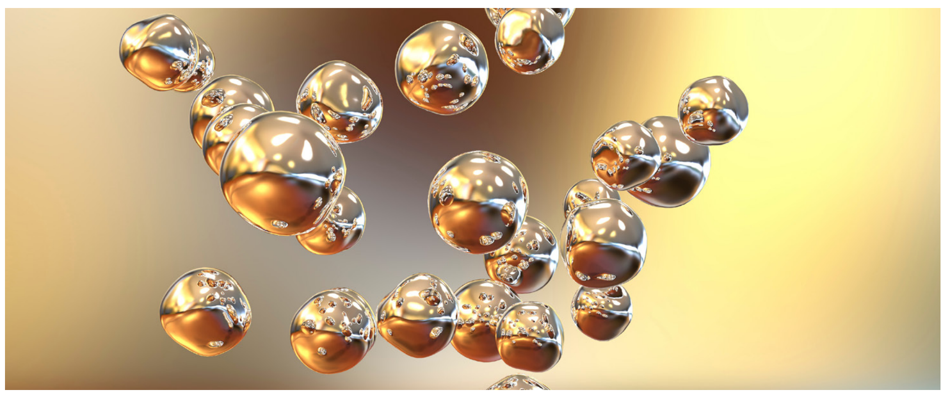
Improving Resolution of Single Nanoparticles Using ICP-MS and Shorter Dwell Times

Advantages of a 50 µs dwell time on a single nanoparticle's signal profile



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Introduction

Single nanoparticles (sNPs) are defined as particles with diameters below 100 nm. Owing to their distinct physical and chemical properties, engineered nanoparticles are incorporated into a wide range of products to enhance performance or functionality. At the same time, they are increasingly recognized as potential contaminants or pollutants. In the semiconductor industry, for example, even single-digit nanometer-sized sNPs present in process chemicals can cause electrical shorting to occur and reduce product yield. Although the effects of sNPs on environmental and biological systems are still being investigated, researchers have developed methods to determine sNPs using single particle-ICP-MS (spICP-MS).[1] Agilent ICP-MS instruments are widely used to characterize sNPs because of their fast-scanning multi-element capability, ultra-high sensitivity, low background, and integrated data analysis software.[2-5]

sNPs are decomposed, atomized, and ionized in the high-energy ICP. Any ions that are generated from a particle enter the vacuum chamber as ion clusters and are then detected as transient signal peaks above the background signal. The signal from each sNP event usually lasts between 400 and 1,300 µs. To detect this short-lived signal with high resolution, a fast time-resolved analysis (fast-TRA) acquisition is employed. Typically, a default dwell time of 100 µs is used. However, if higher peak resolution is required, the Agilent 9500 Triple Quadrupole ICP-MS (ICP-QQQ) can be operated with a dwell time as low as 50 µs. During the development of the 9500 ICP-QQQ, improvements to the instrument's hardware enabled reliable control of TRA at much shorter timing intervals. These enhancements enable the 9500 to operate with high stability at a 50 µs dwell time, making it an effective instrument for high-resolution sNP analysis. The robust plasma of Agilent ICP-MS instruments, as indicated by a CeO^+/Ce^+ ratio < 1%, also reduces matrix effects between standards and samples.

In this study, we conducted a fundamental evaluation of sNP analysis using a dwell time of 50 µs. Gold (Au), silica (SiO_2), and platinum (Pt) nanoparticles were analyzed by the 9500 ICP-QQQ, and the results were compared with those obtained with a 100 µs dwell time.

Experimental

Instrumentation

The Agilent 9500 ICP-QQQ used the standard configuration (Ni cones and u-lens), except for the torch. A quartz torch with a 1.5 mm inner diameter (id) injector was used to minimize diffusion of ion clusters in the ICP and obtain sharper, better-resolved peaks.

Multi-element NP data acquisition and analysis were carried out using the Rapid Multi-Element Nanoparticle Analysis mode of the optional Single Nanoparticle Application Module for the Agilent OpenLab ICP-MS software. In Rapid Multi-Element Nanoparticle Analysis mode, multi-element data are collected sequentially from a single sample acquisition, and all data are combined into a single file. This method saves time, as only one sample uptake and rinse are needed for all analytes. Data quality is likely enhanced, since the risk of sample contamination is considerably lower with a single analysis than with multiple separate analyses.

Table 1. Agilent 9500 ICP-QQQ operating conditions for multi-element nanoparticle analysis.

	No Gas
RF Power (W)	1550
Sampling Depth (mm)	10
Nebulizer Gas Flow Rate (L/min)	0.96
Lens Voltages	Autotune
Dwell Time (µs)	50 or 100

The shaded parameters were defined automatically by selecting the preset method for multi-element nanoparticle analysis in the method wizard or following autotuning.

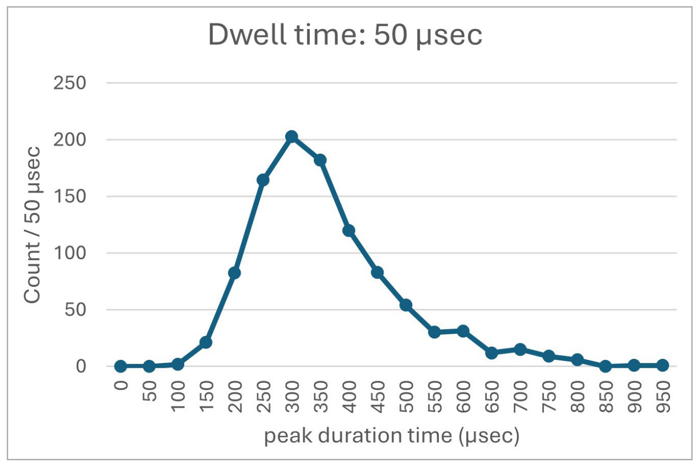
Sample preparation

Seven nanoparticle suspensions comprising 30, 60, 100 nm Au NP; 50, 70 nm Pt NP; 500, 1000 nm SiO_2 NP (nanoComposix, San Diego, CA, USA) were used as NP standards. To measure ionic sensitivity, aqueous Au, Pt, and Si standards (1000 ppm, Kanto Chemicals, Japan) were diluted with ultrapure water.

Results and discussion

Comparison of peak shape using 50 and 100 µs dwell times

A 60 nm Au NP solution was measured using a dwell time of 50 µs. As shown in Figure 1, the nanoparticle signal peak is sharper and more distinctly resolved at a dwell time of 50 µs (top graph) than when the data are reported every 100 µs (bottom graph).



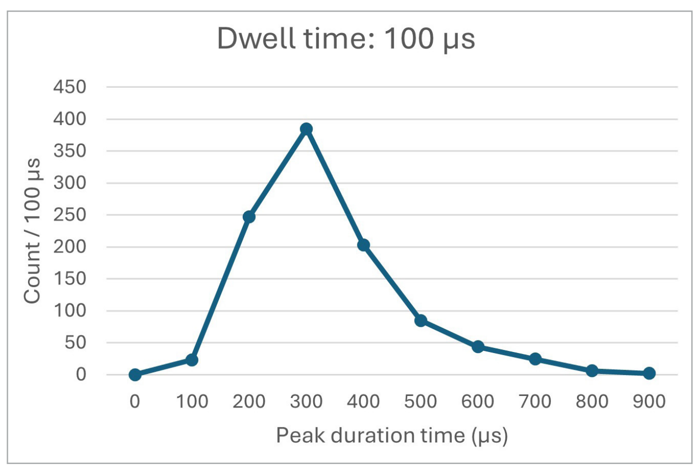


Figure 1. Comparison of peak shape of a 60 nm Au NP using a dwell time of 50 µs (top) and with fewer data points (every 100 µs) (bottom).

In sNP-ICP-MS analysis, peak overlaps can occur, resulting in a positive bias in the particle size distribution and a negative bias in the particle number concentration. While infrequent, these overlaps can be mitigated more effectively by using a shorter dwell time, which increases the likelihood of resolving individual nanoparticle events. Figure 2 shows that two 60 nm Au NPs can be clearly separated within a single 50 µs dwell time interval.

However, as the dwell time decreases, both peak intensity and background signal are sampled over shorter intervals, reducing the signal-to-noise ratio (S/N). Depending on the relative magnitudes of the nanoparticle signals and ion background, the detection efficiency for smaller peaks—previously observable at longer dwell times—may be diminished.

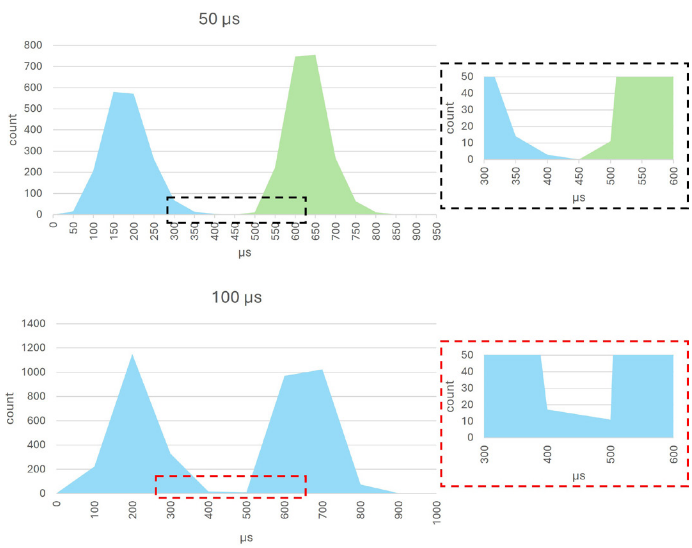


Figure 2. Top: Two adjacent sNP peaks separated by one point (50 µs). Bottom: If the peaks were measured with a 100 µs dwell time, two sNPs would be falsely reported as a single signal, affecting particle size distribution and particle number concentration results.

Comparison of mean particle size results using dwell times of 50 and 100 µs

Seven Au, Pt, and SiO_2 nanoparticle suspensions from nanoComposix were analyzed by the 9500 ICP-QQQ to evaluate mean particle size. Nebulization efficiency was determined using the 60 nm Au material, and this efficiency was applied to convert the Pt and SiO_2 signals to particle size, with additional sensitivity correction using the ionic standards.

At a dwell time of 50 µs, mean particle sizes acquired for all nanomaterials agreed with the manufacturer's certified values (obtained by TEM), and were consistent with the results obtained using a 100 µs dwell time (Table 2).

Table 2. Comparison of mean particle size of three Au, Pt, and SiO_2 nanomaterials measured using dwell times of 50 and 100 µs with certified values.

Element	Certified Size (nm)	Mean Particle Size (nm)	
		50 µs	100 µs
^{197}Au	30 ± 2	29	29
	57 ± 6	57	59
	98 ± 7	100	101
^{195}Pt	46 ± 5	41	41
	71 ± 4	68	68
$^{28}SiO_2$	512 ± 21	498	503
	1013 ± 30	992	987

Comparison of particle size distribution using dwell times of 50 and 100 µs

The signal distribution of the Au nanomaterial with a certified NP size of 57 ± 6 nm was obtained at 50 and 100 µs dwell times. As shown in Figure 3, both measurements produced near-normal size distributions centered around approximately 60 nm, spanning roughly 40 to 80 nm. In both cases, the distributions showed a slight skew towards the lower size range (40–60 nm), consistent with the particle size characteristics described in the certificate of analysis. (The distribution plot provided by nanoComposix cannot be shown here because of copyright restrictions.).

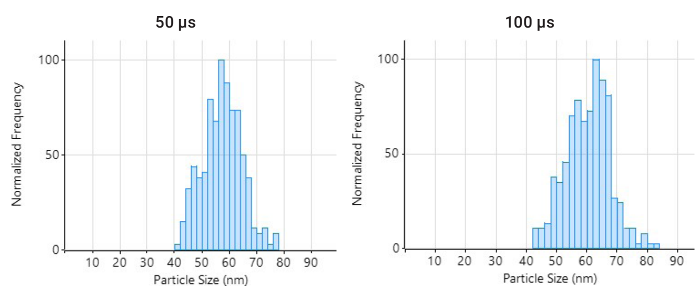


Figure 3. Comparison of particle size distribution of Au 57 ± 6 nm NPs using dwell times of 50 µs (left) and 100 µs (right).

Conclusion

For high-resolution nanoparticle analysis, the Agilent 9500 ICP-QQQ can be operated in single-particle mode with a 50 µs dwell time, as well as the default 100 µs setting. The reduction of dwell time is enabled by advancements in both hardware and software that work together to support higher-resolution single-nanoparticle measurements.

Improved peak resolution was demonstrated for Au, SiO_2, and Pt nanoparticles, while maintaining equivalent performance to the standard 100 µs dwell time setting. The mean particle sizes obtained at 50 µs for the nanoparticle suspensions were within the manufacturer's certified ranges. Likewise, the particle size distributions measured at both 50 and 100 µs closely matched the distributions provided by the manufacturer.

In addition to improved peak resolution, a shorter dwell time reduces the likelihood of multiple particles being detected within a single dwell period, potentially improving data accuracy.

Since the total data volume increases inversely with dwell time, a 50 µs dwell time generates more data points per unit time. To reduce processing time when handling large datasets, Agilent ICP-MS software (both ICP-MS MassHunter and OpenLab ICP-MS) uses multithreaded CPU-based computation for sNP data analysis, maintaining efficient data management.

Although 50 µs may not be necessary for many sNP analyses, having the option to use this shorter dwell time provides greater flexibility. For example, it could enable samples with unexpectedly high particle counts to be analyzed without needing additional dilution.

References

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4. Analysis of 15 nm Iron Nanoparticles in Organic Solvents by spICP-MS, Agilent publication, 5994-1747EN
5. Extending ICP-MS Capabilities to Detect Nanoparticles in Food, Agilent publication, 5994-1748EN

Products used in this application

Agilent products

Product Type	Description	Part Number
Sample Introduction System	1.5 mm torch for 9500 ICP-MS	M5150-67012
Software	Single nanoparticle module	G5714A

www.agilent.com/chem/9500icpqqq

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