Flow Injection Single Particle Inductively Coupled Plasma Mass Spectrometry: A Simplified Approach for the Characterization of Metal-Based Nanoparticles

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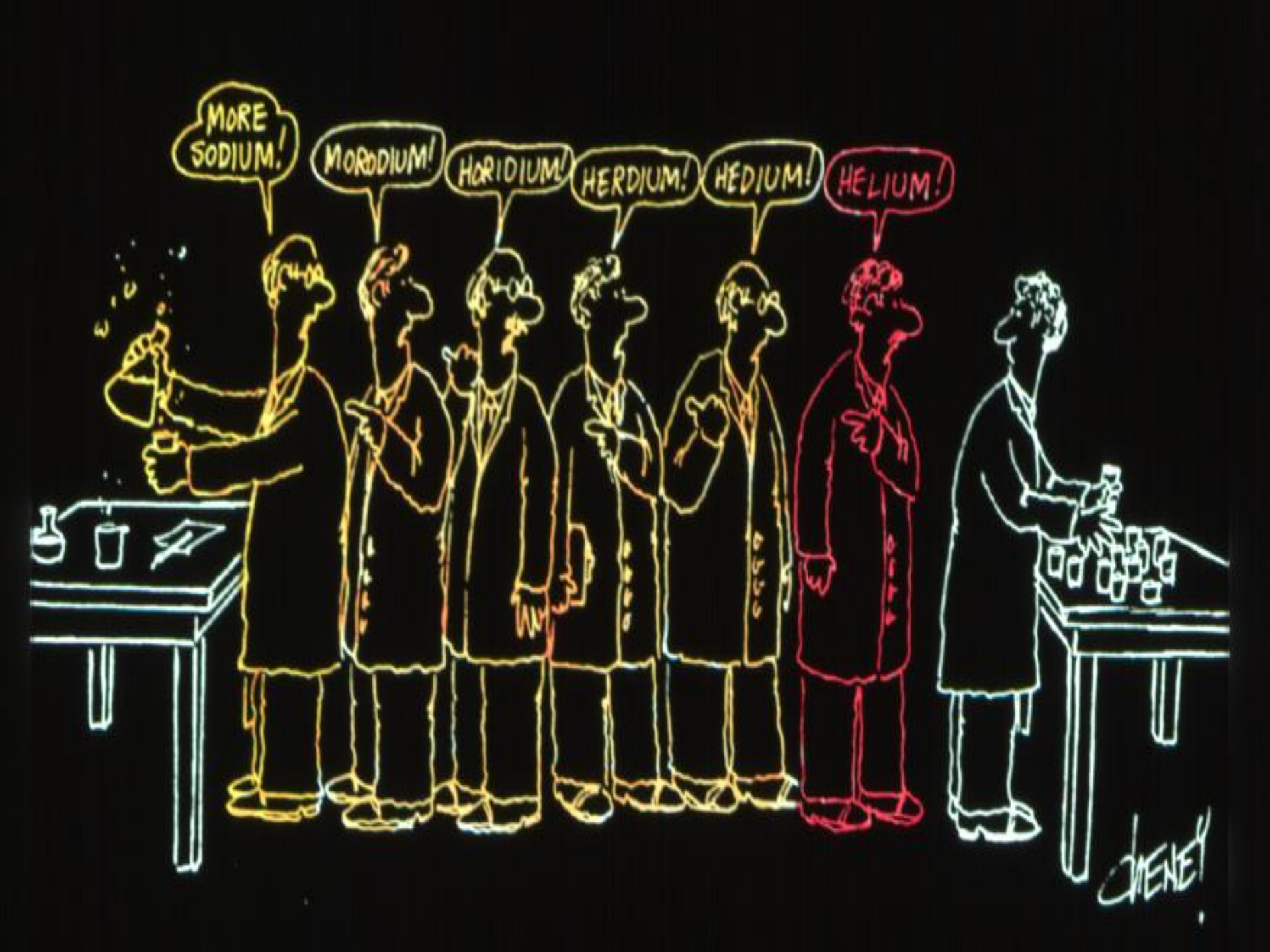

MORE SODIUM!
MORODIUM!
HORIDIUM!
HERDIUM!
HEDIUM!
HELIUM!
CHENEY

Nanoparticles (NPs):

- Possess at least one dimension between 1 and 100 nm.
- Have significantly larger specific surface area than their bulk solid or dissolved form counterparts.
- Have numerous applications
  - Cosmetics
  - Textiles
  - Energy production and storage

Use of NPs in fuel cells

- Efficiency of fuel cells may be improved by increasing the electrochemically active surface area through the loading of NPs on a substrate.
- Need to:
  - determine the NPs mass concentration
  - estimate NPs' size and size distribution.

Single particle inductively coupled plasma mass spectrometry (spICPMS)

- ICPMS operated in time-resolved analysis mode can detect individual particles
- Introduction of very dilute suspension of NPs
  - At the most one particle per droplet in the aerosol produced by nebulisation
    - **signal intensity spike generated for each individual particle following vaporization, atomization and ionization in the plasma.**

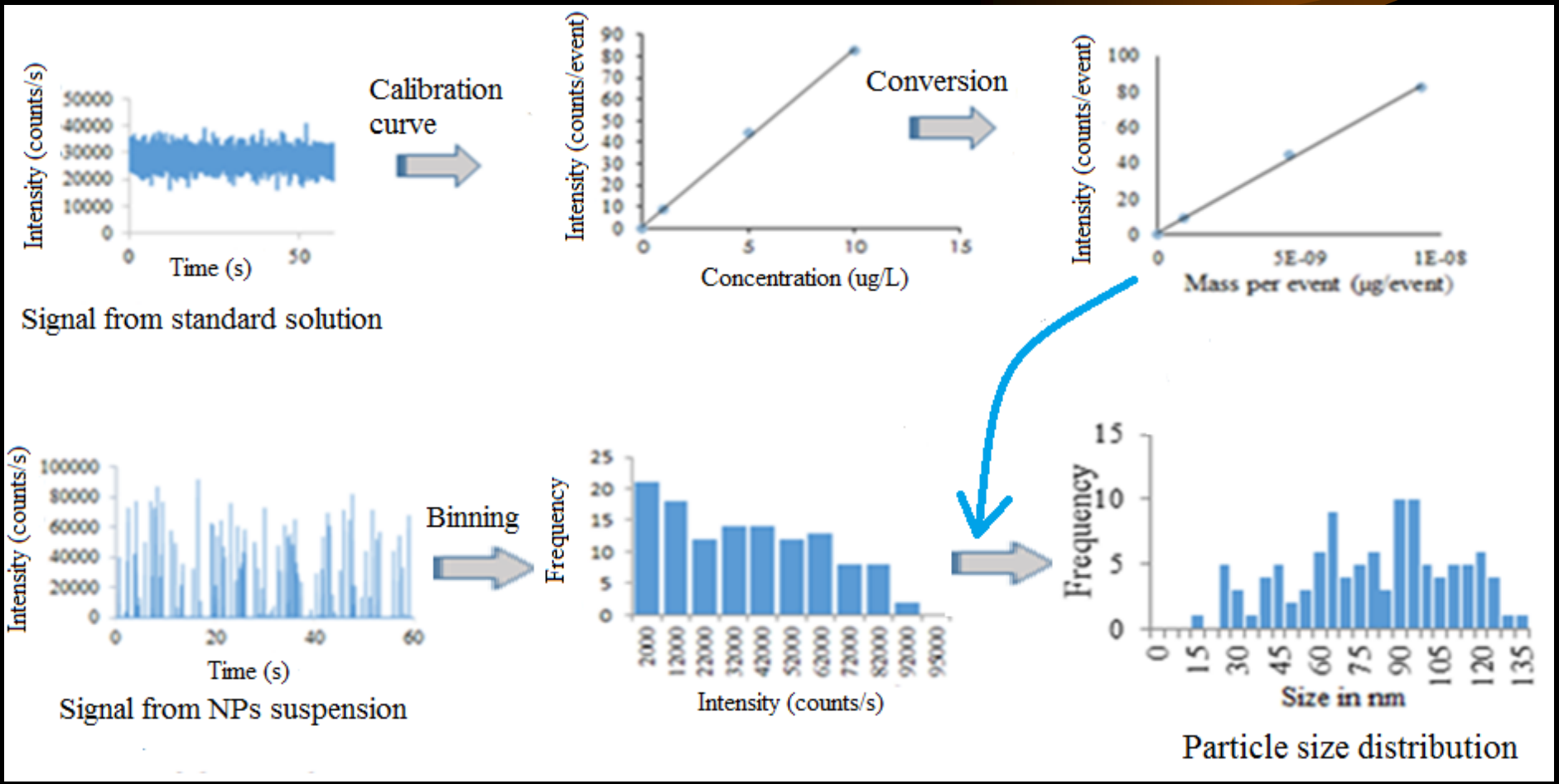
Use of spICPMS information

- Steady-state signal → dissolved metal concentration
- Frequency of pulses → particle number concentration
- Intensity of each pulse → particle mass
  - If the geometry of particles is known, then particle size can also be determined using the density of the bulk metal
    - For Au NPs, assuming a spherical geometry and full ionization of all NPs in the plasma

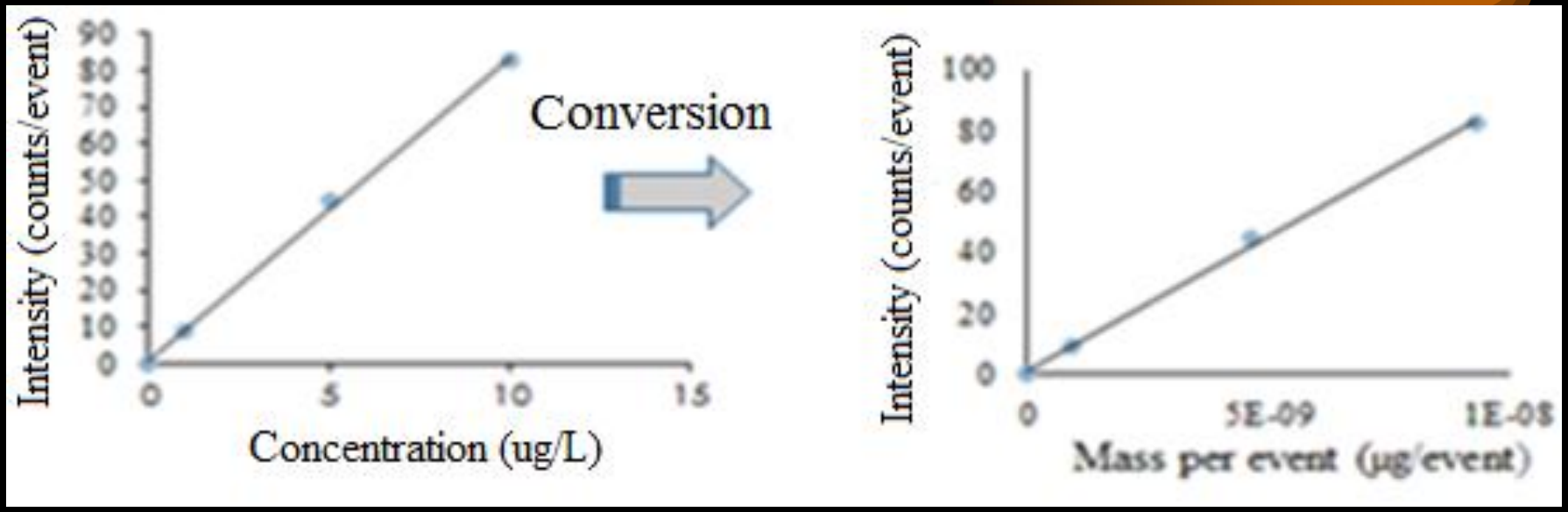
Discriminating NPs from the background

- Multiply signal intensity (in counts/s) of each measurement point by dwell time.
- Compute average intensity (μ) and standard deviation (σ) for the whole data set
  - all data points greater than (μ + 5σ) collected as NP events and removed from the data set.
- Process repeated with new (μ+ 5σ) of remaining data until no more particle events could be identified
  - remaining data correspond to the background signal, unresolved particles and dissolved analyte fraction.

Steps involved in spICPMS



Requirements for the conversion step



Mass per event = concentration × uptake rate × sample introduction efficiency × dwell time.

- Sample introduction efficiency must measured
- Sample uptake rate must be measured

Determination of sample introduction efficiency

- Load a known mass of dry silica gel into a 1-mL micropipette tip (cut so as to match the inner diameter of the torch injector)
- Attach it to the spray chamber to trap the aerosol exiting it.
- The ratio of the mass of solution trapped to that aspirated = sample introduction efficiency (or transport efficiency)
  - 5.2 ± 0.2% (n=3)

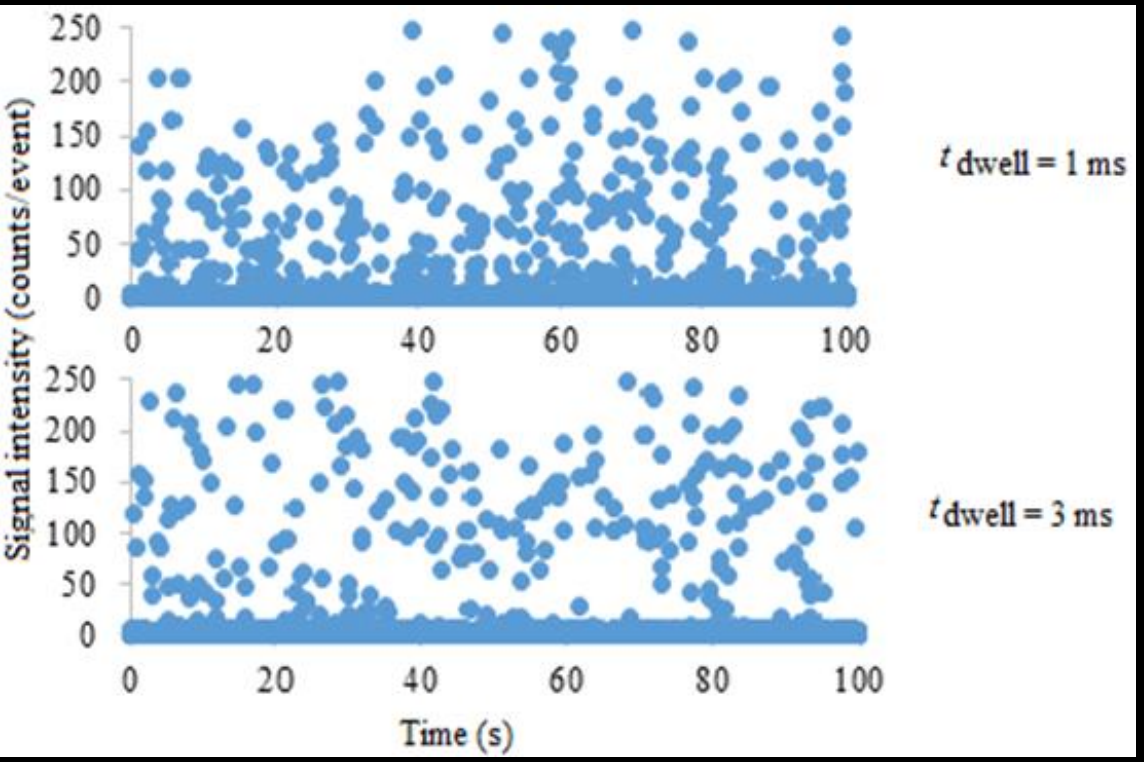
Measurement of sample uptake rate

- Measure the time taken to pump a known volume of solution to the nebulizer
- Sample uptake rate = aspirated volume/time taken (in mL/min).

Operating conditions

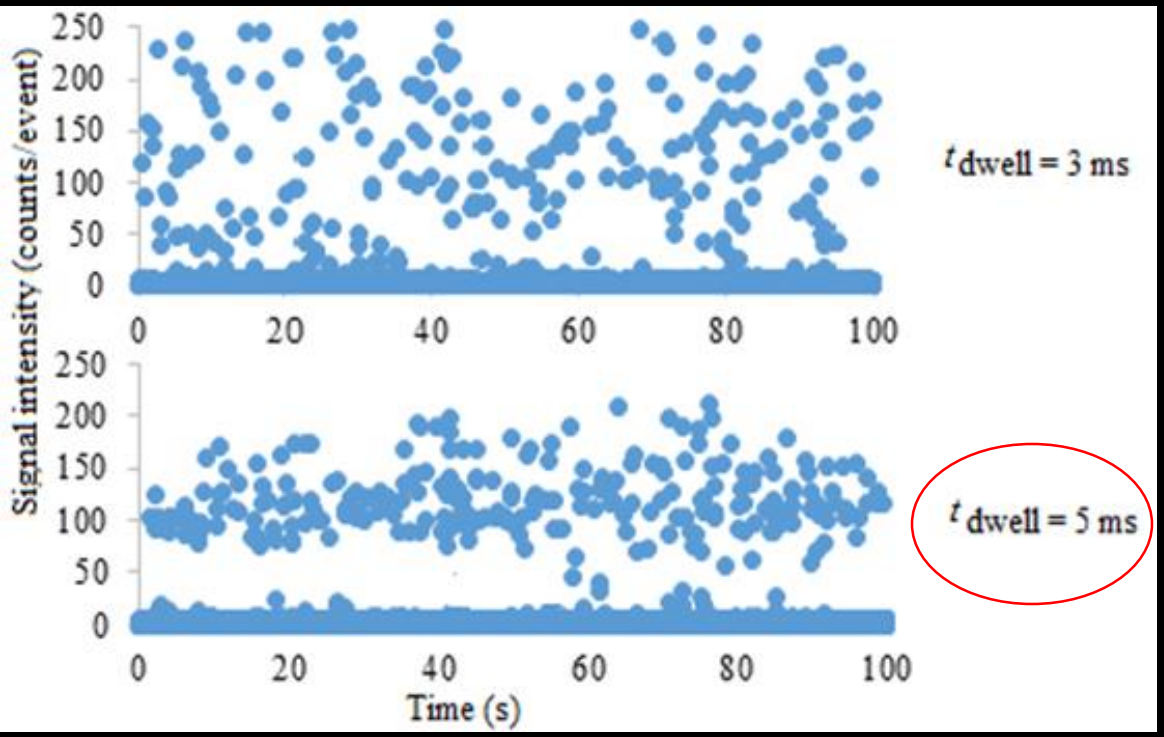
Parameter	Value
ICPMS instrument	Varian 820MS
Nebulizer	MicroMist concentric
Spray chamber	Peltier-cooled double-pass (0°C)
Ar plasma gas flow rate	18 L/min
Ar auxiliary gas flow rate	1.80 L/min
Ar sheath gas flow rate	0.04 L/min
Nebulizer gas flow rate	0.98 L/min
Sample uptake rate	0.25 mL/min
Sampling depth	5.5 mm
RF power	1.40 kW
Dwell time	5 ms
Monitored signal	$^{197}Au^{+}$

Effect of dwell time on the time-resolved signal from 60-nm Au NPs



- 1-ms dwell time
  - Lower mean intensities
  - Higher number of NPs
  - Partial measurement of ion clouds from NP
- Intensity from a NP should not depend on dwell time

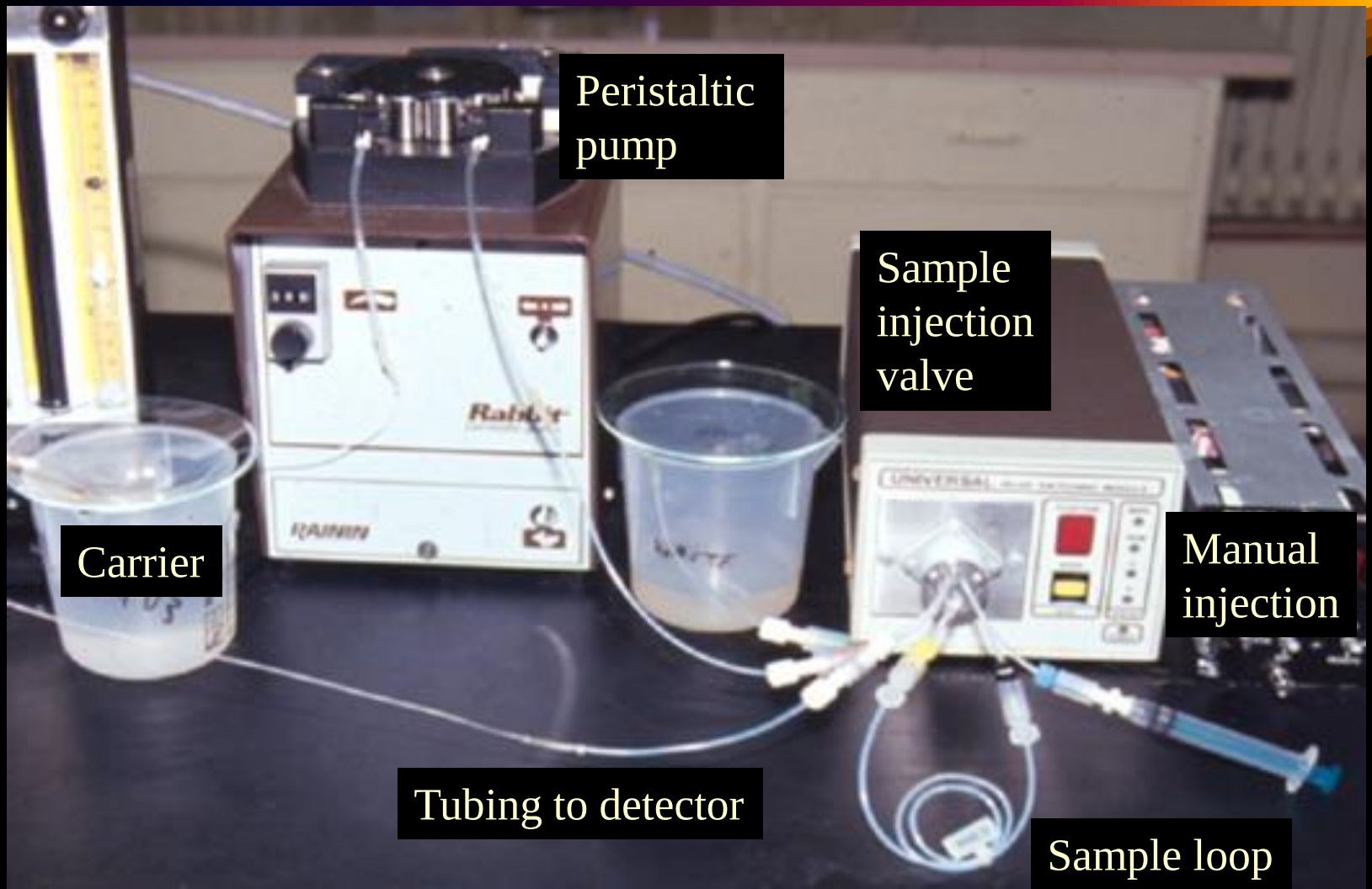
Effect of dwell time on the time-resolved signal from 60-nm Au NPs



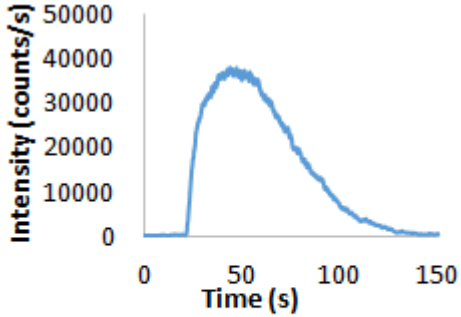
- Frequency of signal splitting drops at longer dwell time
- However, particles coincidence is more likely at longer dwell time

- Dwell time must be selected to minimize both NP splitting and coincidence of NPs
  - 5 ms resulted in relatively stable NPs signals

Example of flow injection set-up

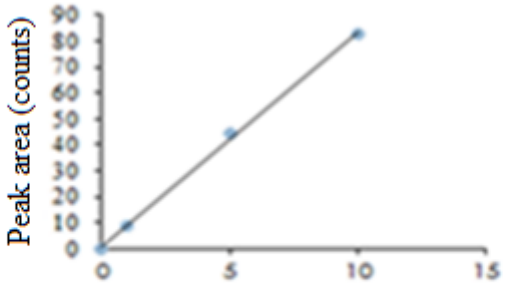


Steps involved in FI-spICPMS

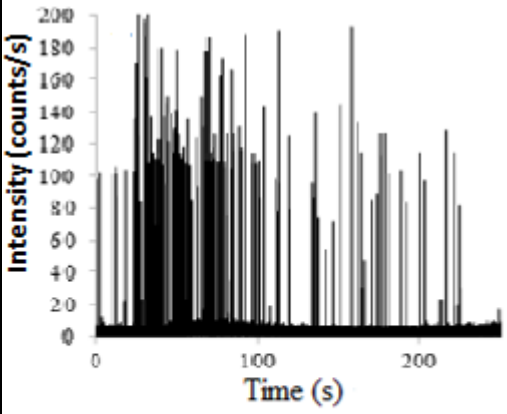


Signal from standard solution

Calibration curve

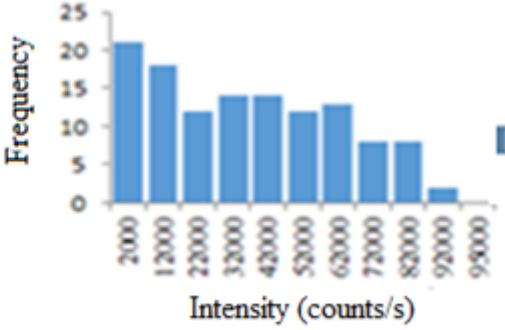


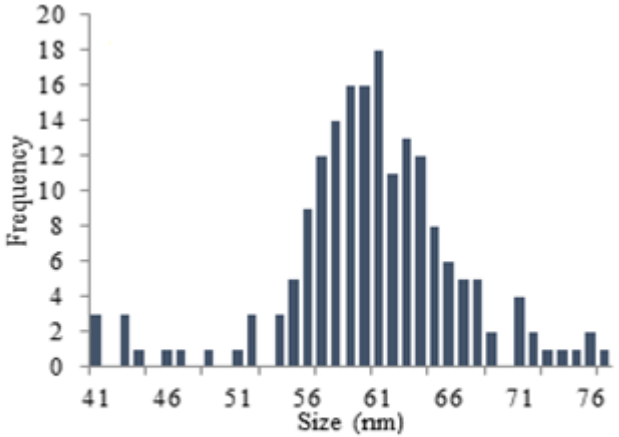
Blank-subtracted peak area of whole injection vs mass of Au injected (= volume × Au concentration)



Signal from NPs suspension

Binning





Particle size distribution

Sample used for this study

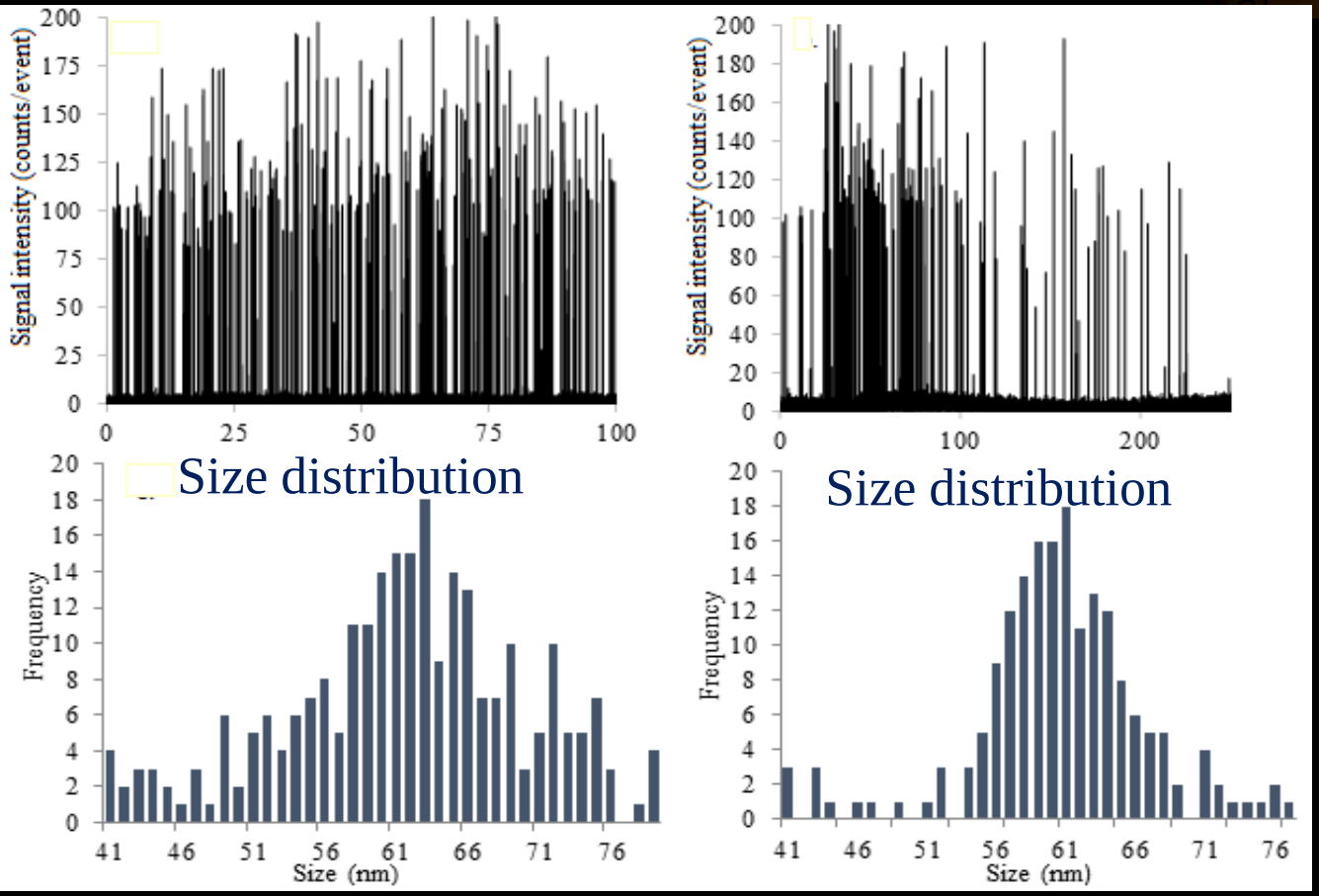
- Au NPs (nanoComposix (San Diego, CA, USA)
  - particle number concentration = 2.3×10^{10} particles/mL
  - solution concentration = 52 ppm Au
- Diluted 1,000,000 fold
  - Au NPs number concentration = 23,000 particles/mL
  - solution concentration = 52 ppt Au

Sample handling

- Commercial Au NPs suspension was diluted with high-purity water in polypropylene vials on the day of the analysis.
- Immediately prior to analysis, the diluted suspensions were sonicated for 10 min to ensure full dispersion of the NPs.
  - A few small blocks of ice were added to the ultrasonic bath to prevent temperature increase during sonication.

Comparison of spICPMS and FI-spICPMS for 60-nm Au NPs

spICPMS



FI-spICPMS

- With FI-spICPMS, no measurement of:
  - sample introduction efficiency
  - sample uptake rate

Effect of mass concentration on the measured diameter of 60-nm Au NPs

Mass concentration (ng/L)	Average diameter (nm)		Reference value* (nm)
	spICPMS	FI-spICPMS	
50	61.8 ± 0.9	60.2 ± 0.6	60.6 ± 6.0
100	64.4 ± 4.8	64.0 ± 4.2	
175	67.2 ± 7.3	66.4 ± 5.6	

* From transmission electron microscopy measurements

- Similar results with FI
- Better precision at greater dilution
  - Less NPs coincidence

- Detection limit (3σ, n=10): 20 nm with or without FI

Determination of NPs number concentration by spICPMS

- Sampling time = 100 s
- Number of NPs detected during 100 s = 421
- Number of NPs in 1 min = 253
- NPs number concentration = $f(I_p)/(q_{liq} \times TE)$ = 253/(0.25 × 0.05) = 20240 particles/mL
  - $f(I_p)$ = frequency of NP events (pulses/min)
  - q_{liq} = sample uptake rate = 0.25 mL/min
  - TE = transport efficiency = 0.050

Determination of NPs number concentration by FI-spICPMS

- 50-µL injection used to determine the transport efficiency
  - # of detected particles in 50 µL = 73
  - Expected # of particles in 50 µL = 23000 × 0.1 = 1150
  - TE = transport efficiency = 132/2300= 0.063
- 100-µL injection used to determine the NPs number concentration
  - # of detected particles in 100 µL = 132
  - NPs number concentration = 132/0.063 = 2095

60-nm Au NPs number concentration by spICPMS and FI-spICPMS (n=3)

Method	Transport efficiency	Measured NPs number/mL	Recovery (%)
spICPMS	0.052 ± 0.002	(2.011 ± 0.045) $\times 10^{10}$	87.5 ± 2.0
FI-spICPMS	0.057±0.006	(2.260 ± 0.080) $\times 10^{10}$	96.2 ± 3.5

- Better recovery with FI
- No measurement of sample uptake rate
  - Eliminates one source of error

Additional feature of FI-spICPMS

- Verification of mass balance can readily be done with the injection of a standard of NPs
  - With 100-µL loop: 5.20×10^{-6} µg of Au injected
  - $(4.97 \pm 0.05) \times 10^{-6}$ µg of Au measured
  - Recovery = 95.6 ± 1.0 %
- With spICPMS, mass balance is time-dependent
  - Assumes no change in sample uptake rate
- No need to know the sample uptake rate with FI-spICPMS

Conclusions

- FI-spICPMS provides similar results to spICPMS without requiring a measurement of the sample uptake rate.
- If only the mass of particles is desired, then measurement of the sample introduction efficiency is also not required with FI-spICPMS

ACKNOWLEDGEMENTS

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