Agilent's Solutions for Nanoparticles Analysis
ICP-MS, ICP-MS/MS, software

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The Total Solution

Choice of Mass Spectrometers

- 7800 quadrupole ICP-MS – cost-effective, 3 ms dwell time
- 7900 quadrupole ICP-MS – ultra-sensitive, ultra-fast 0.1 ms dwell time
- 8900 ICP-QQQ – highest sensitivity and lowest background, MS/MS for interference-free determination of SiO_2 and TiO_2 nanoparticles

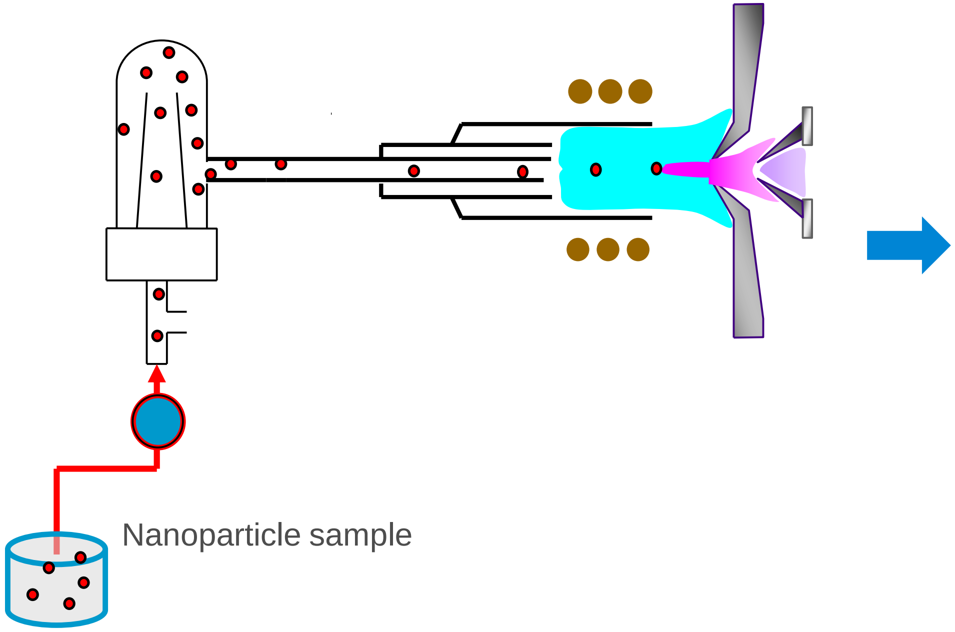
Fully automated acquisition and data analysis configuration within MassHunter 4.3 software guided by Method Wizard

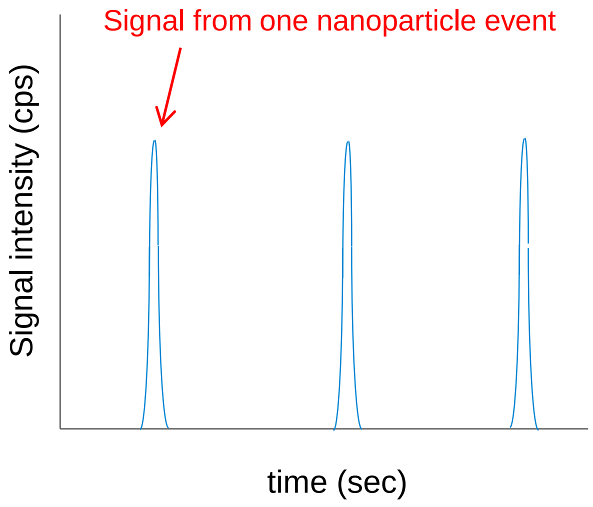
- Supports single particle mode with 1 or 2 elements and field-flow fractionation (FFF) coupling

7800 ICP-MS 7900 ICP-MS 8900 ICP-QQQ

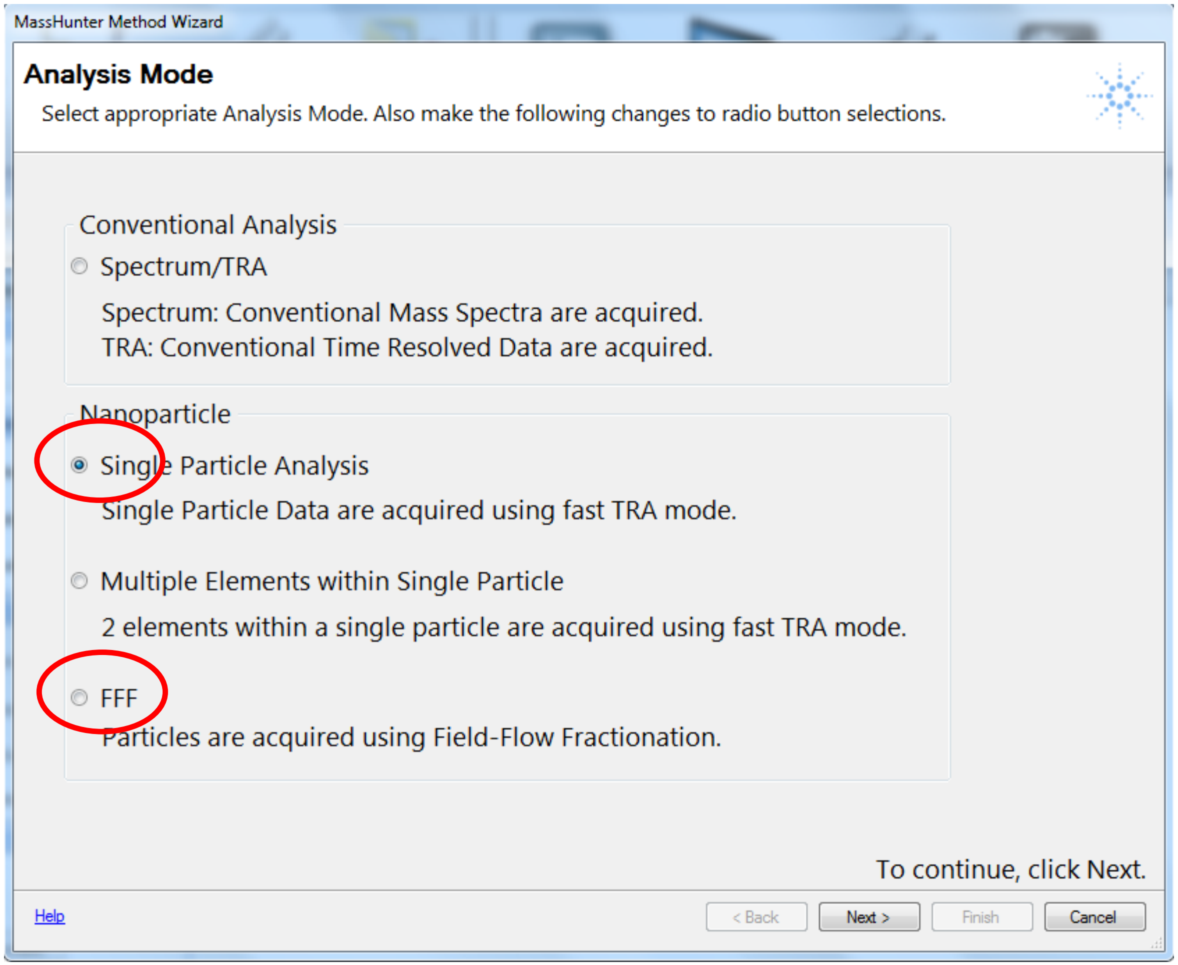
Single Particle-ICP-MS (spICP-MS)

- Uses normal sample intro system and TRA data collection method
- If sample is sufficiently dilute, each nanoparticle gives a distinct transient signal
- Particle concentration, particle size (diameter), size distribution and composition are obtained



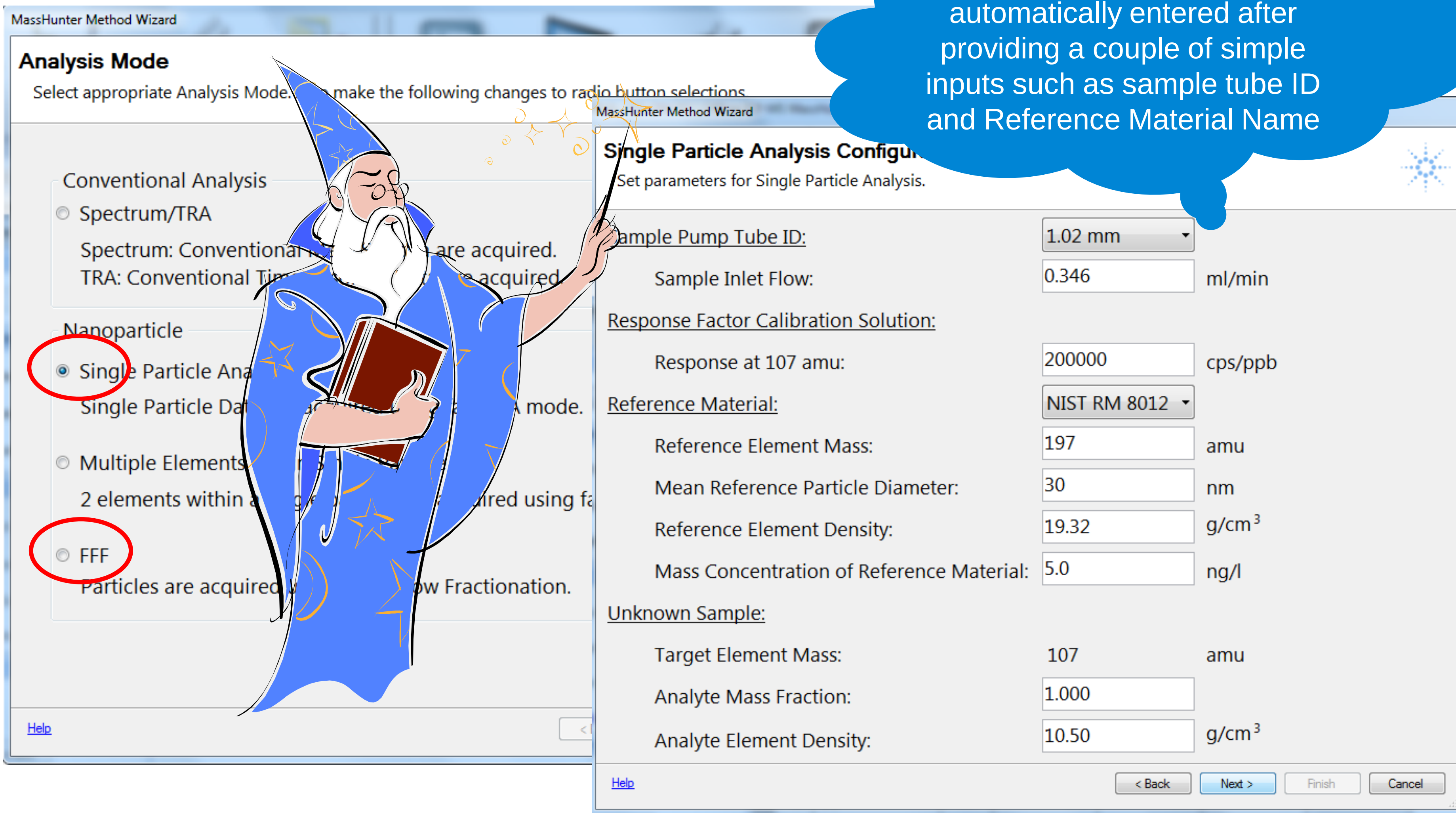


Method Wizard now supports nano analysis by both sNP and FFF modes

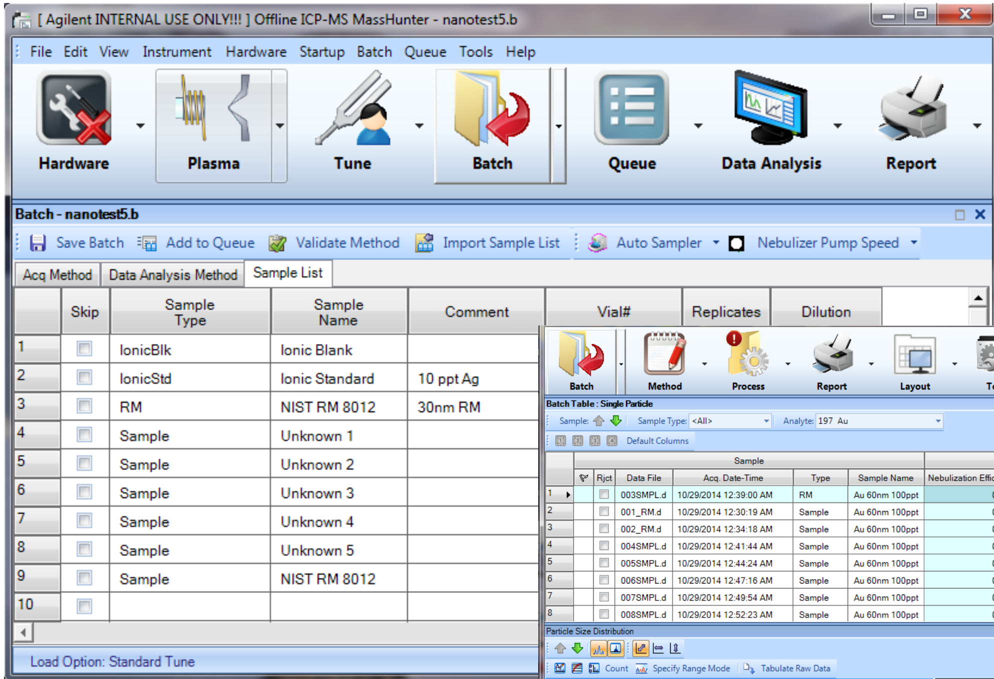


Method Wizard now supports nano analysis by both sNP and FFF modes

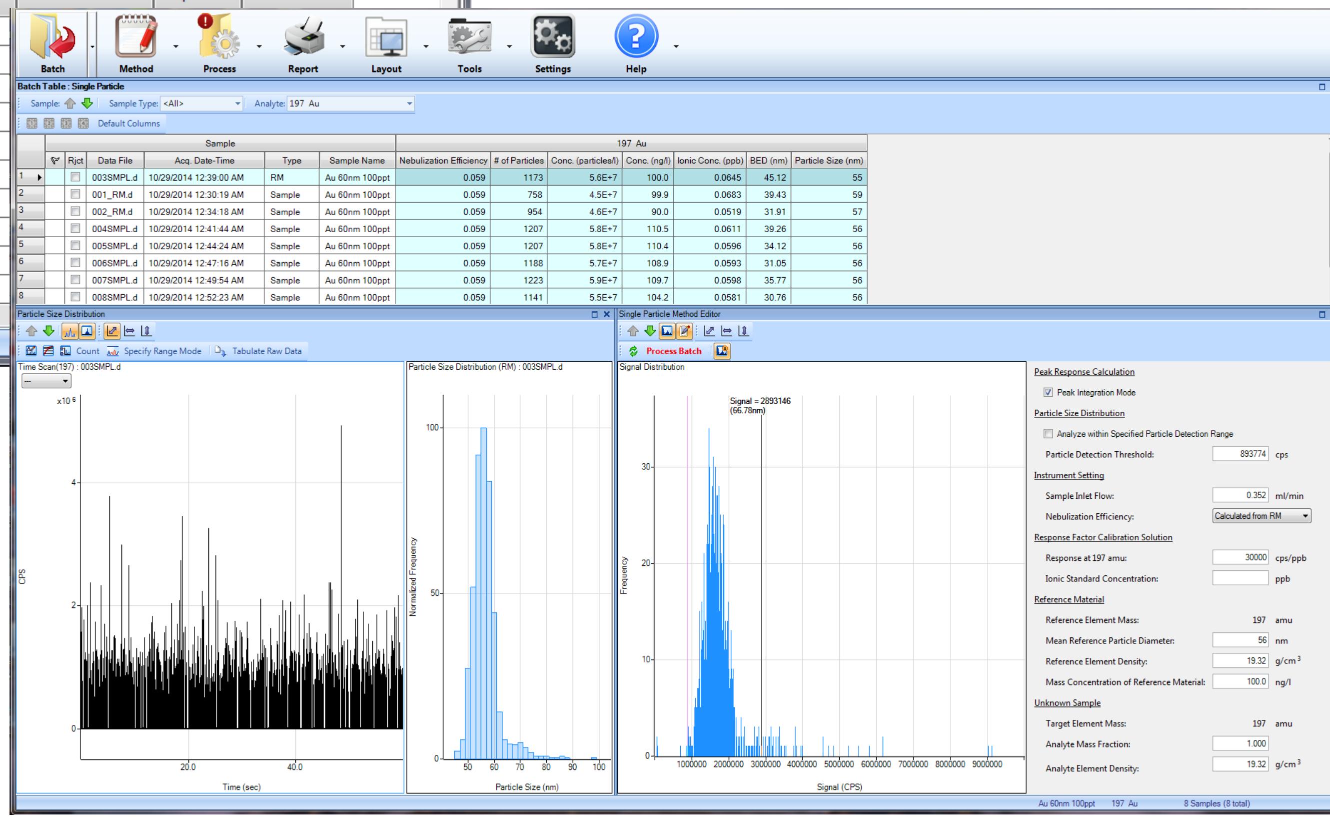
Most parameters are automatically entered after providing a couple of simple inputs such as sample tube ID and Reference Material Name



Just Complete the Sample List, Add it to the Queue…

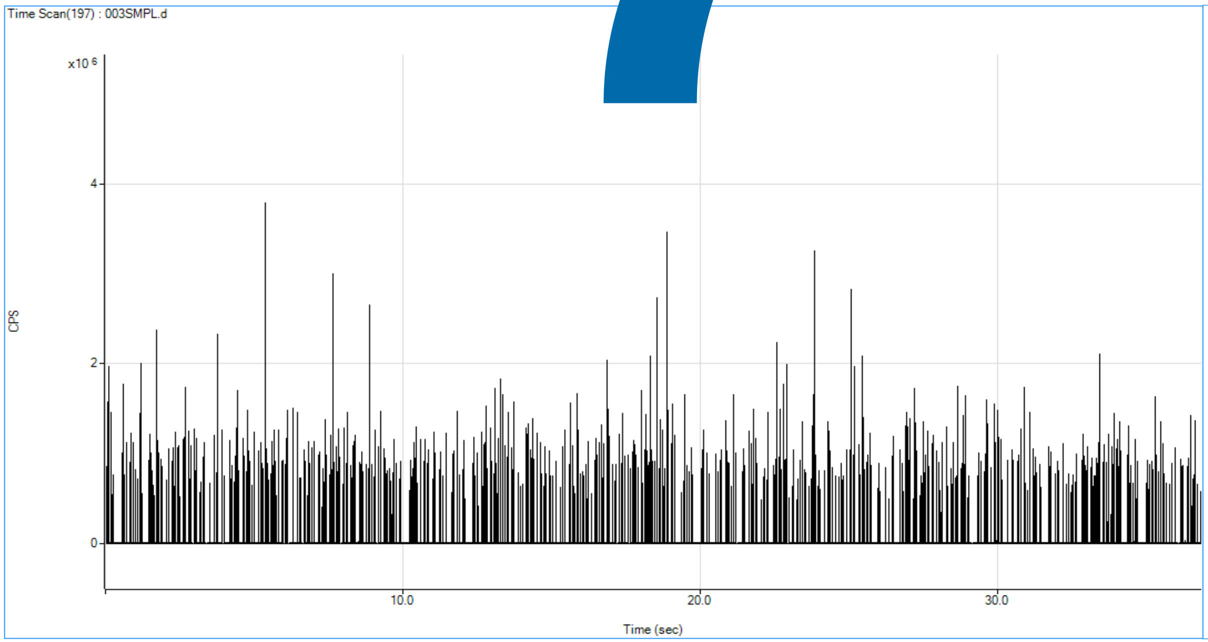


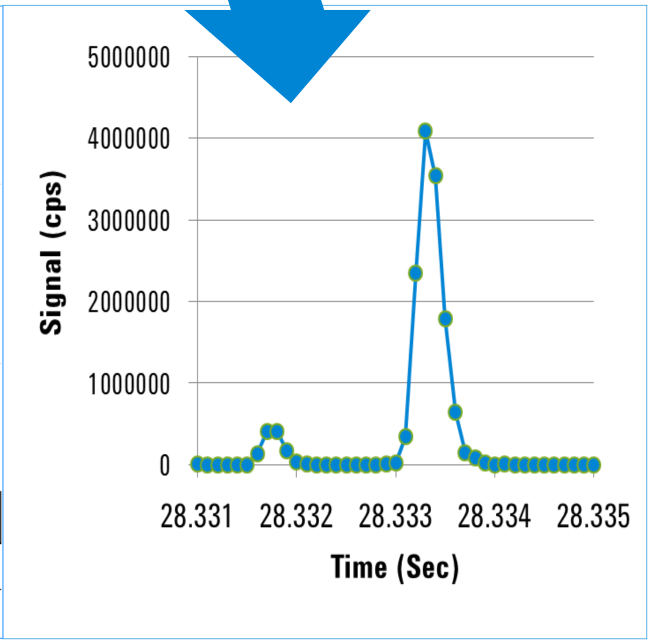
And Review the Results



100µs integration time and no settling time with the Agilent 8900 and 7900 captures all the data

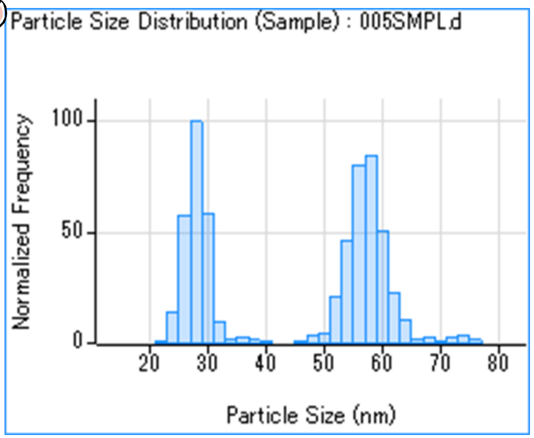
Zoom in…





Raw Data to Right Results in Seconds

Composite Sample	Observed concentration (particles/L)	Observed concentration (ng/L)	Prepared total concentration (ng/L)	Recovery
60nm (NIST 8013) 50 ng/L + 30nm (NIST 8012) 5 ng/L	4.78 x10^7	57.6	55	**105%**



Reference particle size by TEM (nm)	Observed particle size (nm)	Prepared particle number ratio (%)	Observed particle number ratio (%)
56.0±0.5	58	55.6	57.8
27.6±2.1	28	44.4	42.2

Determining Really Small Nanoparticles
What are the limitations and how can ICP-MS/MS solve them?

There are only 2 things that limit the minimum size nanoparticle that can be detected in single particle mode.

1. Sensitivity
2. Background (raw instrument background, spectral interferences, dissolved ionic background)

Everything else is secondary.

Nanoparticle size (diameter) is a function of the cube root of the mass. If the diameter of a particle is reduced by half, the mass and therefore the signal is reduced by 8X. HIGH SENSITIVITY IS THE CRITICAL FACTOR FOR DETECTING SMALL PARTICLES.

Background is also critical because nanoparticle peaks are detected as x times the signal to noise. Small peaks can be lost in the noise.


High sensitivity analysis of SiO_2 nanoparticles using the Agilent 8900 ICP-QQQ in MS/MS mode

Application note

Materials, environmental, food

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Introduction

Nanomaterials are increasingly used in industrial processes, manufactured goods, medicines, and consumer products such as cosmetics, sunscreen, and food. The measurement of nanoparticles (NPs) is the focus of attention because the fate of NPs in the environment and the potential for toxic effects once absorbed into the body are not yet well understood.

ICP-MS is a well-established technique for measuring the elemental content of materials; the relatively recent development of Single Particle acquisition mode (spICP-MS) now provides a powerful method to characterize the NP content of a sample. spICP-MS is used to record the target element signals generated from individual NPs in the solution analyzed, allowing simultaneous determination of the number, concentration, and size of particles present, as well as the dissolved element concentration. This approach has been developed by many researchers [1-4], and modern ICP-MS instruments can now offer automated acquisition and calibration approaches to support NP characterization. Current ICP-MS systems use short dwell times and acquire data continuously for a single isotope with no

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Agilent application note 5991-6596

Challenge of Si or Ti Measurement by Conventional (Single) Quadrupole ICP-MS

- **Interferences**
  - Si is interfered by C, N and O overlaps (ubiquitous in most aqueous/organic samples)
  - Ti is interfered by polyatomic overlaps in P, S, Si and C matrices

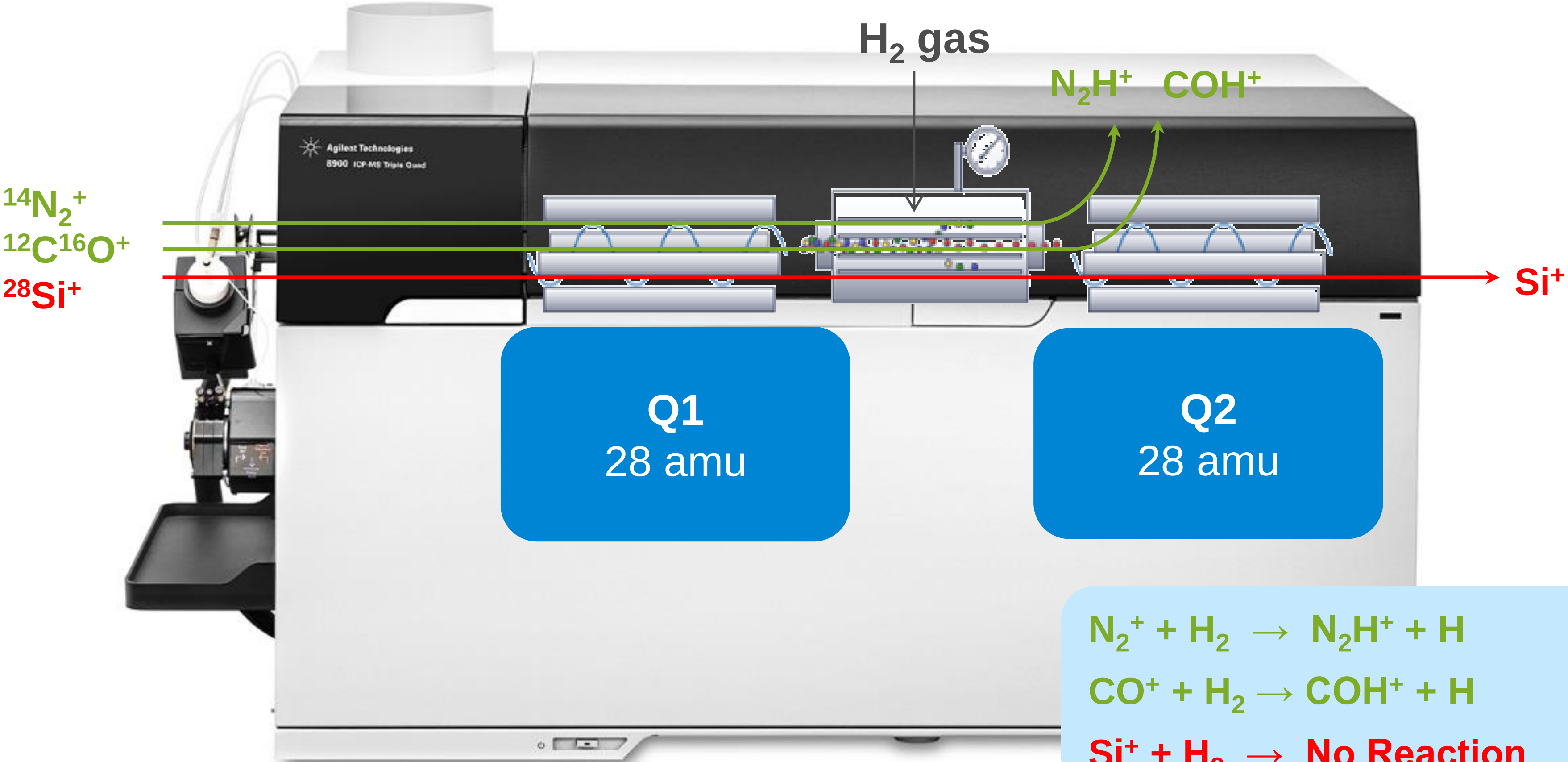
  These interferences make the analysis of SiO_2 or TiO_2 NPs in real samples difficult

- **^{48}Ti (74% abundance) cannot be measured reliably by ICP-QMS, due to the ^{48}Ca isobaric interference**
  - Less interfered ^{49}Ti (5.4% abundance) has less sensitivity, so detection of smaller particles is compromised

➡ ICP-MS/MS can solve these problems

ICP-MS/MS Technique for Si (On-Mass Method)

ICP-MS/MS uses two quadrupoles separated by a collision/reaction cell



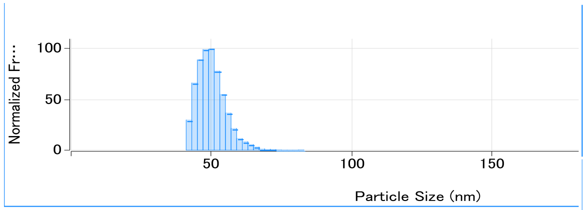
$N_2^+ + H_2 \rightarrow N_2H^+ + H$

$CO^+ + H_2 \rightarrow COH^+ + H$

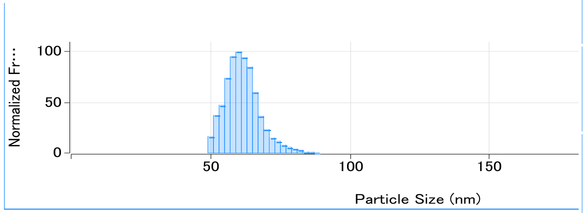
$Si^+ + H_2 \rightarrow$ **No Reaction**

SiO_2 Nanoparticle Reference Material Results

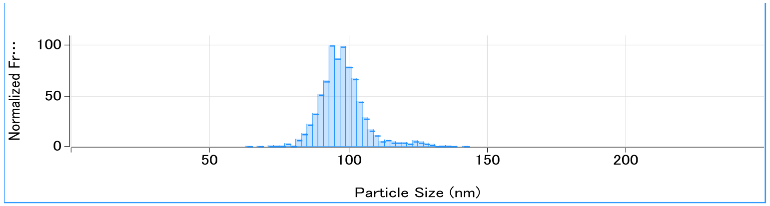
50 nm



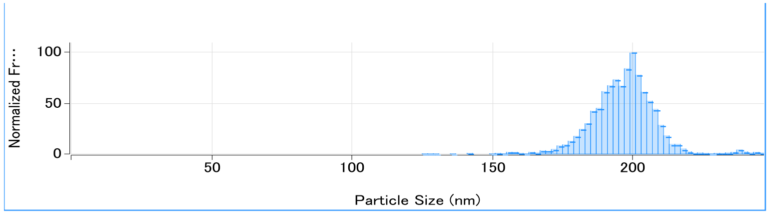
60 nm



100 nm



200 nm



Nominal size (nm)	Median size (nm)	Most Freq. Size (nm)	Mean Size (nm)	TEM Diameter (1) (nm)	BED (2) (nm)
50	49	50	49	46.3 ± 3.1	23
60	59	58	60	57.8 ± 3.5	22
100	99	100	100	97.0 ± 4.8	25
200	199	204	199	198.5 ± 10.5	25

(1) values supplied by nanoComposix

(2) Background equivalent diameter ~ size detection limit – most likely limited by dissolved Si.

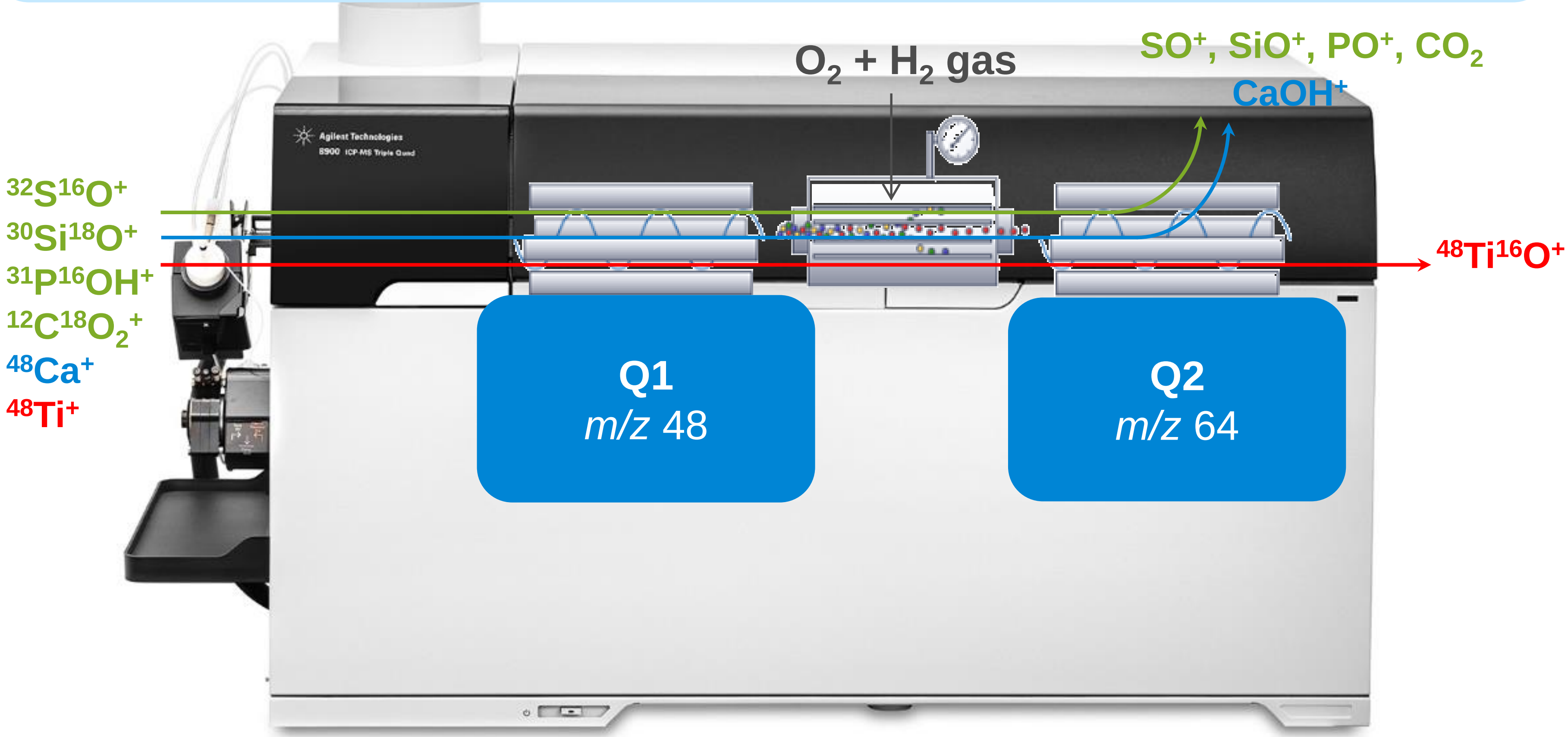
ICP-MS/MS Technique for Ti (Mass-Shift Method)

$SO^+ + O_2 \rightarrow$ No Reaction
$SiO^+ + O_2 \rightarrow$ No Reaction
$POH^+ \rightarrow PO^+ + H$ (collision)
$CO_2^+ + O_2 \rightarrow CO_2 + O_2^+$

$Ca^+ + O_2 \rightarrow CaO^+ + O$

→ $CaO^+ + H_2 \rightarrow CaOH^+ + H$

$Ti^+ + O_2 \rightarrow TiO^+ + O$



TiO_2 analysis - Interference Removal by O_2-H_2 Mode

Determining interferences in ionic matrix solutions

Mode	Sensitivity (cps/ppb)	**BEC (ppb)**	Quantitative result as Ti (ppb)					
			P 100 ppm	S 100 ppm	Ca 50 ppm	Si 50 ppm	Ethanol 0.1%	Matrix mixture
No gas	155000	**0.016**	1.7	6.0	225	0.39	0.14	261
$O_2 + H_2$	79000	**0.001**	0.010	0.001	0.18	0.054	0.001	0.023

No gas : Single Quad mode, Q2=48
$O_2 + H_2$: MS/MS mode, Q1=48, Q2=64

Advantage of $O_2 + H_2$ mode

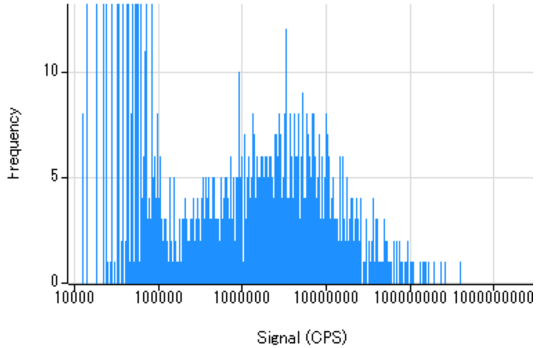
- Can use the most abundant isotope of Ti (mass 48, 73.7% relative abundance) for highest sensitivity
- Can remove almost all interferences including ^{48}Ca

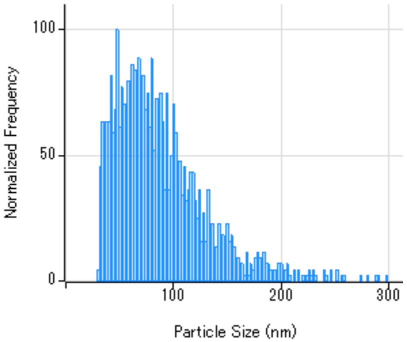
TiO_2 NPs in Matrix Samples

O_2-H_2 MS/MS mode

	Signal Distribution	Size Distribution	

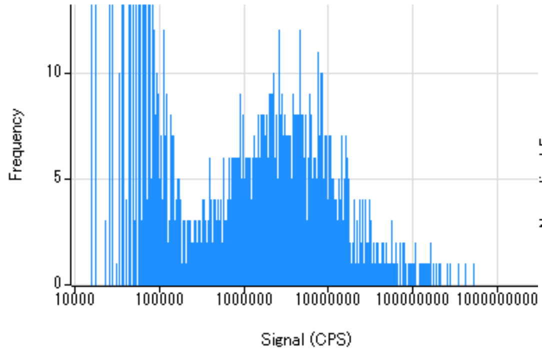
Sunscreen in DI water

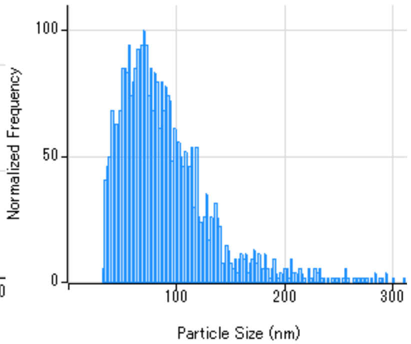




- Mean size : 77 nm
- BED : 16 nm

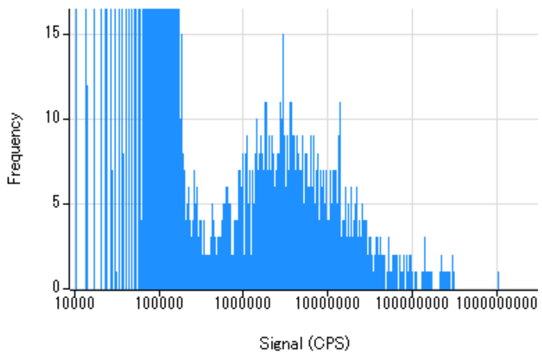
Sunscreen in tap water

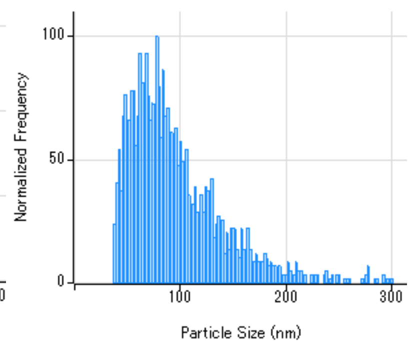




- Mean size : 79 nm
- BED : 10 nm

Sunscreen
in matrix mixture
(100 ppm S & P, 50 ppm Ca & Si, 0.1% ethanol)





- Mean size : 84 nm
- BED : 22 nm

Conclusions

The sp-ICP-MS/MS method with MS/MS for SiO_2 and TiO_2 nanoparticle analysis:

- Provides high sensitivity for Si and Ti
- Effectively eliminates polyatomic ions which interfere with Si or Ti analysis thereby significantly lowering the minimum detectable particle size even in complex matrices
- Permits the use of major isotopes (^{28}Si, ^{48}Ti), even in the presence of polyatomic and isobaric (^{48}Ca) overlaps
- Provides quick and accurate results for SiO_2 and TiO_2 particles smaller than 100 nm

Thank You