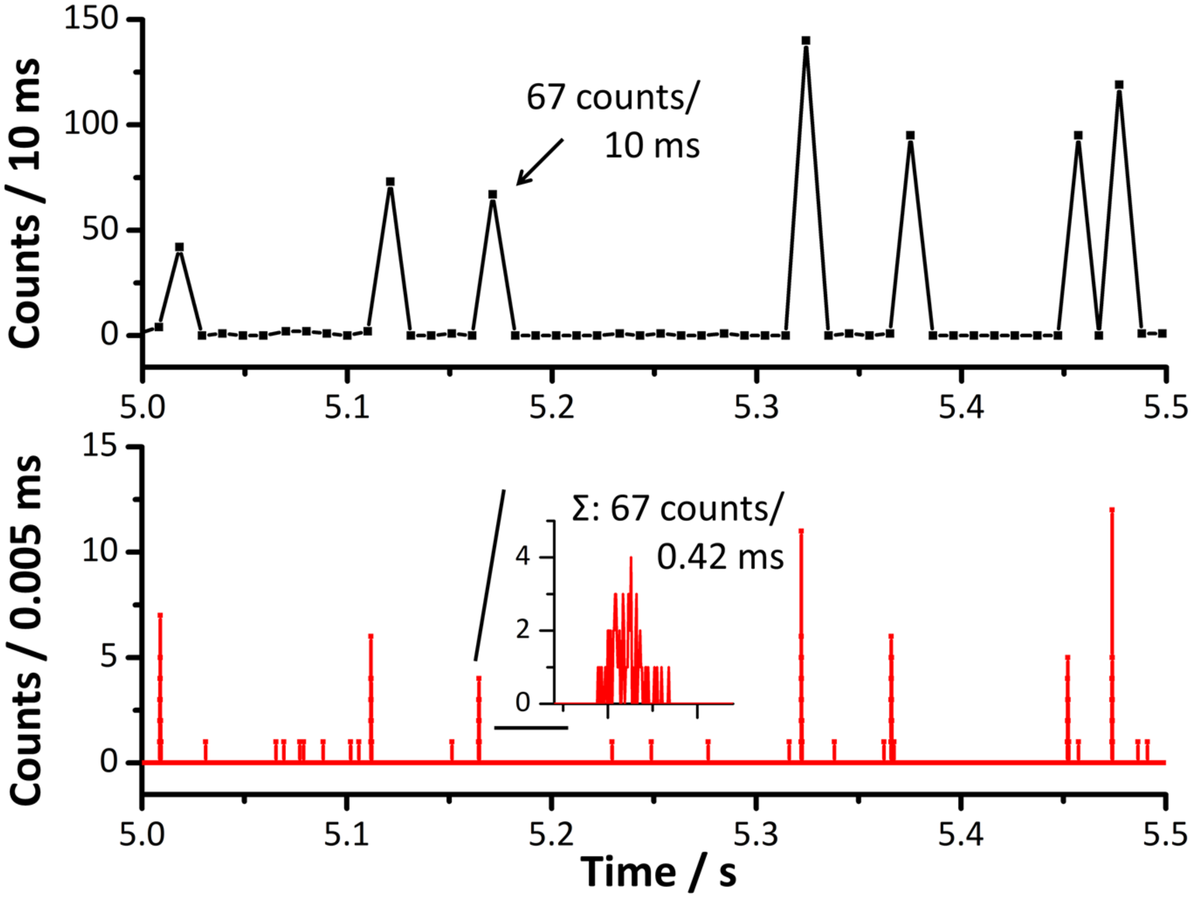


Figure SI-1: Representative signal of the model ELAN 6000 ICP-MS instrument (monitoring *m/z* ^{197}Au) due to 90 nm AuNPs (c_{NP} = 2.5x10^5 NP mL^{-1}) acquired simultaneously for 0.5 s with 10-ms dwell time (top, vendor software) and 5-µs dwell time (bottom, home-built DAQ). A detailed view showing a transient signal of a single-particle event is depicted in the small insert. In this case, 67 counts were obtained with both acquisition techniques.

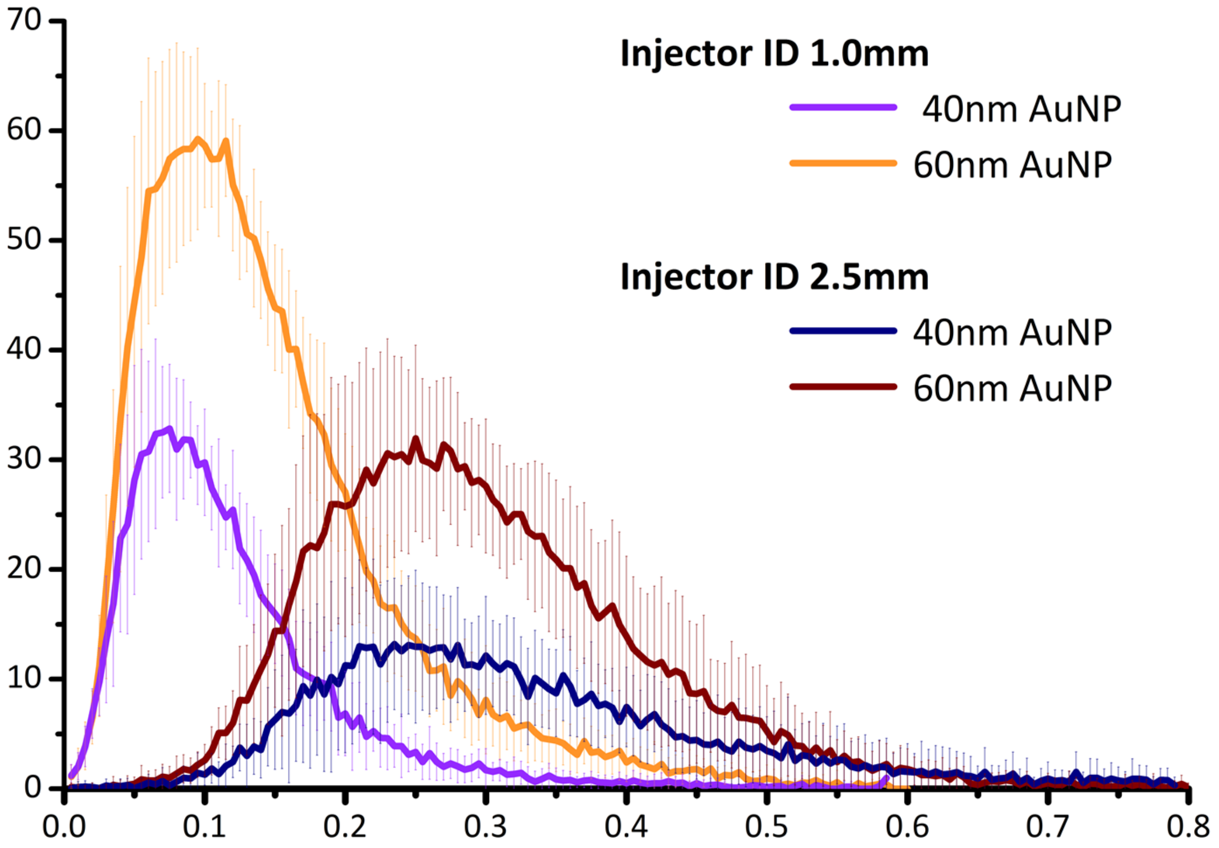
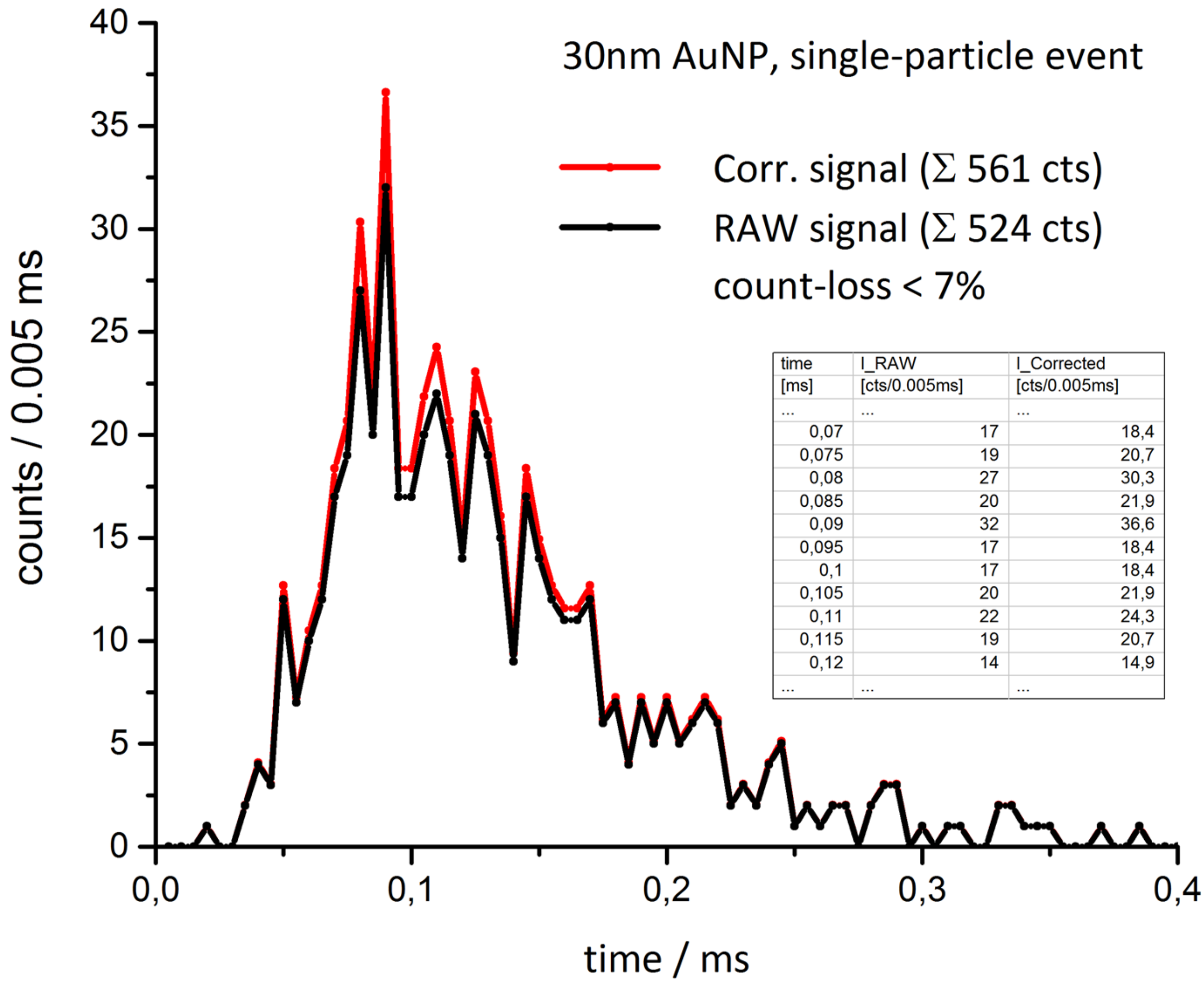


Figure SI-2: Average temporal profiles (each n=20, SD given as thin bars) of transient signals from 40 nm AuNP and 60 nm AuNP, respectively. Data acquired at two different operational conditions, using either a torch injector with inner diameter of 1.0 mm or 2.5 mm (gas flows were carefully adjusted to meet comparable sensitivity).



time	I_RAW	I_Corrected
[ms]	[cts/0.005ms]	[cts/0.005ms]
...	...	...
0,07	17	18,4
0,075	19	20,7
0,08	27	30,3
0,085	20	21,9
0,09	32	36,6
0,095	17	18,4
0,1	17	18,4
0,105	20	21,9
0,11	22	24,3
0,115	19	20,7
0,12	14	14,9
...	...	...

Figure SI-3: Typical transient signal from 30 nm AuNP, acquired with home-built DAQ. Raw data (black) depicts actual count values as derived from the detection electronics, whereas corrected data (red) represents the corresponding count rates, if supposed count losses due to bandwidth limitations are taken into account (based on Poisson statistics and assuming a dead time of 50 ns).

Considerations on particle coincidence and split-particle events

Probability for the occurrence of particle coincidence

All calculations are based on Poisson distribution:

$$P_\lambda(k) = \frac{\lambda^k}{k!} e^{-\lambda}$$

The expected value $\lambda_{NP\_in\_dwell}$ describes the probability for a NP to occur in a given timeframe t_{dwell} and for a given particle number concentration c_{NP}, if the sample introduction rate q_{neb} is assumed to be 2.6 µL/min.

$$\lambda_{\mathrm{NP\_in\_dwell}} = \frac{f_{\mathrm{NP}}}{n_{\mathrm{dwell}}}$$

$$f_{\mathrm{NP}} = c_{\mathrm{NP}} * q_{\mathrm{neb}}$$

$$n_{\mathrm{dwell}} = \frac{1\mathrm{s}}{t_{\mathrm{dwell}}}$$

The probability for one NP, P(1), to five NP, P(5), to occur in a certain timeframe is used to determine the number of NP which theoretically got into the ICP ($n_{NP,theor}$) versus the number of NP, which in fact are supposed to be counted ($n_{NP,eff}$). Here, it is assumed that in all cases, P(1) to P(5), no information on the actual number of NP occurring per dwell time is present and in all cases only one NP is counted.

$$n_{\mathrm{NP,theor}} = [P(1) * 1 + P(2) * 2 + P(3) * 3 + P(4) * 4 + P(5) * 5] * n_{\mathrm{dwell}}$$

$$n_{\mathrm{NP,eff}} = [P(1) * 1 + P(2) * 1 + P(3) * 1 + P(4) * 1 + P(5) * 1] * n_{\mathrm{dwell}}$$

The percentage given describes the ratio of observed NP compared to the number of NP, which were introduced into the ICP in a specific timeframe.

$$r = \frac{n_{\mathrm{NP,\ eff}}}{n_{\mathrm{NP,theor}}}$$

Table SI-1: Effect of particle number concentration and average duration of a particle's ion cloud (increases with particle size) on the probability for particle coincidence.

	10nm AuNP (t_{NP} ~ 400 us)				**30nm AuNP (t_{NP} ~ 600 us)**				
c_{NP}	$5x10^5$ NP mL^{-1}		$2.5x10^6$ NP mL^{-1}		$2.5x10^5$ NP mL^{-1}		$2.5x10^6$ NP mL^{-1}		
	DAQ	**Vendor**	**DAQ**	**Vendor**	**DAQ**	**Vendor**	**DAQ**	**Vendor**	
t_{dwell}	0.4 ms	10 ms	0.4 ms	10 ms	0.6 ms	10 ms	0.6 ms	2.5 ms	10 ms
$\lambda_{NP\_in\_dwell}$	0.009	0.217	0.043	1.083	0.007	0.108	0.065	0.271	1.083
P_λ (1NP)	0.009	0.174	0.041	0.367	0.006	0.097	0.061	0.207	0.367
P_λ (2NP)	0.000	0.019	0.001	0.199	0.000	0.005	0.002	0.028	0.199
$n_{NP,eff}$	21.66 NP s^{-1}	19.5 NP s^{-1}	106.0 NP s^{-1}	63.7 NP s^{-1}	10.8 NP s^{-1}	10.3 NP s^{-1}	104.9 NP s^{-1}	94.8 NP s^{-1}	63.7 NP s^{-1}
$n_{NP,theor}$	21.66 NP s^{-1}		108.33 NP s^{-1}		10.83 NP s^{-1}		108.33 NP s^{-1}		

r	100%	90%	98%	59%	100%	95%	97%	88%	59%

Probability for the occurrence of split-particle events

All calculations are based on Poisson distribution.

The expected value $\lambda_{split\text{-}NP}$ describes the probability for the occurrence of split-particle events per second for a given particle number concentration c_{NP} with a sample introduction rate q_{neb} of 2.6 µL/min. For this, every dwell time t_{dwell} is divided into equal bins having a length of the average temporal duration t_{NP} of a single particle event. The ratio $r_{lastbins}$ then only describes the duration of all dwell time's last bins per second.

$$\lambda_{\text{split - NP}} = r_{\text{lastbins}} * f_{\text{NP}}$$

$$r_{\text{lastbins}} = \frac{n_{\text{dwell}} * t_{\text{NP}}}{1\text{s}}$$

$$f_{\text{NP}} = c_{\text{NP}} * q_{\text{neb}}$$

$$n_{\text{dwell}} = \frac{1\text{s}}{t_{\text{dwell}}}$$

Table SI-2: Effect of dwell time on the probability for split-particle events for different particle number concentrations.

	10nm AuNP (t_{NP} ~ 400 us)	**30nm AuNP (t_{NP} ~ 600 us)**		
c_{NP}	5x10^5 NP mL^{-1}	2.5x10^5 NP mL^{-1}	2.5x10^6 NP mL^{-1}	
t_{dwell}	10 ms	10 ms	2.5 ms	10 ms
n_{dwells}	100	100	400	100
f_{NP}	21.66 NP s^{-1}	10.83 NP s^{-1}	108.33 NP s^{-1}	
$r_{lastbins}$	0.04 s / s	0.06 s / s	0.24 s / s	0.06 s / s
$\lambda_{split\text{-}NP}$	0.87 NP s^{-1} (4.0%)	0.65 NP s^{-1} (6.0%)	26 NP s^{-1} (24%)	6.5 NP s^{-1} (6.0%)

Considerations on SEM detector pulse pile-up

All calculations are based on Poisson distribution.

The expected value $\lambda_{pile\text{-}up}$ describes the probability for the occurrence of a SEM signal pulse during a given dead time t_d of 50 ns dependent on the maximum observed number of counts I_{max}.

$$\lambda_{\text{pile - up}} = I_{\text{max}} * t_{\text{d}}$$

The probability for one signal, P(1), to five signals, P(5), to occur in a given dead time is used to determine the number of signals which theoretically were present (I_{theor}) in a 5 µs integration time window versus the number of signals, which in fact were counted (I_{eff}). Here, it is assumed that in all cases, P(1) to P(5), no information on the actual number of signals occurring per 5 µs is present and in all cases only one signal is counted.

$$I_{\text{theor}} = [P(1) * 1 + P(2) * 2 + P(3) * 3 + P(4) * 4 + P(5) * 5] * \frac{5000 \text{ ns}}{50 \text{ ns}}$$

$$I_{\text{eff}} = [P(1) * 1 + P(2) * 1 + P(3) * 1 + P(4) * 1 + P(5) * 1] * \frac{5000 \text{ ns}}{50 \text{ ns}}$$

The percentage given describes the ratio of observed signal counts to the number of signals, which are supposed to be counted at a count rate I_{max}.

$$r = \frac{I_{\text{eff}}}{I_{\text{theor}}}$$

Table SI-3: Influence of ICP-MS operating conditions on the count rate during transient signals, affecting the probability for potential SEM detector pulse pile-up (assuming a dead time of 50 ns).

I_{max}	**10 cts / 5 µs**	**20 cts / 5 µs**	**40 cts / 5 µs**	**80 cts / 5 µs**
$\lambda_{pile\text{-}up}$	0.1 cts / 50 ns	0.2 cts / 50 ns	0.4 cts / 50 ns	0.8 cts / 50ns
P(1)	0.0905	0.1637	0.2681	0.3594
P(2)	0.0045	0.0164	0.0536	0.1438
P(3)	0.0002	0.0011	0.0072	0.0383
$I_{eff.}$	9.52 cts / 5 µs	18.13 cts / 5 µs	32.97 cts / 5 µs	55.05 cts / 5 µs
r	95.2%	90.7%	82.4%	68.8%
Lost counts	4.8%	9.3%	17.6%	31.2%