Supplementary Information

Statistical properties of spikes in single particle ICP-MS time scans

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S1 Monte Carlo simulations

Synthetic time scans were generated with the following procedure:

- First, the points of discontinuity of a homogeneous Poisson process of intensity λ were randomly drawn. These points model the starts of the particle events left by the ions clouds stemming from the nanoparticles in the time scan. To perform this step, a series of random interarrival times, distributed according to an exponential law of parameter λ, was generated.
- Then, the duration of each particle event was drawn from one of the three distributions mentioned in Sec S2.
- If the intersection between a particle event and a given time bin of the synthetic time scan was not void, a nonzero value was affected to the corresponding reading. All the readings of the time scan that did not belong to a fraction of any particle event were set equal to 0.

The number of nanoparticles having entered the instrument is equal to the number of discontinuities of the homogeneous Poisson process generated during the first step of the algorithm, up to a duration τ_{obs}. The spike count is the number of blocks made of contiguous nonzero readings in the synthetic signal.
All the Monte Carlo results reported in this work are based on 10,000 trials.

S2 Effect of the probability distribution ruling the particle event duration on the average number of particles per spike

To check that the average number of particles per spike $\mathcal{N}$ depends only on the average of the duration τ of particle events and not on the shape of the probability distribution function of this random variable (a feature named "universality" in the article), Monte-Carlo simulations for three possible distributions were run:

- Constant-valued (i.e. Dirac-distributed) $\tau = \tau_p$;
- Gamma (G) distribution: $\mathrm{PDF}(\tau) = \frac{1}{\Gamma(k)\theta^k}\tau^{k-1}e^{-\tau/\theta}$, where Γ denotes the gamma function – $\Gamma(x) = \int_0^{+\infty} t^{x-1}e^{-t}\,\mathrm{d}t$ for $x > 0$;
- Inverse Gaussian (IG) distribution: $\mathrm{PDF}(\tau) = \sqrt{\frac{\lambda}{2\pi\tau^3}}\exp\Big(-\frac{\lambda(\tau-\tau_m)^2}{2\tau_m^2\tau}\Big)$.

Gamma and inverse Gaussian distributions are commonly employed to model nonnegative real random variables.
The relationships between the parameters of these distributions and their first two moments (average and variance) are given in Tab. S1.

Table S1: Dirac, Gamma and inverse Gaussian distributions average and variance.

Particle event duration PDF	Average	Variance
δ_{τ_p}	τ_{p}	0
$\mathrm{Gamma}(k,\theta)$	$k\theta$	$k\theta^2$
$\mathrm{IG}(\tau_m,\lambda)$	τ_m	τ_m^3/λ

Fig. S1 confirms that the average number of particles per spike is universal, i.e. it only depends on the average value of τ regardless of the underlying probability distribution of τ.

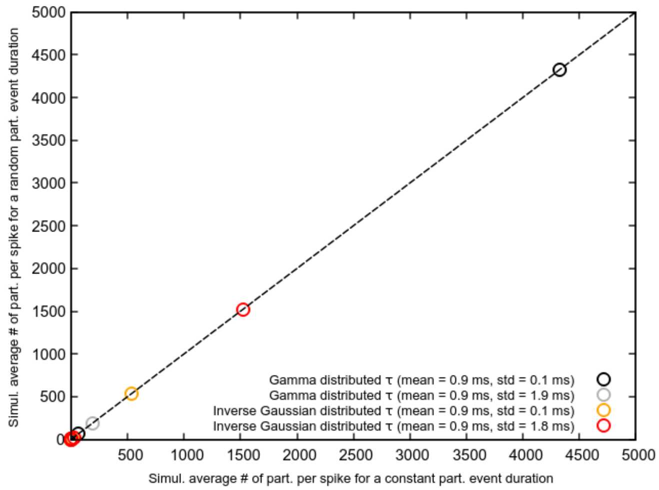

Figure S1: Comparison between the average number of particles per spike when the particle event duration is random with an average equal to 0.9 ms and when it is constant and equal to 0.9 ms. Data were obtained by Monte Carlo simulation. The dashed line is the identity line and is here to guide the eye.

S3 Effect of the probability distribution ruling the particle event duration on the probability distribution governing the number of particles per spike

It is shown in the manuscript that the number of particle per spikes is geometrically distributed in the zero dwell time and constant particle event case, and that it is no longer rigorously true when one of these assumptions is waived. However, the deviation from the geometric distribution is expected to be gradual.

The p-values stemming from the Pearson's χ^2 statistics obtained from the comparison between the distributions obtained numerically and the geometric distribution with parameter $e^{-2\lambda\tau_{\mathrm{dw}}}\,\frac{e^{\lambda\tau_{\mathrm{dw}}}-1}{\lambda\tau_{\mathrm{dw}}}\,e^{-\lambda}$ are displayed in Tab. S2. The p-values equal to unity when λ is greater than $4\times10^3\,\mathrm{s}^{-1}$ should be interpreted with caution: empirical frequencies can be low in this case and the Pearson's χ^2 test is not very reliable in such a situation.

S4 Effect of the probability distribution ruling particle event duration on the average spike duration

S4.1 Zero dwell time and constant particle duration case

Calculating the average spike duration $\langle\tau_s\rangle$ when the duration of particle events is constant is straightforward. According to the law of total expectation, it is equal to $\sum_{k=1}^{+\infty}\mathrm{E}(\tau_s|k)\,\mathrm{P}(X=k)$, $\mathrm{E}(\tau_s|k)$ being the expected value of the spike duration τ_s given that the spike is the outcome of k particle events, while $\mathrm{P}(X=k)$ denotes the probability that a spike stems for k particle events. Given that $\mathrm{E}(\tau_s|k)=(k-1)\mathrm{E}(t|t\leq\tau_p)+\tau_p$ and $\mathrm{P}(X=k)=p(1-p)^{k-1}$ for a zero dwell time and a constant particle event duration,

$$\langle\tau_s\rangle=\sum_{k=1}^{+\infty}\big((k-1)\mathrm{E}(t|t\leq\tau_p)+\tau_p\big)p(1-p)^{k-1}. \tag{1}$$

Table S2: Pearson's χ^2 test: p-values resulting from Monte Carlo simulations. Column δ_9 corresponds to a constant particle event duration τ equal to 0.9 ms. Column $\mathrm{G}_{n,m}$ denotes a Gamma distributed particle event duration τ with average $n \times 10^{-4}$ s and standard deviation $m \times 10^{-4}$ s. Column $\mathrm{IG}_{n,m}$ denotes a particle event duration τ following an inverse Gaussian distribution with average $n \times 10^{-4}$ s and standard deviation $m \times 10^{-4}$ s.

Flux rate (s^{-1})	δ_9	$\mathrm{G}_{9,1}$	$\mathrm{G}_{9,3}$	$\mathrm{G}_{9,6}$	$\mathrm{G}_{9,9}$	$\mathrm{G}_{9,18}$	$\mathrm{IG}_{9,1}$	$\mathrm{IG}_{9,3}$	$\mathrm{IG}_{9,6}$	$\mathrm{IG}_{9,9}$	$\mathrm{IG}_{9,18}$
10	1.000	1.000	1.000	0.996	0.996	0.565	1.000	1.000	0.997	0.987	0.588
20	1.000	1.000	1.000	0.998	0.998	0.074	1.000	1.000	0.997	0.963	0.063
30	1.000	1.000	1.000	0.998	0.998	0.001	1.000	1.000	0.998	0.942	0.000
40	1.000	1.000	1.000	0.998	0.998	0.000	1.000	1.000	0.999	0.815	0.000
50	1.000	1.000	1.000	0.994	0.994	0.000	1.000	1.000	0.998	0.738	0.000
60	1.000	1.000	1.000	0.985	0.985	0.000	1.000	1.000	0.995	0.645	0.000
70	1.000	1.000	1.000	0.987	0.987	0.000	1.000	1.000	0.986	0.444	0.000
80	1.000	1.000	1.000	0.987	0.987	0.000	1.000	1.000	0.970	0.258	0.000
90	1.000	1.000	1.000	0.971	0.971	0.000	1.000	1.000	0.947	0.261	0.000
100	1.000	1.000	1.000	0.941	0.941	0.000	1.000	1.000	0.950	0.131	0.000
200	1.000	1.000	1.000	0.545	0.545	0.000	1.000	1.000	0.659	0.000	0.000
300	1.000	1.000	1.000	0.126	0.126	0.000	1.000	1.000	0.097	0.000	0.000
400	1.000	1.000	1.000	0.004	0.004	0.000	1.000	1.000	0.004	0.000	0.000
500	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
600	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
700	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
800	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
900	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
1000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
2000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
3000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.000	0.000	0.000
4000	1.000	1.000	1.000	0.000	0.000	0.000	1.000	1.000	0.965	0.000	0.000
5000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	0.000	0.000
6000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	0.000
7000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	0.000
8000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	0.000
9000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	0.000

Since $\sum_{k=1}^{+\infty}(k-1)x^{k-1} = x/(1-x)^2$ for $|x| < 1$, one gets in the zero dwell time and constant valued particle event duration case

$$\langle \tau_s \rangle = \left(\frac{1}{p} - 1\right)\mathrm{E}(t | t \leq \tau_p) + \tau_p, \tag{2}$$

as stated in Sec. 2.3.1. t being exponentially distributed with parameter λ (t is the interarrival time between successive events of a homogeneous Poisson process of rate λ), $\mathrm{E}(t \,|\, t \leq \tau_p) = (1 - e^{-\lambda\tau_p})^{-1} \int_0^{\tau_p} \lambda t e^{-\lambda t}\,\mathrm{d}t$, and finally,

$$\langle \tau_s \rangle = (e^{\lambda\tau_p} - 1)\big(1 - (1 + \lambda\tau_p)e^{-\lambda\tau_p}\big)/\big(\lambda(1 - e^{-\lambda\tau_p})\big) + \tau_p. \tag{3}$$

Monte Carlo simulations displayed in Fig. S2 are in perfect agreement with this formula.

S4.2 Nonnegative dwell time and random particle duration case

A universal tight upper bound was derived in the article for the average spike duration. Additionally, Monte Carlo simulations demonstrate numerically that the average spike duration itself is universal, i.e. does not depend on the whole probability distribution of the particle event duration τ, but only on its average. This interesting feature is illustrated in Fig. S3.

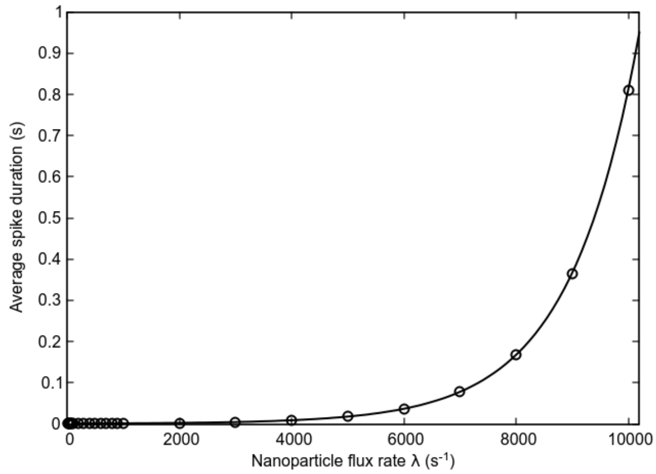

Figure S2: Average spike duration calculated by Monte Carlo simulation (circles) and theoretical estimation (black line) for a zero dwell time and a constant valued particle event duration (equal to 0.9 ms in this case).

S5 Average size of nanoparticles in a 3:1 mixture of 60 and 150 nm-sized AuNPs

Single particle ICP-MS experiments were performed with dispersions composed of a mixture of 60 and 150 nm-sized gold nanoparticles stabilized with a citrate buffer (Sigma-Aldrich). The particle number concentration of the 60 nm stock dispersion was $\approx 1.9 \times 10^{10}\,\mathrm{mL}^{-1}$, while it was $\approx 3.6 \times 10^{9}\,\mathrm{mL}^{-1}$ for the 150 nm stock dispersion.

The most dilute dispersion analyzed was made from a mixture between the $250,000\times$ diluted 60 nm dispersion and the $150,000\times$ diluted 150 nm dispersion. According to the particle number concentrations of the stock solutions, 76% of the particles of this dispersion had a 60 nm size and 24% a 150 nm size, a ratio consistent with sp-ICP-MS measurements. More concentrated dispersions were also analyzed, always with the same ratio between the numbers of 60 and 150 nm-sized nanoparticles.

The expected average diameter of the nanoparticles in all these dispersions is thus equal to $0.76 \times 60\,\mathrm{nm} + 0.24 \times 150\,\mathrm{nm} = 81.6\,\mathrm{nm}$. According to the sp-ICP-MS experiments, with the operating parameters that were employed, the average number of counts associated with the 60 nm sized nanoparticles is 992, while the mean number of counts associated with the spikes in the sp-ICP-MS time scans averaged over all the nanoparticle flux rates that were measured is 2569 (cf. Tab. S3). Assuming that the nominal diameter of the 60 nm nanoparticles is genuinely equal to 60 nm, the average nanoparticle diameter than can be inferred from the experimental data is $(2569/992)^{1/3} \times 60\,\mathrm{nm} = 82.4\,\mathrm{nm}$, a value that differs by less than 1% from the expected one.

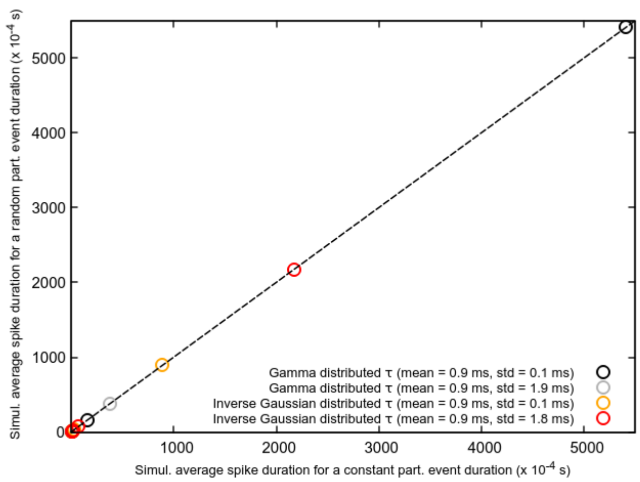

Figure S3: Comparison between the average spike duration when the particle event duration is random with an average equal to 0.9 ms and when it is constant and equal to 0.9 ms. Data were obtained from Monte Carlo simulations. The dashed line is the identity line and is here to guide the eye.

Table S3: Average number of particles per spike and average number of counts per particle as a function of the nanoparticle flux rate λ for the analyzed 3:1 mixture of 60 and 150 nm sized gold nanoparticles.

Flux rate λ (s^{-1})	$\mathcal{N}$	Average number of counts per particle
25	1	3052
821	2	3015
1642	5	2961
2463	10	3095
3283	22	2510
4104	48	2507
4925	103	2847
5748	222	2593
6563	477	2235
7390	1036	2466
8208	2227	2654
9027	4789	2632
9850	10338	2101
10669	22225	2138
11486	47612	2100
12313	102972	2202