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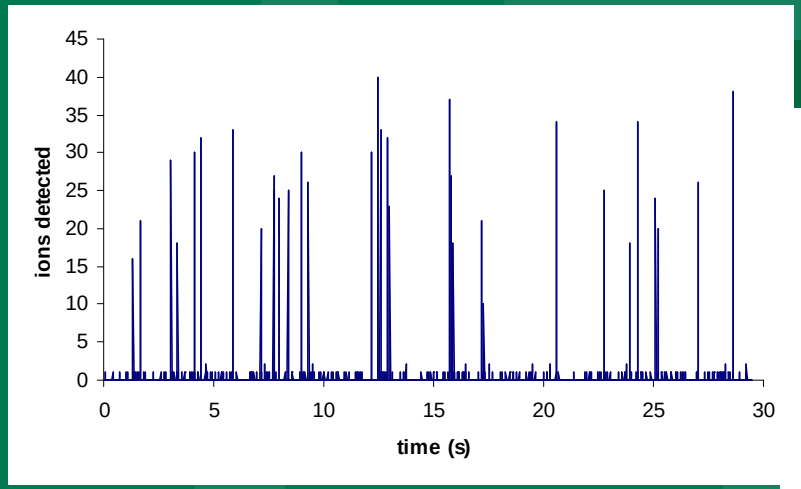
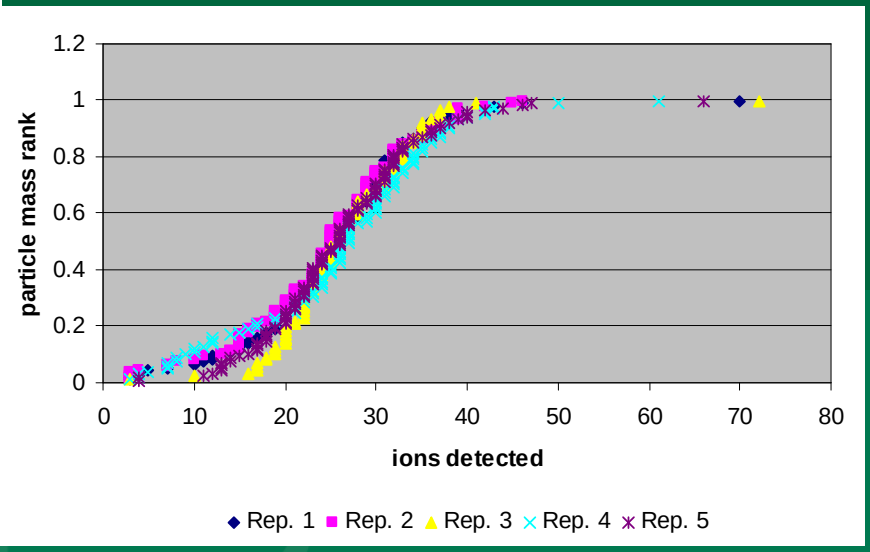
Recent applications of single particle - inductively coupled plasma for metal-based nanomaterial determinations in surface water

National Exposure Research Laboratory

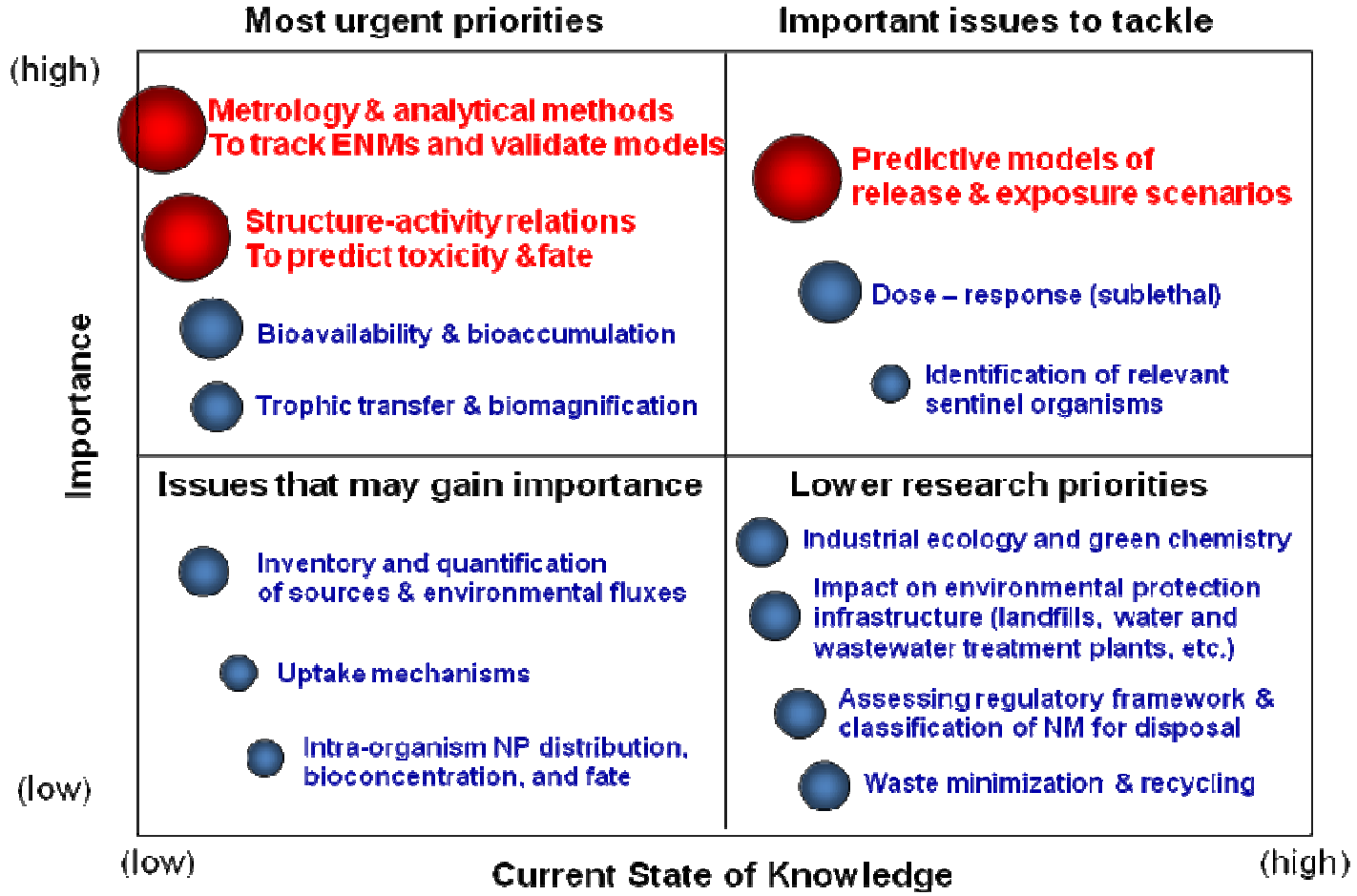
U.S. Environmental Protection Agency

Ed Heithmar



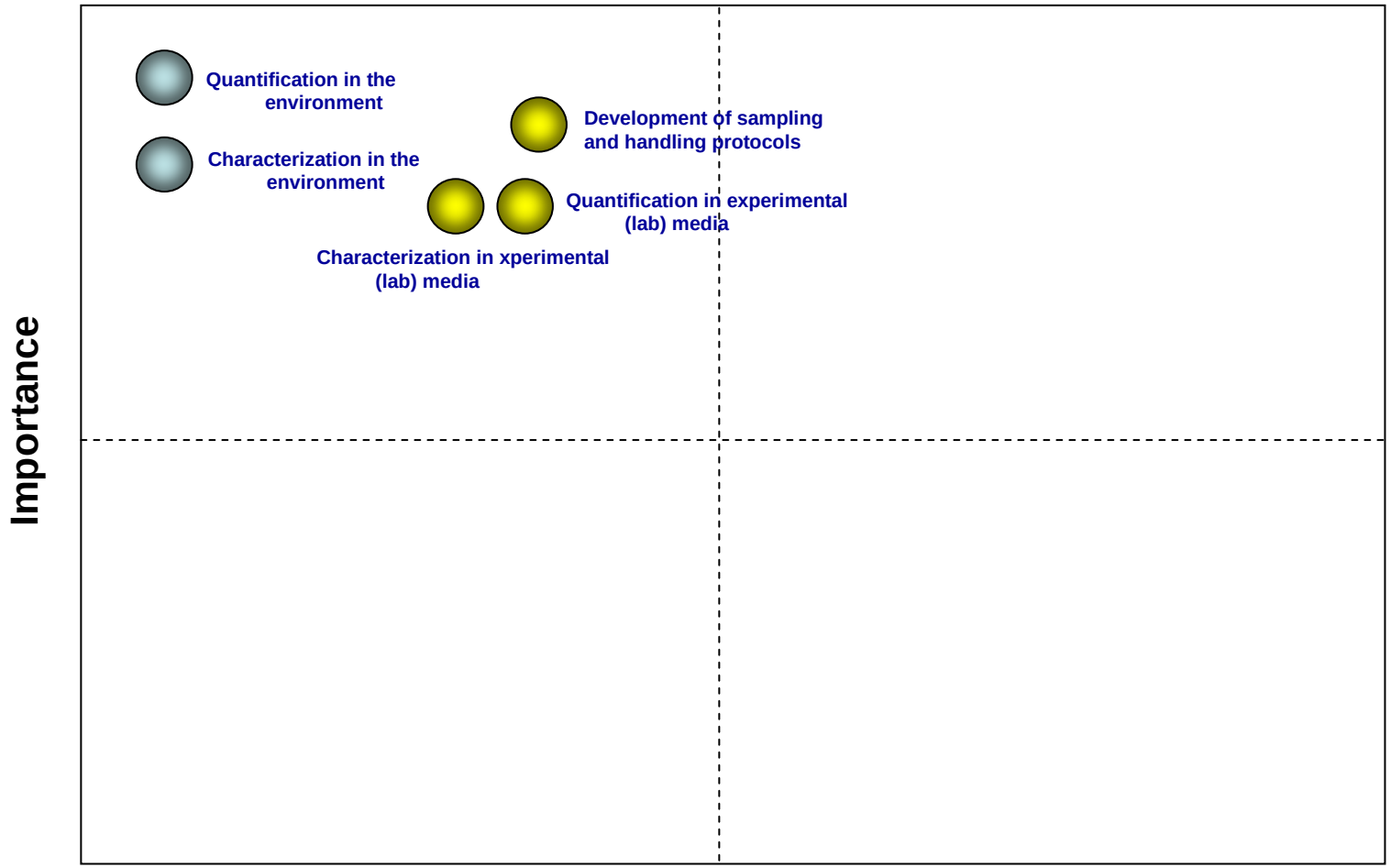


Consensus ranking of priorities for ENM EH&S research



ICON Workshop on the Eco-Responsible Design of ENMs. With permission: Alvarez, P. J. J., V. Colvin, et al. (2009). "Research Priorities to Advance Eco-Responsible Nanotechnology." ACS Nano 3(7): 1616-1619.

Ranking metrology research needs



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Measuring metal-based ENMs in the environment

- Ensemble methods allow representative samples, provide good particle size resolution. high elemental sensitivity.
    - Light-scattering methods are useful for characterizing starting materials and, in limited cases, simple experimental systems.
    - Hyphenated methods, e.g., flow-field flow fractionation coupled with ICPMS, offer higher sensitivity and elemental selectivity, so are more useful for characterizing metal-based ENMs in complex media.

- Ensemble methods provide total metal concentration associated with a size fraction of nanoparticles.

- Single particle – ICPMS is a complementary method to ensemble methods.

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SP-ICPMS - complementary to hyphenated methods

SP-ICPMS

- Provides concentration of metal-based nanoparticles, and mass of metal in each nanoparticle.
- No direct information on particle diameters.

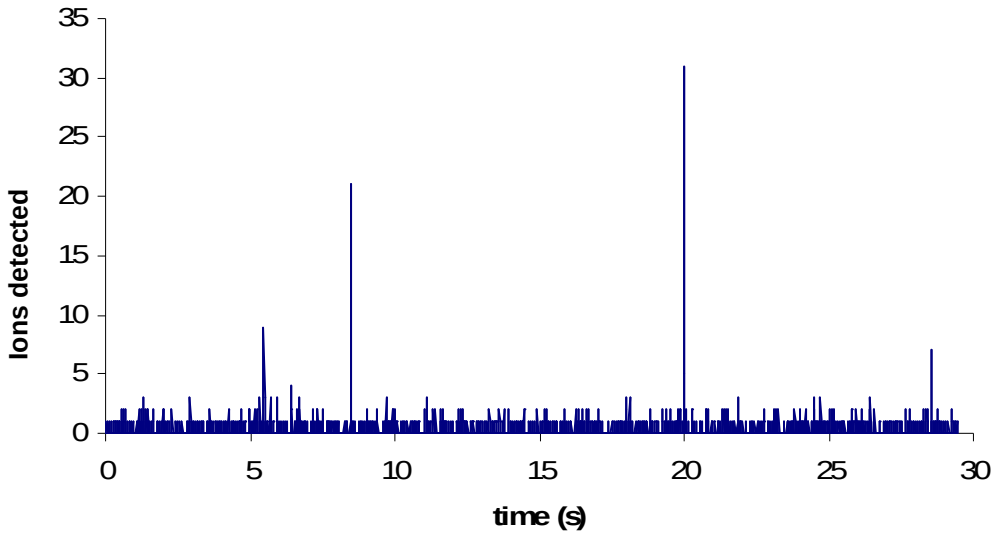
Hyphenated Methods

- Provide separation of nanoparticles according to hydrodynamic diameter, and determines total metal concentration associated with each nanoparticle size.
- No direct information on number or composition of metal-based nanoparticles.

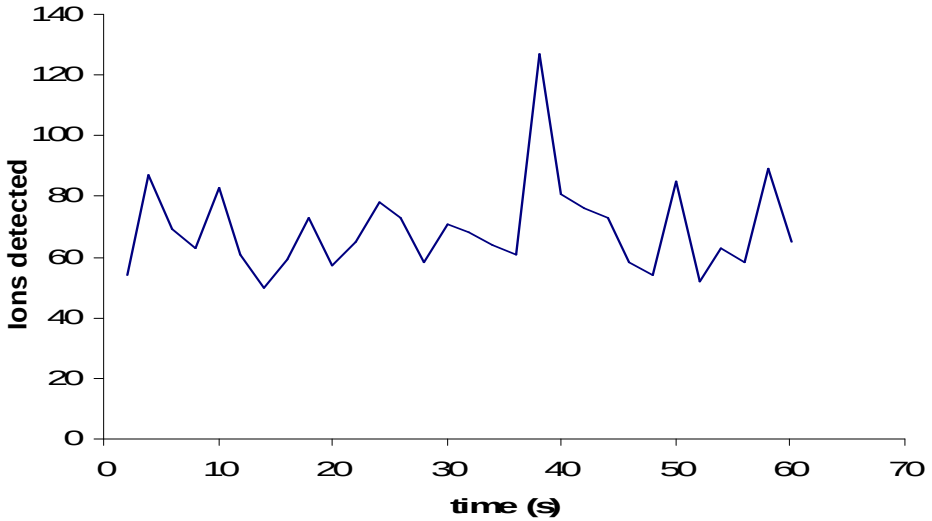
Conventional ICPMS analysis – long integration time improves S/N

30 pg mL^{-1} dissolved gold

0.01 s integration



2 s integration



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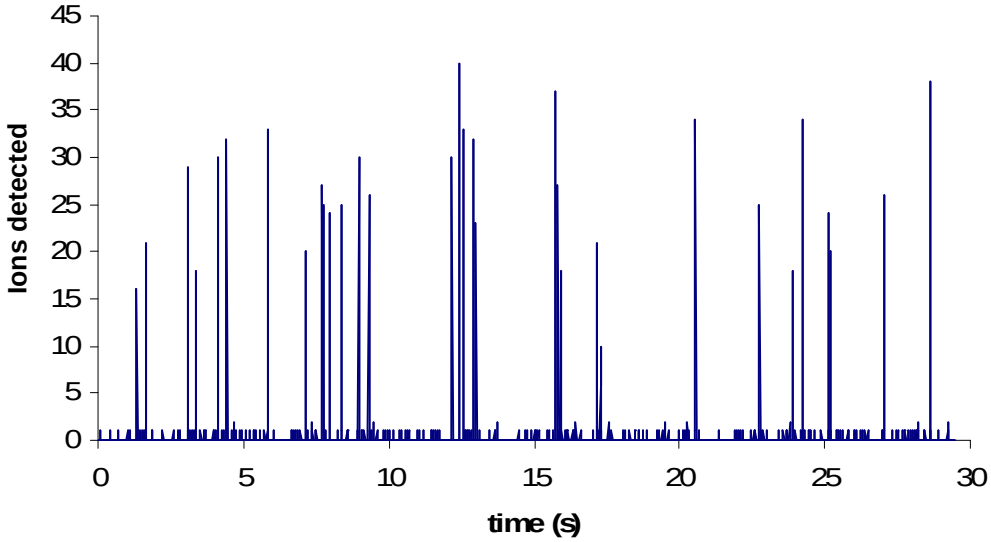
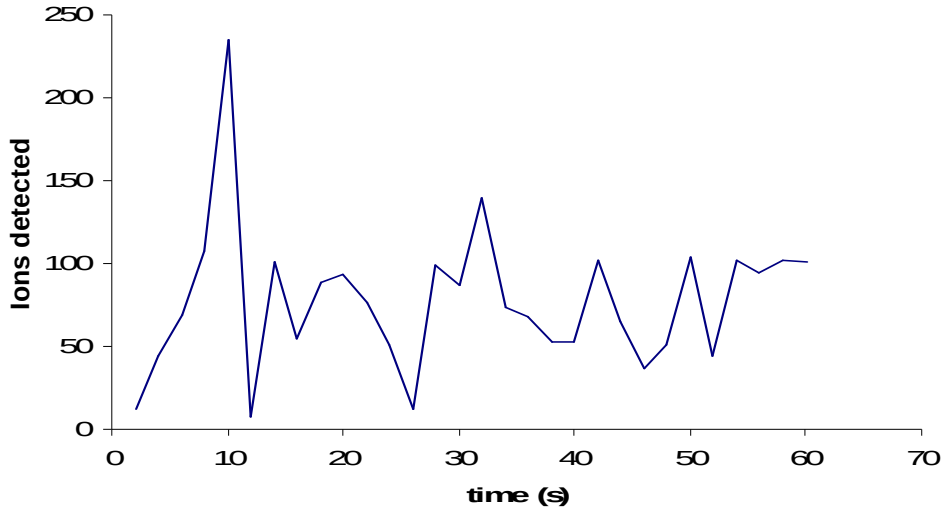
Single particle - ICPMS analysis

30 pg mL^{-1} 50 nm gold nanoparticles

0.01 s integration



2 s integration



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Keys to SP-ICPMS

- ICPMS sensitivity is the same for dissolved element and element in nanoparticle.
- Each ion pulse is produced by a single nanoparticle (assuming low nanoparticle concentration).
- Number of ion pulses counted during total acquisition time is proportional to nanoparticle concentration in sample.
  - This proportionality is the same for all elements, so only one nanoparticle standard of any element detectable by ICPMS is needed.
- Number of ions in each pulse is proportional to the mass of the element in the nanoparticle that produced the pulse.
  - A conventional ICPMS analysis with standard of dissolved element (along with the particle proportionality determined above) establishes the proportionality.
- Shorter integration times per point improve nanoparticle concentration dynamic range, as well as nanoparticle elemental mass S/N.

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Potential Applications of SP-ICPMS

- Characterizing metal-based ENMs in experimental test media.
  - – High particle concentration sensitivity allows characterizing ENMs at environmentally relevant concentrations.
  - – Elemental selectivity allows characterizing ENMs in presence of large amounts of background particles.
- Monitoring transformation processes.
  - – Transformations at low particle concentrations can be monitored.
  - – Rates of fast transformations can be monitored.
- Screening environmental waters for potential metal-based ENMs.
  - – Cannot selectively identify ENMs.
  - – Rapidly identifies “suspect” water samples for more definitive analysis.

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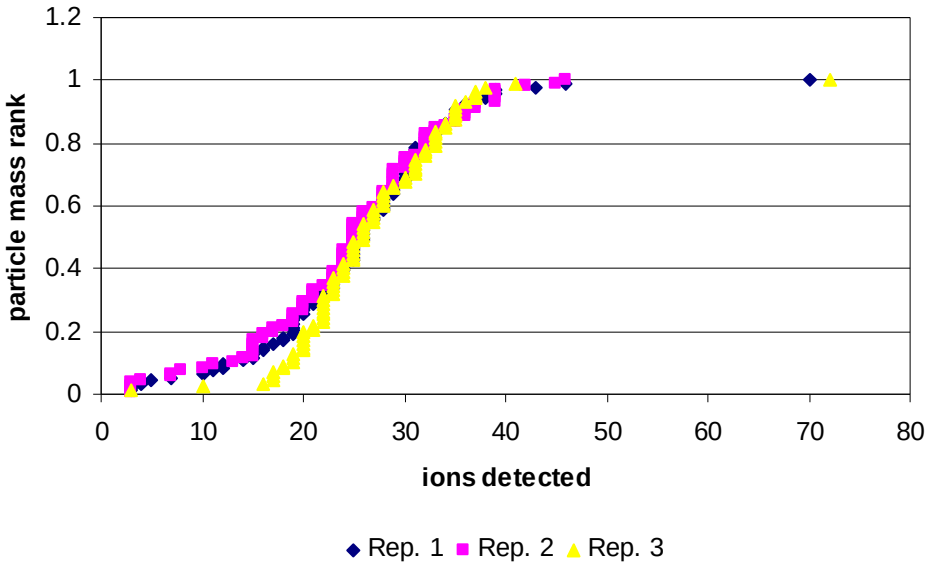
Measuring low concentration ENMs

Replicate analyses of
50 nm Au - $4x10^3$ mL^{-1} (5 ng L^{-1})



Particle statistics

	mean # ions	# particles
Rep. 1	25.6	94
Rep. 2	25.0	105
Rep. 3	26.4	87

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Measuring low concentration ENMs in complex media

Replicate analyses of
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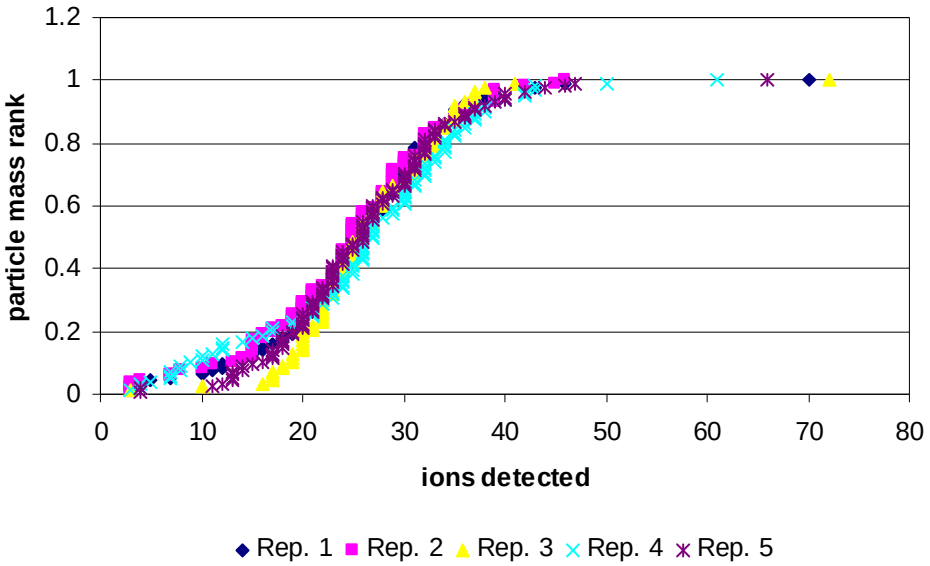

Particle statistics

	mean # ions	# particles
Rep. 1	25.6	94
Rep. 2	25.0	105
Rep. 3	26.4	87
Rep. 4	26.3	101
Rep. 5	25.9	115
Mean	25.8	101
%rsd	2.2[1]	11

[1]Corresponds to less than 0.8% rsd in diameter.

Replicates 4 & 5 analyzed in 5x10^7 silver particles

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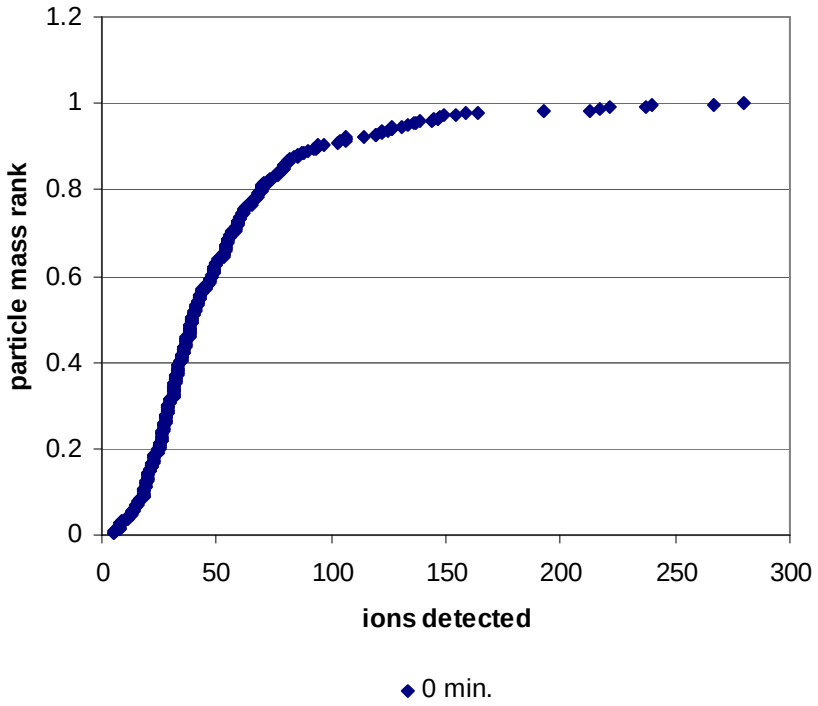
Monitoring aggregation of Ag by $CaCl_2$

$4x10^8$ mL^{-1} Ag (60 nm) + 200 mM $CaCl_2$



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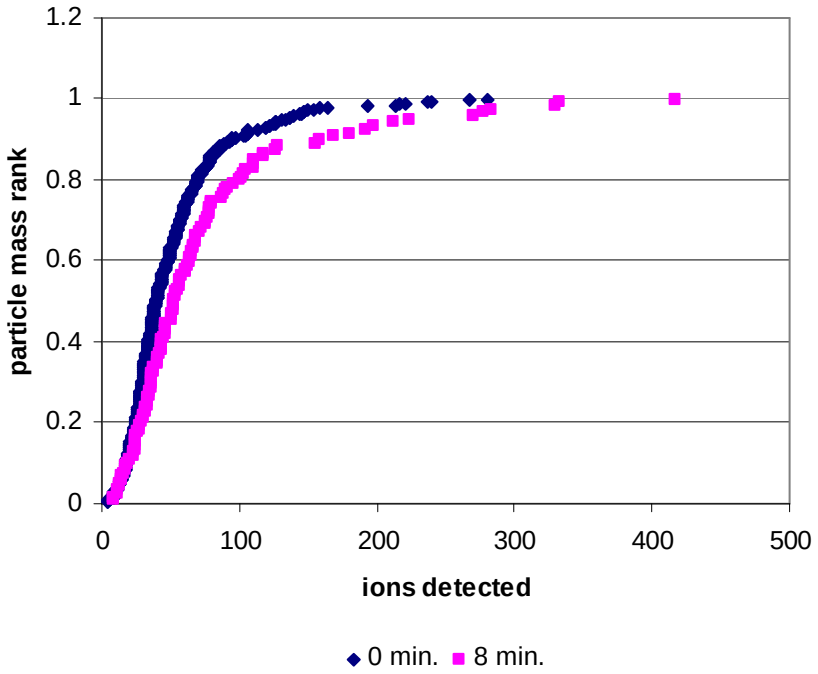

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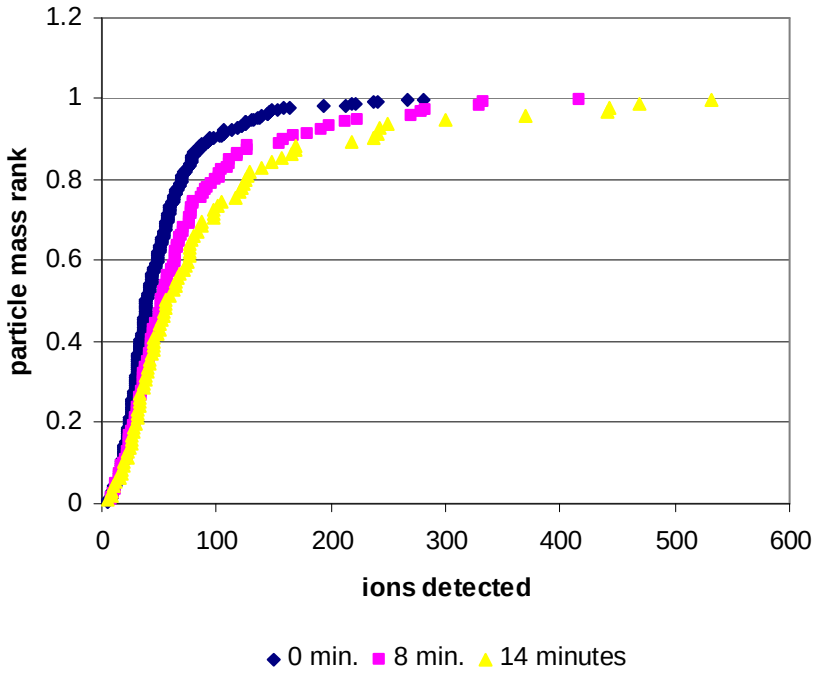

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Feasibility study of screening Las Vegas Wash water for metal-based ENMs

- Filtering media evaluated.
- Las Vegas Wash sampled at 36°06.826’ N, 115°08.741’, ca. 1 mile downstream from Las Vegas Strip.
- 10 mL water filtered in the field and analyzed within 4 hours.

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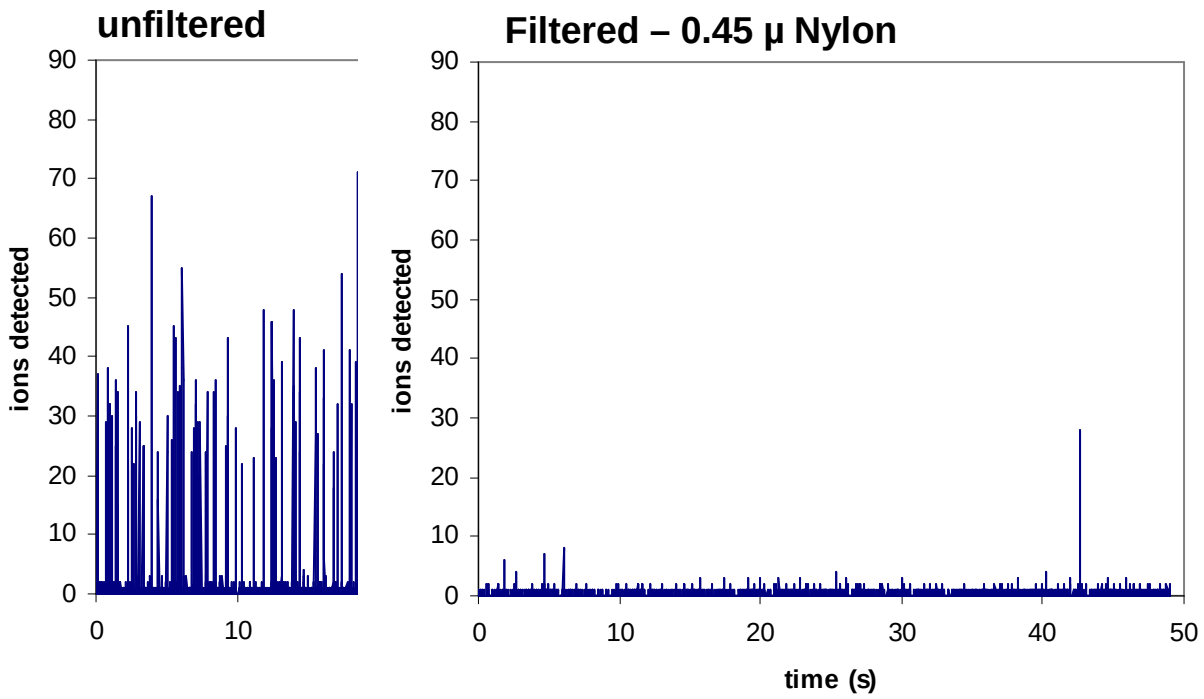
Effect of 0.45µfiltering on recovery of 50 nm Au in reagent water



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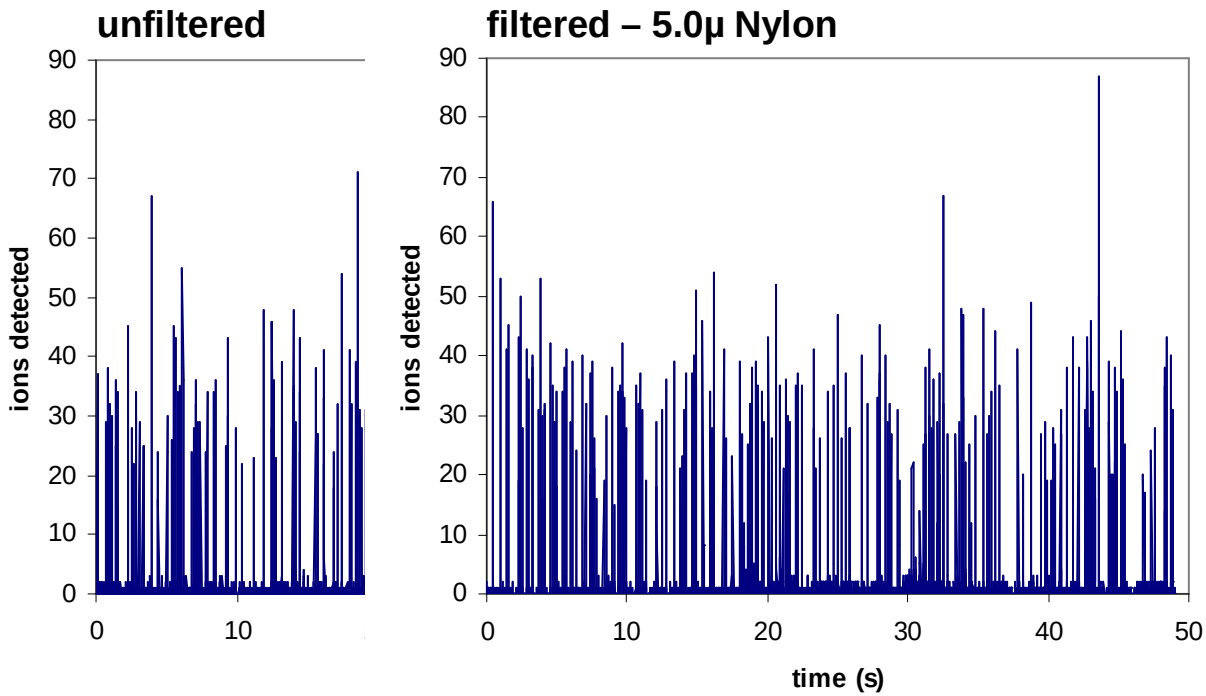
Effect of 5µfiltering on recovery of 50 nm Au in reagent water



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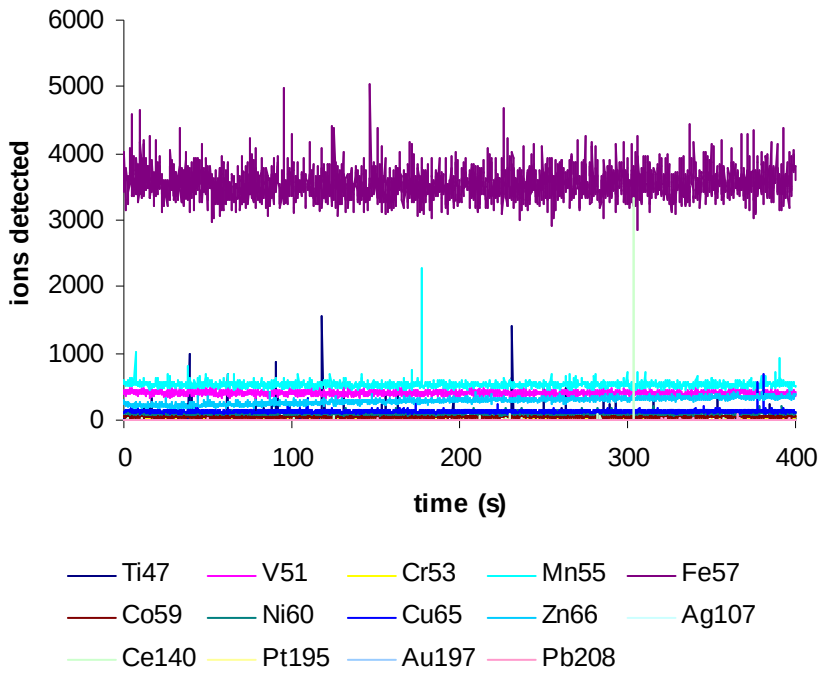
SP-ICPMS analysis of Las Vegas Wash water for 14 elements



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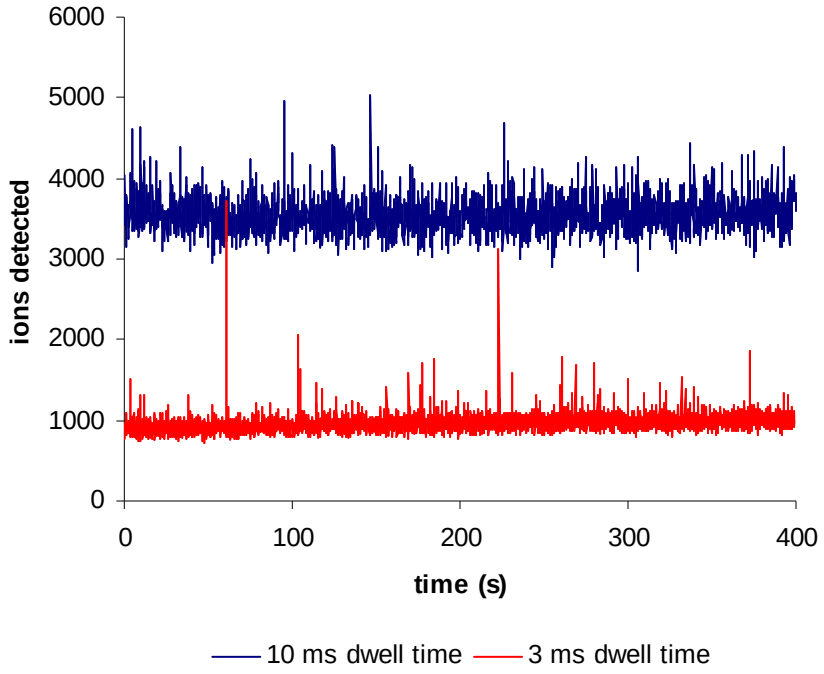
SP-ICPMS analysis of Las Vegas Wash water for iron-containing nanoparticles



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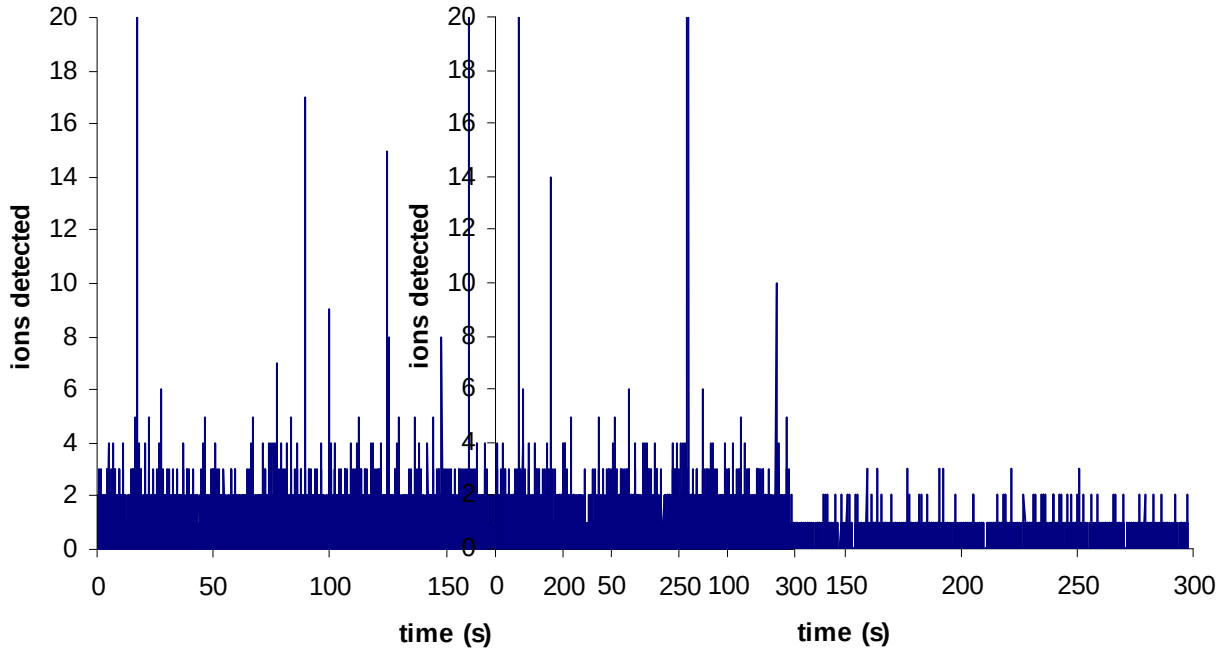
Silver-containing nanoparticles in Las Vegas Wash water



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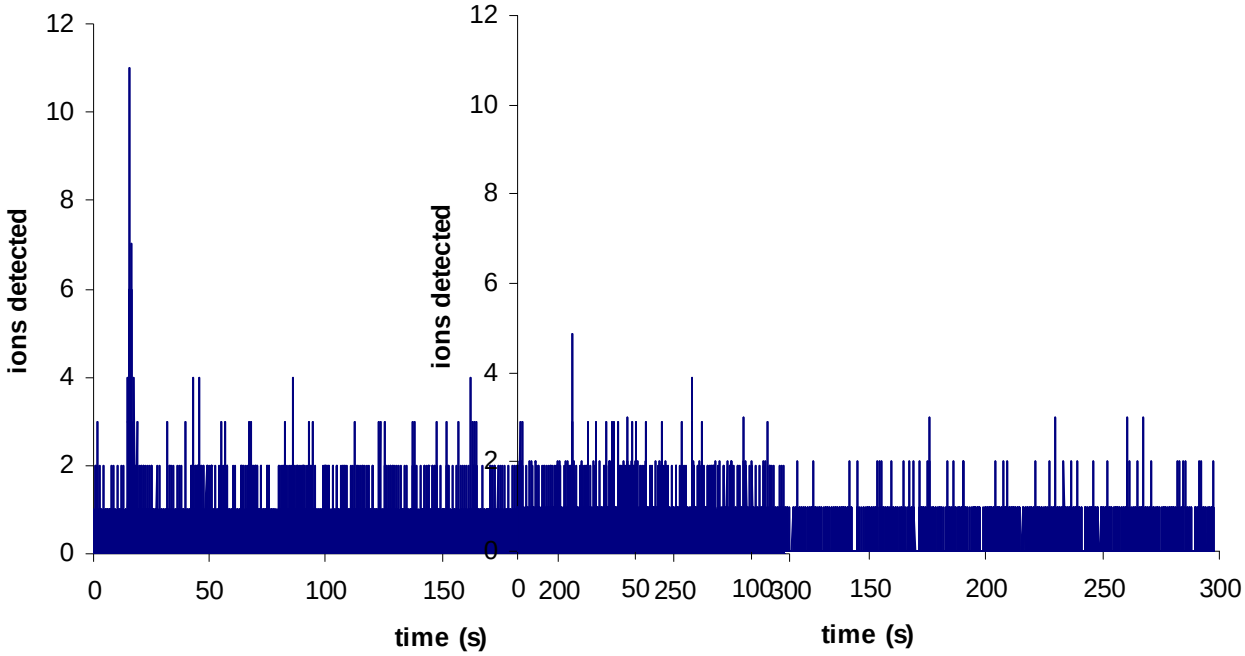
Gold-containing nanoparticles in Las Vegas Wash water



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Conclusions and ongoing work

- SP-ICPMS holds promise for rapid screening of surface water for metal-based ENMs.
- Issues related to pre-filtration need to be investigated.
- SP-ICPMS alone is not a selective technique.
  - Coupling with flow-field flow fractionation is being studied.
- Faster dwell times yield superior S/N and dynamic range.
  - Limited by current commercial ICPMS architecture.

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Acknowledgements

I thank Emily Siska for valuable assistance in the laboratory, and Charlita Rosal for helpful discussions and comments on this presentation