Making newly-developed nanoanalysis tools (spICP-MS, FFF-ICP-MS) more readily utilized for exposure studies

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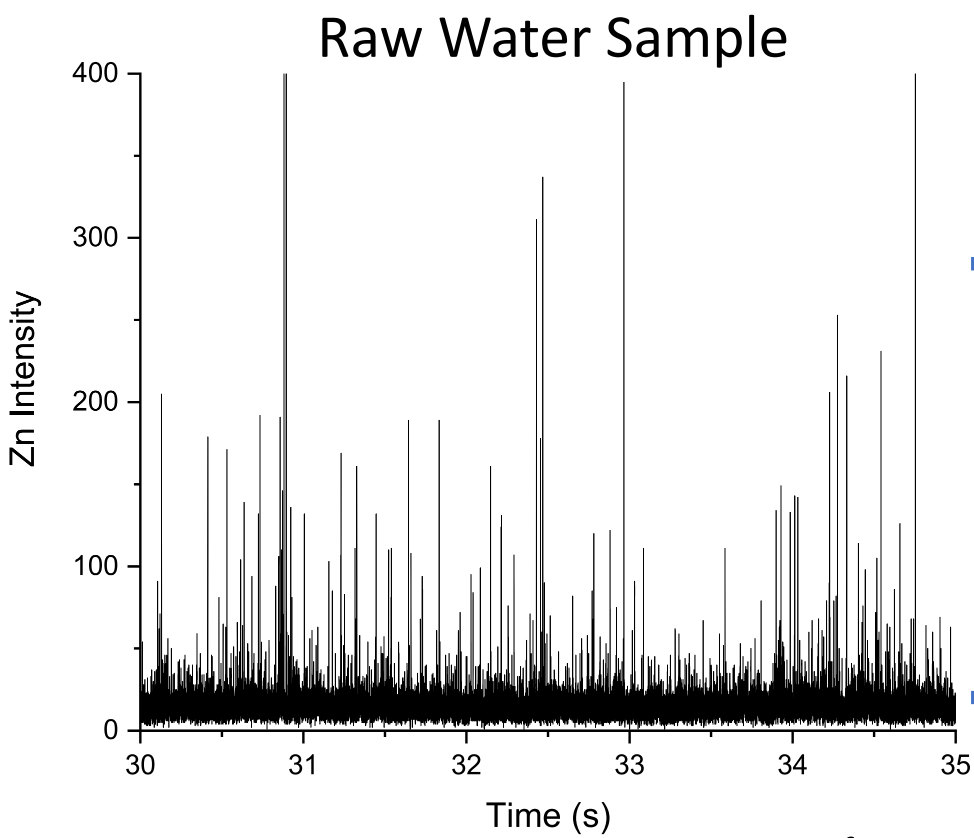
Presented at QEEN II
Characterization Discussion
October 10, 2018

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # RD83558001

Recognize What Does single-element spICP-MS tells us (and what it doesn't)

PE Syngistix Software used
Graphs prepared with OriginPro

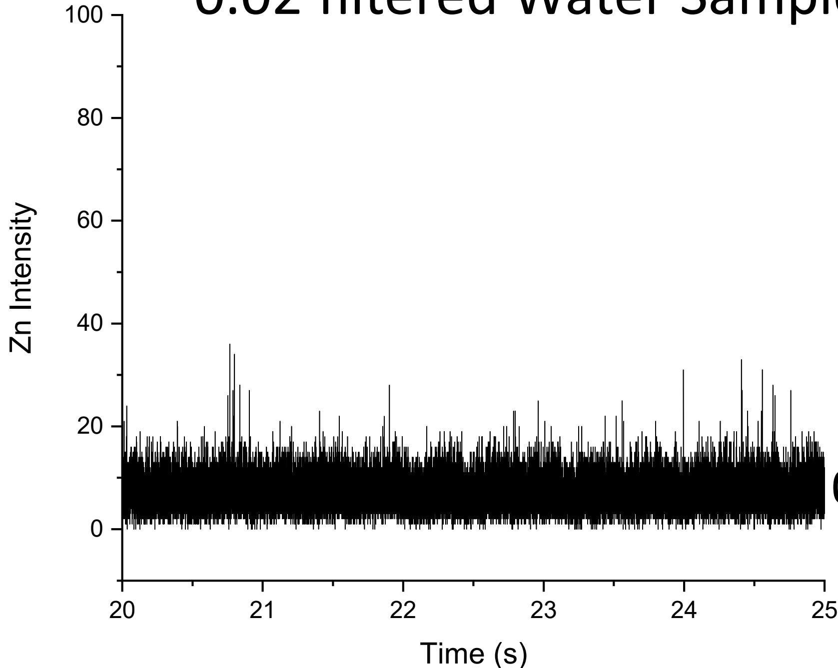


5 sec out of 60 sec total

Particle # = 2564
Mean Peak Area = 205 counts
Average Size = 98 nm

"Dissolved" = 6.1 ppb

0.02 filtered Water Sample

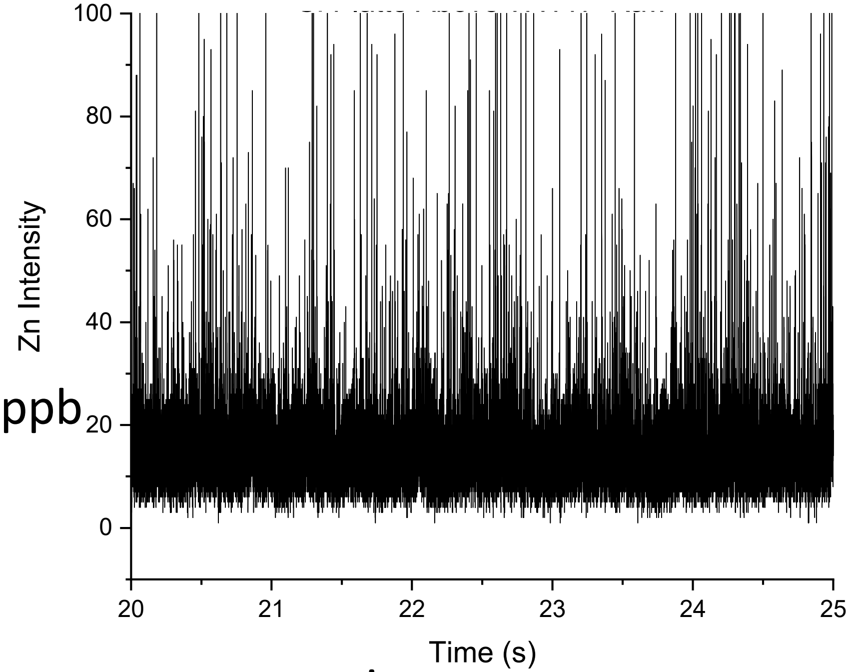


0.8 ppb

"Dissolved"

6.1 ppb

Raw Water Sample



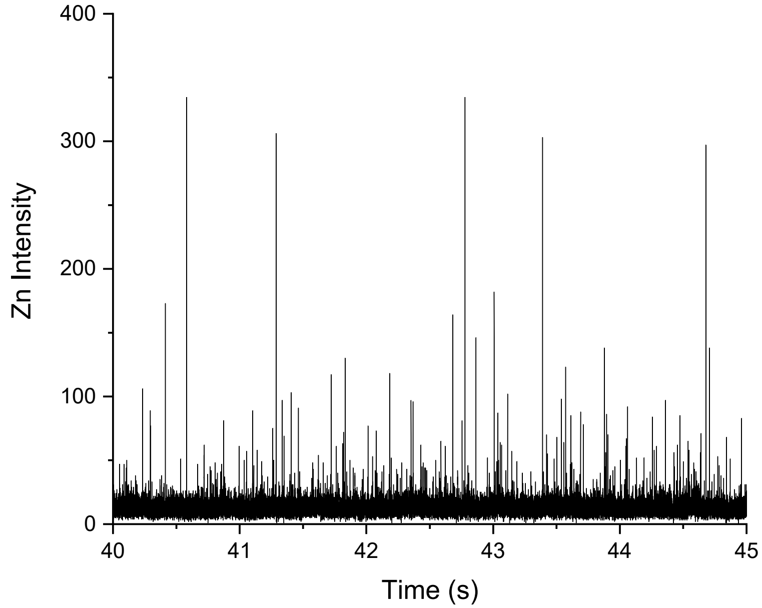
Non-Resolved NPs = 5.3 ppb mass concentration

= unknown

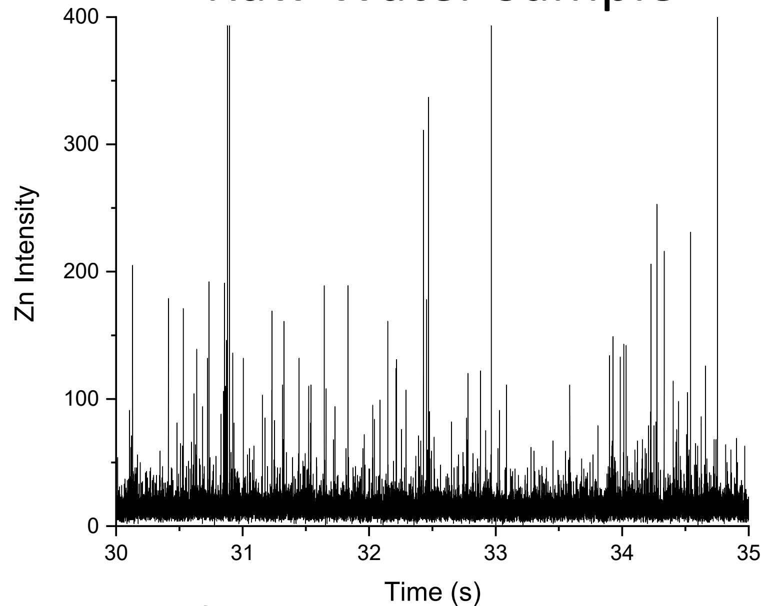
Particle # = 178
Mean Peak Area = 28 counts
Average Size = 54 nm

Particle # = 2564
Mean Peak Area = 205 counts
Average Size = 98 nm

< 5 Micron Settled Water Sample (70 min)



Raw Water Sample



Form is not measured

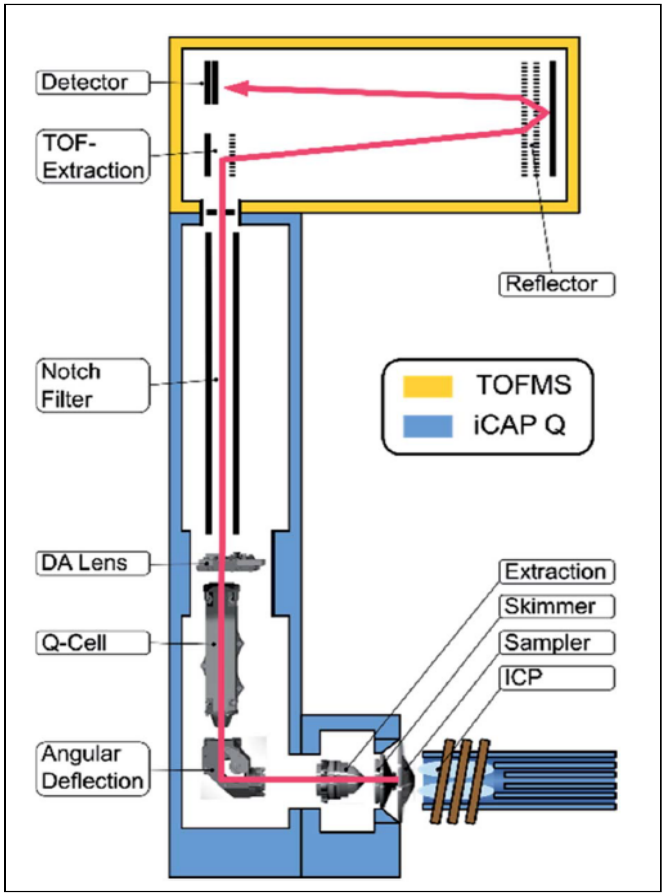
Particle # = 1752
Mean Peak Area = 144 counts
Average Size = 85 nm

Particle # = 2564
Mean Peak Area = 205 counts
Average Size = 98 nm

68 % as many NPs as raw
70 % less mass (intensity) per NP
Average Size 15 % smaller

Why does 5 micron settling affect < 100 nm sized NPs?
Heteroaggregates
or
Minor amounts of Zn in > 5 micron particles

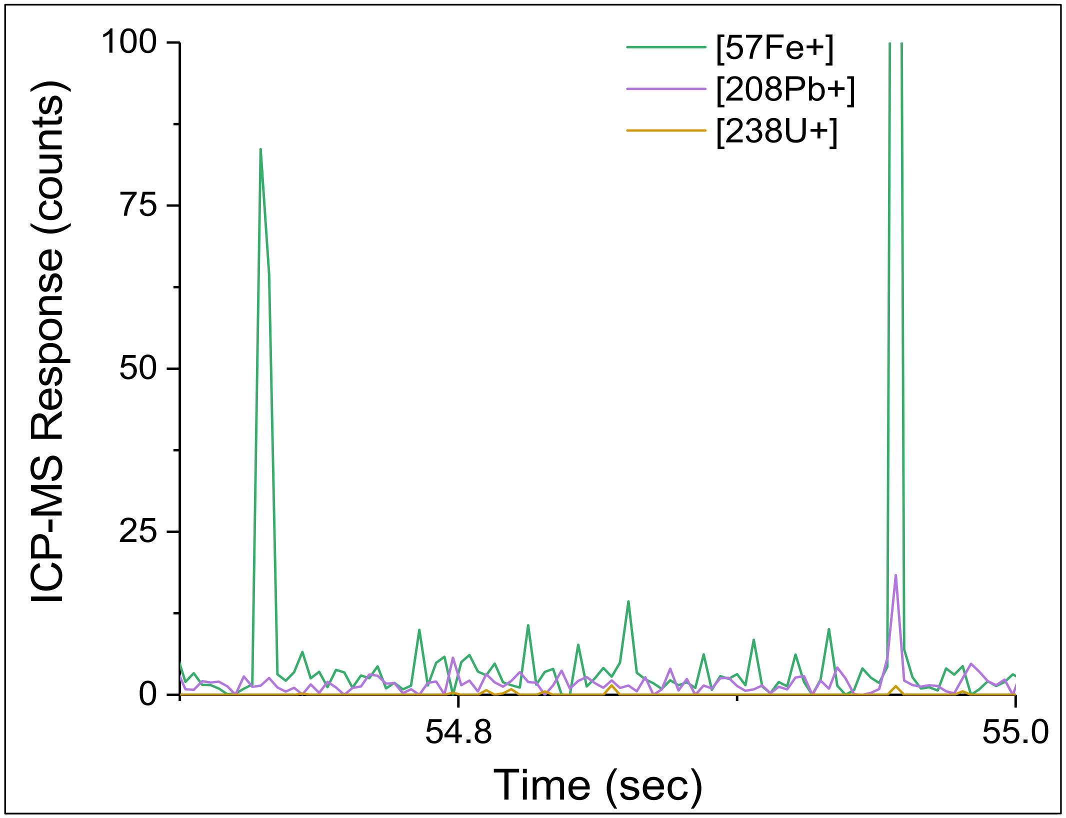
ICP-time-of-flight-Mass Spectrometry : More Info on Form



Montaño, M. et al., **2017**

Hendriks, L. et al. *Journal of Analytical Atomic Spectroscopy*, **2017**

- ICP-TOF-MS detects all elements quasi-simultaneously
- A full mass spectrum is collected every dwell time (46µs)
- Could potentially be used to examine elemental ratios on a particle-by-particle basis



spICP-MS: Plus, minus, and opportunities

There are reasonably low barriers to increased application but:

- reasonable expectations need to be set
- inherent limitations must be accepted

Single-Element

- ICP-QMS instruments are common
- Versatility make them cost-effective ($150 K)
- spICP-MS software widely-available
- Gives # concentration
- But data interpretation requires some specialized training

Multi-Element (TOF-MS)

- ICP-TOF MS instruments are not common (yet)
- Still expensive ($500 K)
- Limited sensitivity means not all (or any) of the nano-range can be measured (lets not forget importance of colloids though)

Inherent spICP-MS Limitations

- Instrument range (theoretical)
  - At 0.1 msec
  - 2 count/dwell equals 20,000 cps
  - 1500 counts/dwell equals 15 million CPS
  - Range of 750 in counts (mass) translates to 9 x range in diameter (cube root function)
    - Typical observation 20 -200 nm
    - Instrument range influences our perception of size distributions

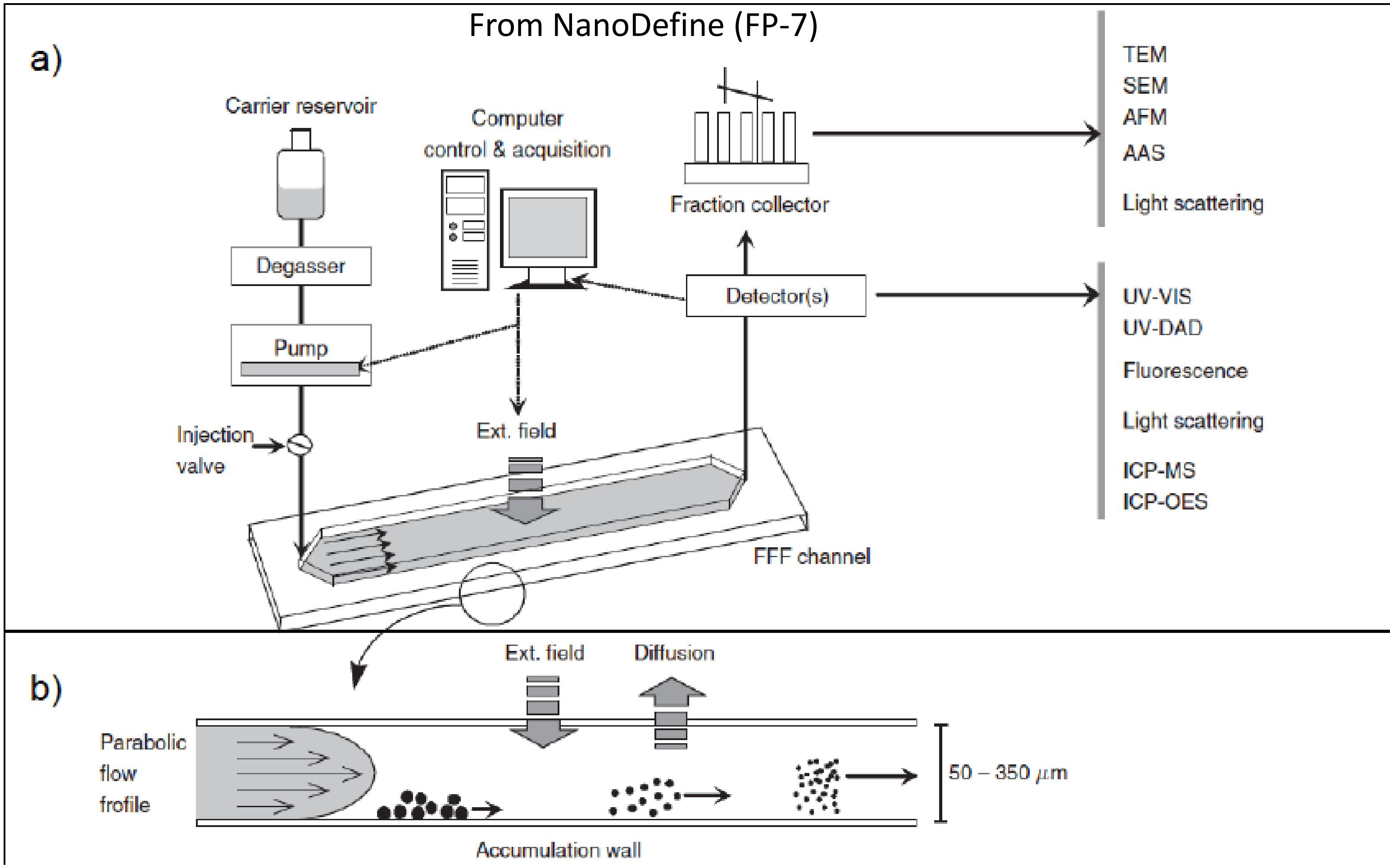
- Particle Number Distribution
- Pareto's Law
  - Log # versus log size (slope about 3)
  - 10x more 10 nm than 100 nm
  - 10x more 1nm than 10 nm
  - Typical Observed particle numbers in the low thousands
  - Example: 900 1nm, 90 10nm, 9 100nm
    - Poor counting statistics in upper range
    - Background high at size DL
    - Influences our perception of size distributions

Field Flow Fractionation with ICP-MS detection

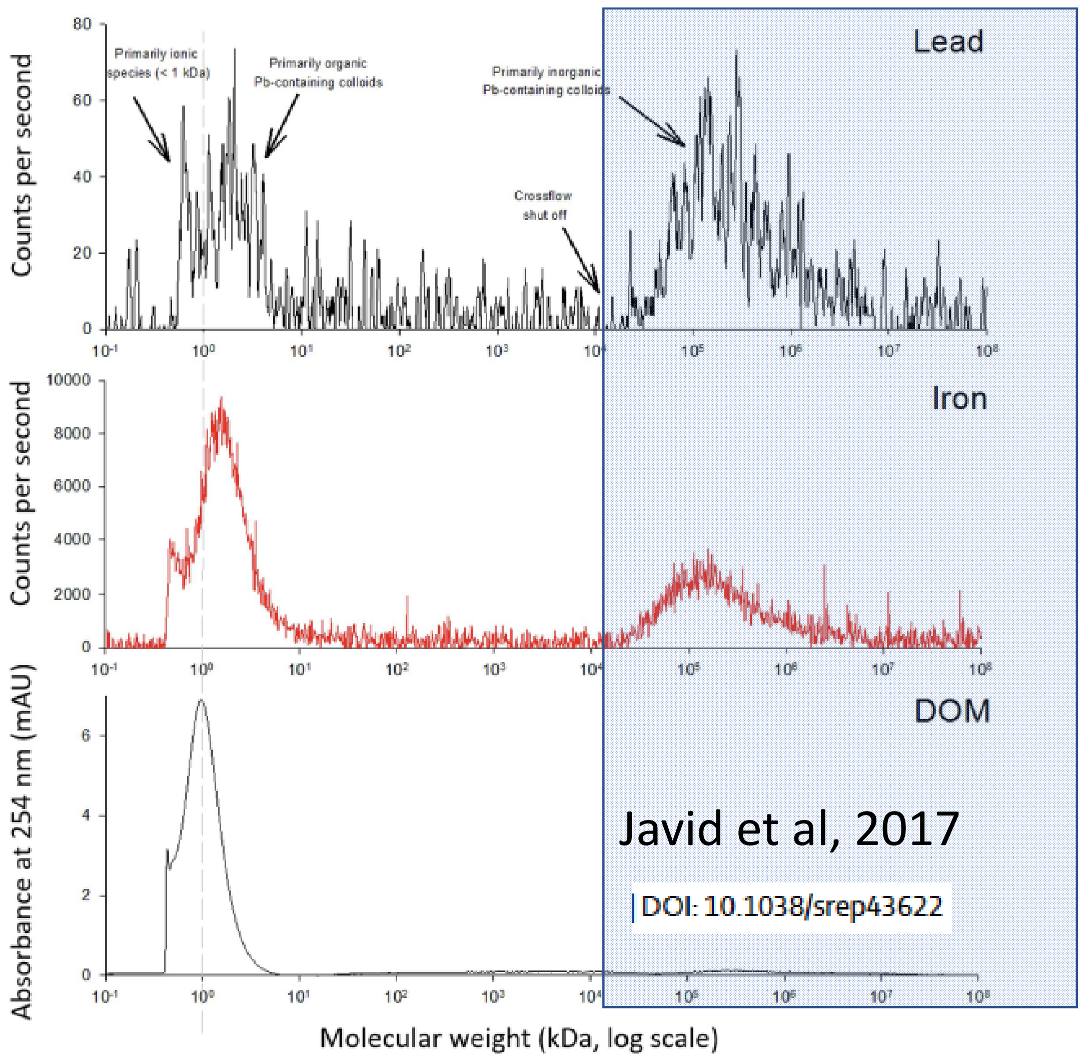
Provides sizing (hydrodynamic radius) with quantitative multi-element analysis.

Applicable down to about 1-2 nm

FFF recently had its 50th birthday, coupled with ICP-MS 25 years ago



From NanoDefine (FP-7)



Co-elution of elements suggests co-existence in NPs but independent, same-sized particles would also co-elute.

Turning field off allows analysis (but not sizing) of large particles (non-nano) that are outside separation range (colloids).

FFF-ICP-MS: Plus, minus, and opportunities

There are unfortunately still moderate barriers to increased application

Challenge

- Two instruments needed
- FFF less versatile than ICP-MS and expensive $75-120K
- Size separation only over about a 10-20 fold range in a given run
- Slow - run time up to one hour depending on size range
- Technique can be unforgiving
  - poor recovery (nothing comes out) usual biggest issue

Opportunity/Needs

- Need more Labs (academic/ Gov/Commercial) with equipment and expertise. COLLABORATE!
- Over 85 FFF sold in NA over past decade (< 15 for Env) so expertise exists.
- Will likely remain superior to sp ICP-MS for < 5-10 nm NPs
- Other online detectors give additional information (DOC,etc)

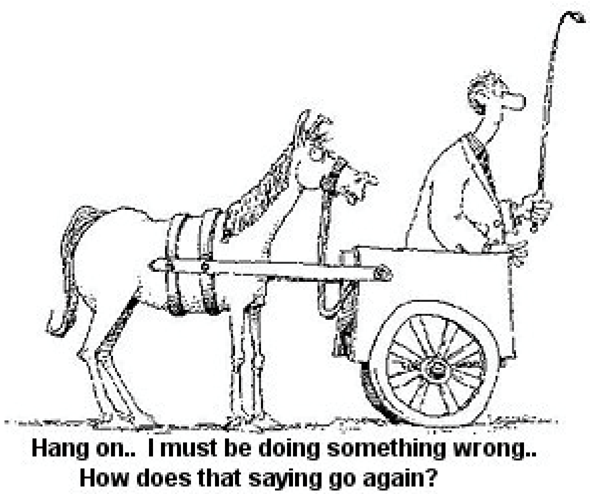
Risk **Exposure** Hazard

Advanced Analytical Methods for **Exposure Assessment**

→ Predict/Prevent Adverse Effects

Understand and mitigate real-world health effects ← Functional Assays for Environmental Adverse Effects

Number Concentration
Mass Concentration
Available Surface Area



Biological markers of stress
Environmental products of NP exposure (ROS, etc)