

# Determination of Hg nanoparticles in produced water associated to crude oil production by single particle inductively coupled plasma mass spectrometry (sp-ICP-MS)

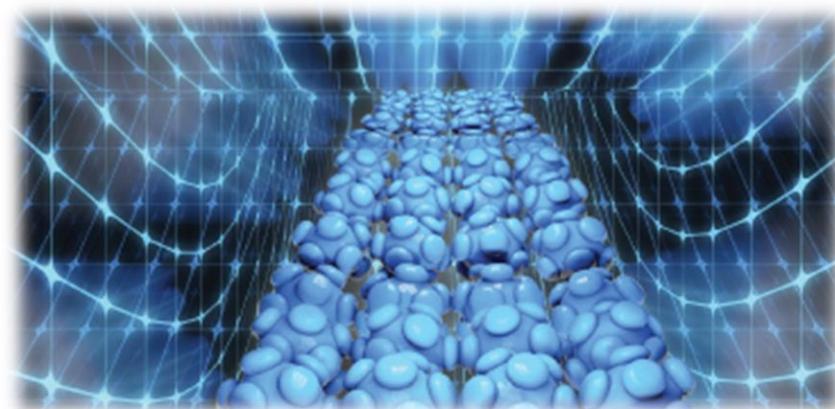


Jenny Nelson, Michiko Yamanaka, Bert Woods  
Agilent Technologies



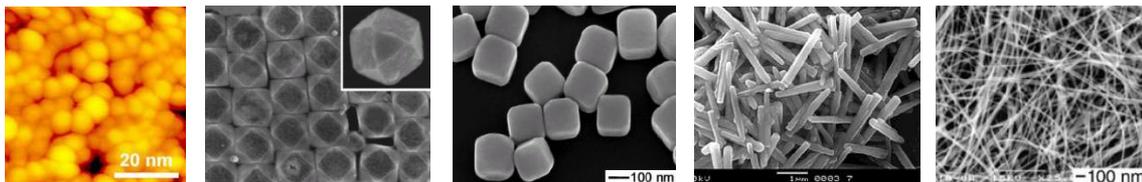
# Outline

- Nanoparticle (NP) characterization
- NP analysis by ICP-MS:
  - Important concepts
  - Instrumentation
  - NP workflow
- Application:
  - Hg analysis in produced water



# What are nanoparticles and where do they come from?

Particles with at least one dimension in the nano-scale (1-100nm)  $10^{-9}$  m



## Natural Sources

Produced by redox reactions, weathering, mining, volcanos, dust storms...



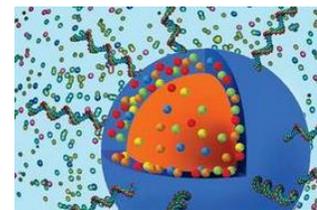
## Unintentionally produced NPs

Emitted to air, water and soil from combustion, wear, metal polishing and metal working, electric motors etc.



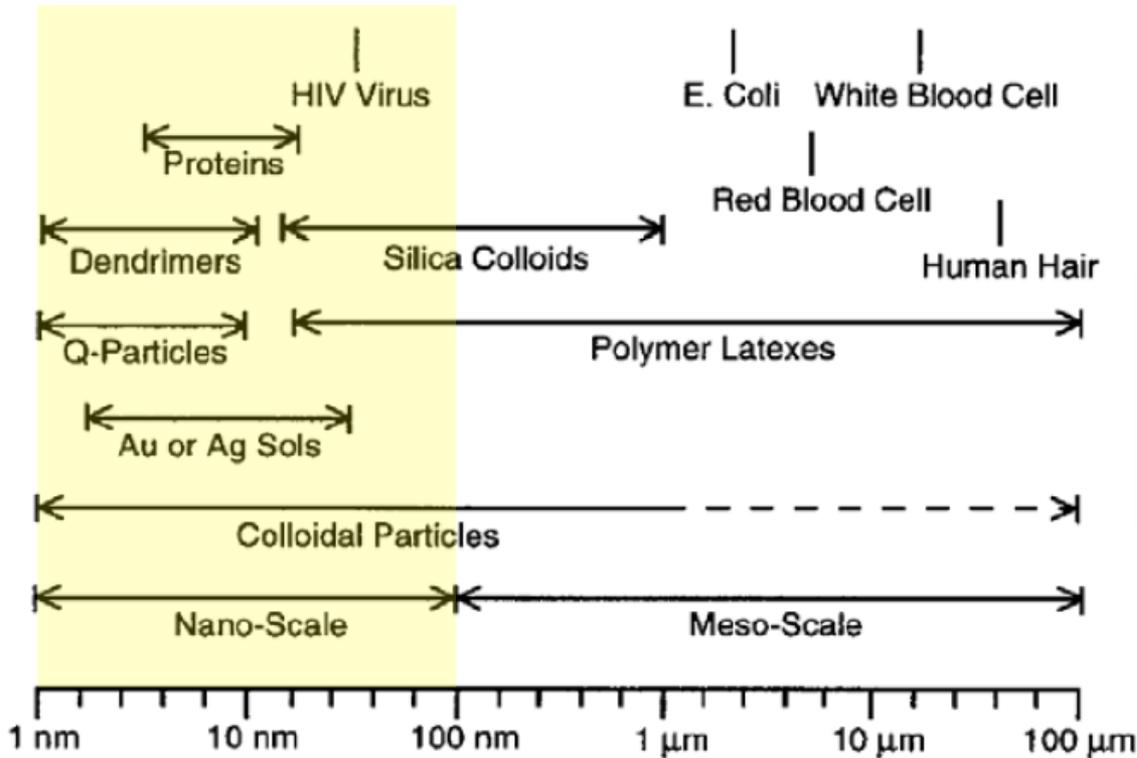
## Engineered NPs

Synthesized for a specific purpose by design



# Relative size of nanoparticles (log scale)

## Colloidal Domain – Characteristic Sizes



**Orlin D. Velev**

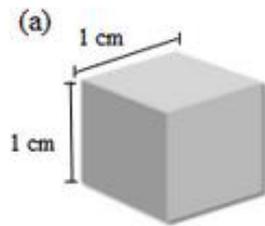
*Department of Chemical and Biomolecular Engineering  
North Carolina State University  
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# Why are nanoparticles so important?

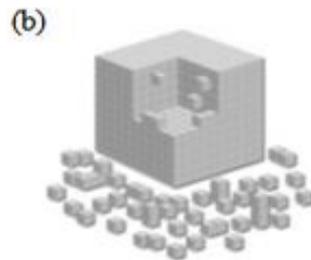
## Novel physical and chemical characteristics

Very large surface area to volume ratio → large role of intermolecular (surface) forces

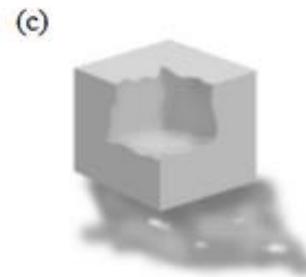
- Increased solubility
- Increased vapor pressure (lower melting temperature)
- Very high surface energy
- Ability to cross biological membranes



Total surface area:  $6 \text{ cm}^2$



Total surface area:  $60 \text{ cm}^2$   
(All 1 mm cube)



Total surface area:  $60,000,000 \text{ cm}^2$   
(All 1 nm cube)

# Nanoparticles in the environment - considerations

- Environmental health and safety concerns of nanoparticles
  - ◆ Potential to be released into environment
  - ◆ May be toxic to beneficial microbes
  - ◆ Potential impact on aquatic species
  - ◆ Poorly characterized toxicity to humans
- Analytical needs
  - ◆ Chemical composition
  - ◆ Size and size distribution
  - ◆ Mass/number concentration
  - ◆ Agglomeration state
  - ◆ Shape
  - ◆ Surface area/charge
  - ◆ .....

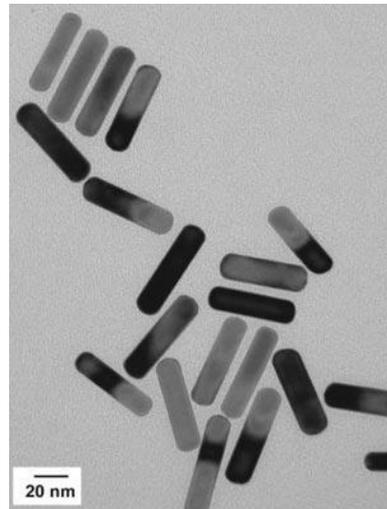
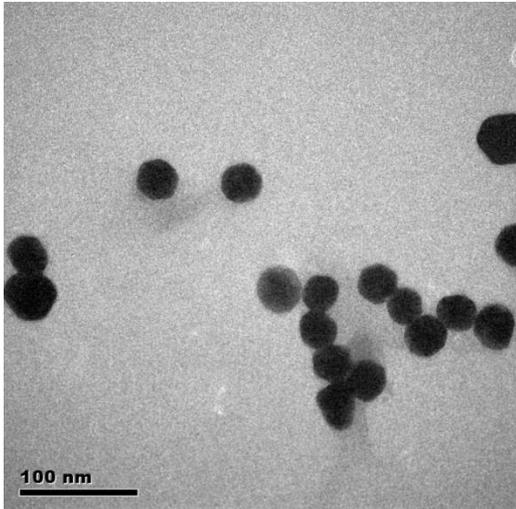
How many of these needs can ICP-MS related methods meet?

# Methods for NP characterization

- **Imaging** methods (TEM, SEM, AFM) are often definitive for detection, shape and size determination. Not quantitative nor representative.

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Transmission Electron Microscopy (TEM)

## Benefits

Excellent size and shape characterization for individual particles

Capability to detect very small particles

## Limitations

Time consuming preparation

Subject to preparation artifacts

No elemental information

# Methods for NP characterization

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- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering) simple, but subject to interferences. No elemental information.

# Methods for NP characterization

- **Imaging** methods (TEM, SEM, AFM) are often definitive for detection, shape and size determination. Not quantitative nor representative.
- **Spectroscopic/optical** methods (UV-Vis, dynamic light scattering) simple, but subject to interferences. No elemental information.
- **Hyphenated techniques** (Chromatographic (or other online) separation coupled with ICP-MS detection). Allow representative samples, provide good particle size resolution, high elemental sensitivity but no information on individual particles

FFF-ICP-MS

CE -ICP-MS

HPLC-ICP-MS

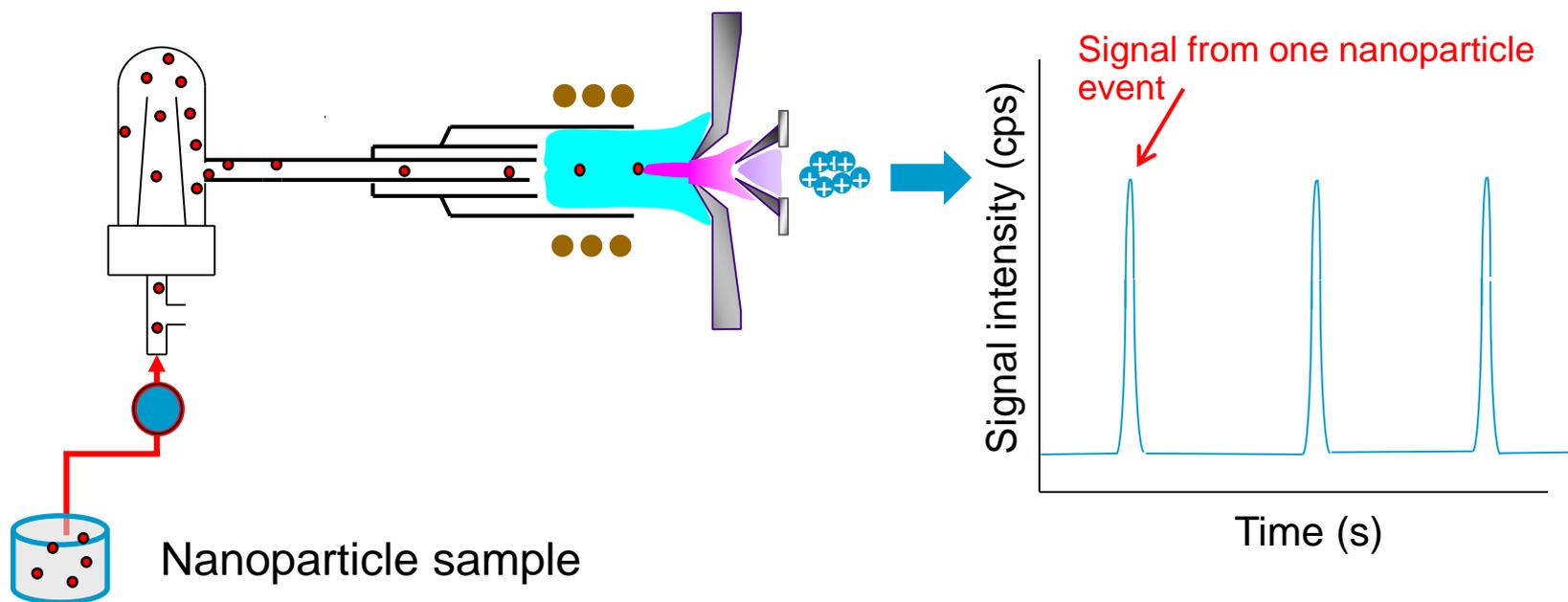


- **Single particle ICP-MS**

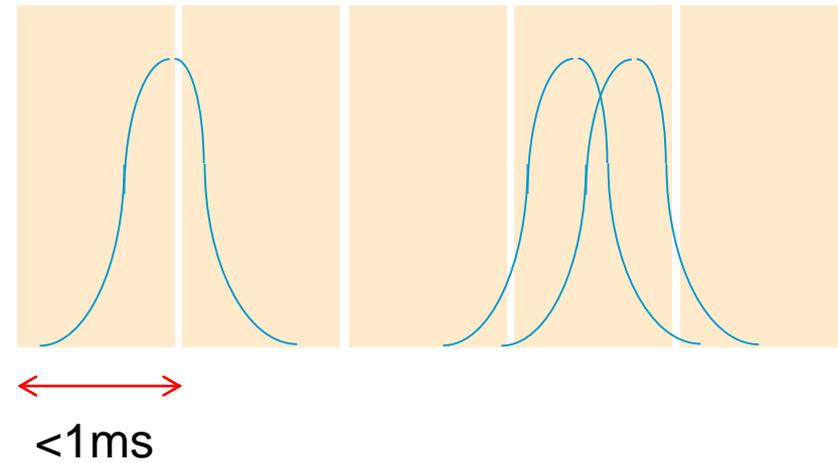
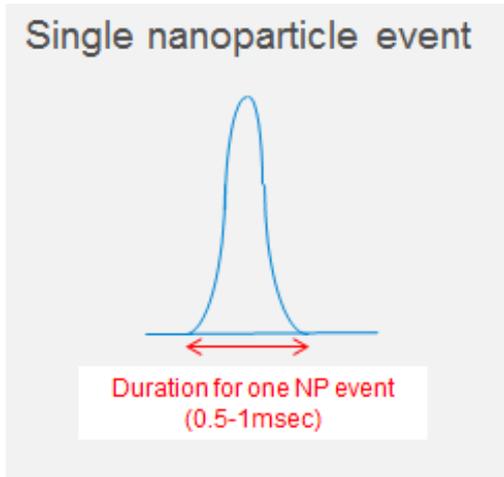
# Methods for NP characterization

- **Single Particle - ICP-MS**

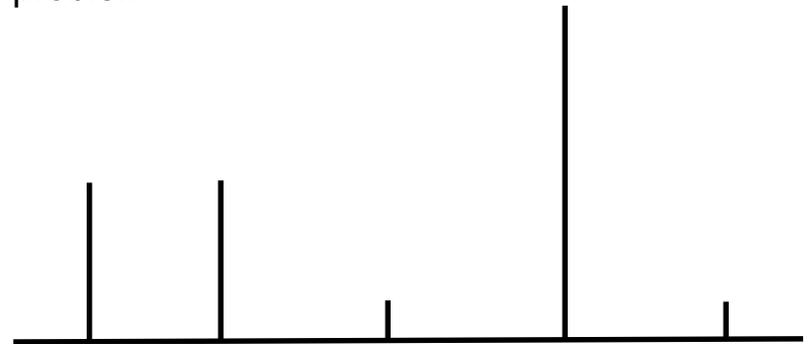
- Each nanoparticle gives a transient signal (a plume of ions generated from the particle)
- Use Time Resolved data acquisition and analysis
- Particle concentration, particle diameter, composition and size distribution are obtained



# Some important concepts for single nanoparticle analysis



- Just shortening the dwell time alone does not solve the problem
- Need a way to integrate signal over multiple scans to:
  - Accurately quantify signal from single particle
  - Help identify overlapping peaks

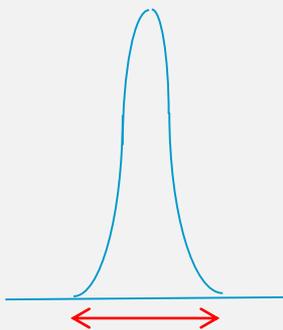


# Microsecond Scanning with no Settling Time

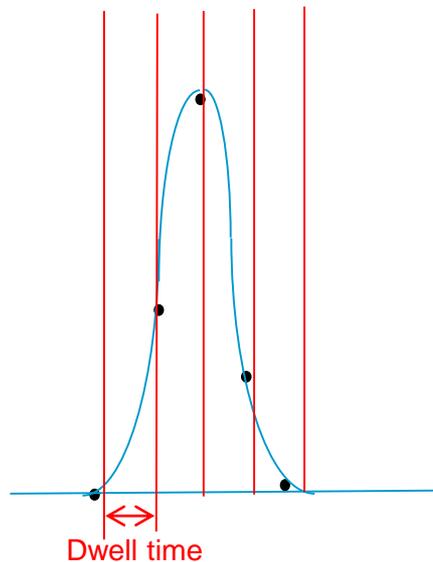
## - Short Dwell Time (0.1ms)

- Peak Integration Mode

Single nanoparticle event

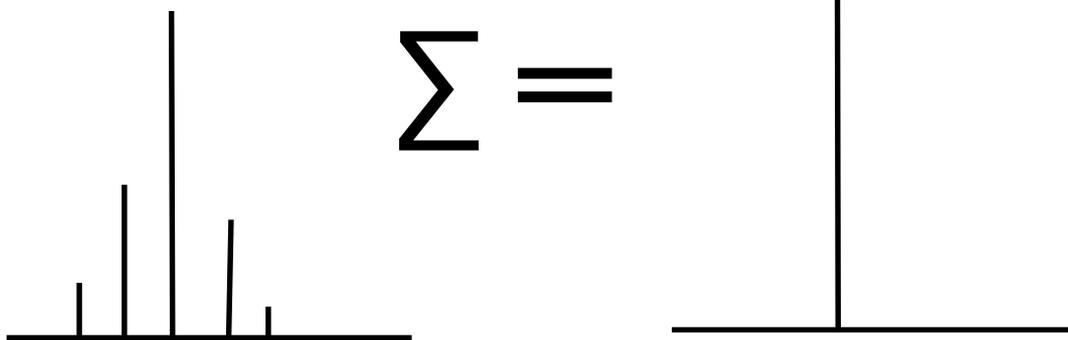


Duration for one NP event  
(0.5-1msec)



Dwell time

- “Peak Integration Mode” is automatically enabled by sNP
- Data Analysis software when dwell time is <1ms



# Choice of Mass Spectrometers

In this study I used both the 7900 SQ ICP-MS and TQ 8900 ICP-QQQ

- 7900 quadrupole ICP-MS – ultra-sensitive, ultra-fast 0.1 ms dwell
- 8900 ICP-QQQ – highest sensitivity and lowest background, MS/MS for interference-free determination of nanoparticles, ultra-fast 0.1 ms dwell
- 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



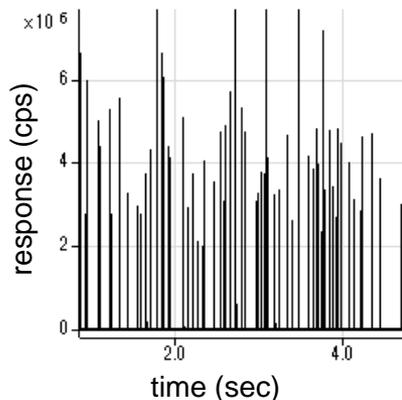
7900 ICP-MS



8900 ICP-MS/MS

# Workflow for NP characterization

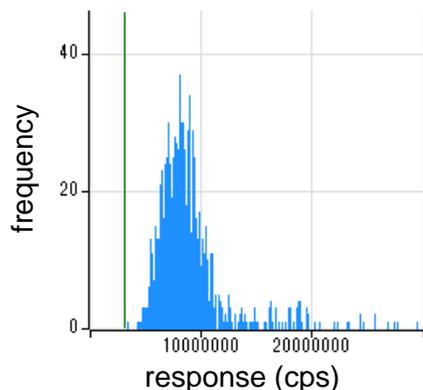
ICP-MS TRA data



convert



Response vs frequency



Input



- Analyte response factor > Mass of analyte in particle
- Nebulization efficiency (calculated from reference material)
- Analyte density
- Analyte mass fraction in sample particle

Calculate

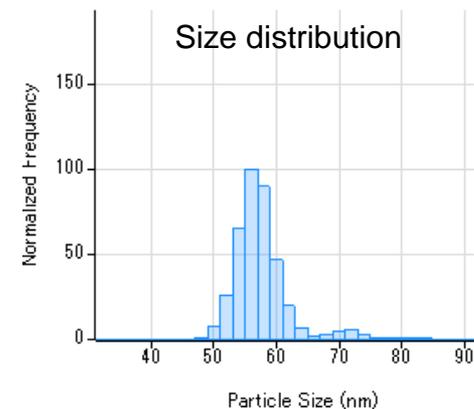


Tabulate and Report



Sample				197 Au						
Data File	Acq. Date-Time	Type	Sample Name	Nebulization Efficiency	# of Particles	Conc. (particles/l)	Conc. (ng/l)	Ionic Conc. (ppb)	BED (nm)	Particle Size (nm)
001IONB.d	5/13/2015 3:10:19 AM	IonicBlk	blank							
002IONS.d	5/13/2015 3:13:07 AM	IonicStd	1ppb							
003_RM.d	5/13/2015 3:15:21 AM	RM	30nm 5ppt	0.071	619	2.5E+7	5.0	0.0178	4.21	27
004SMPL.d	5/13/2015 3:18:20 AM	Sample	60nm 50ppt	0.071	617	2.5E+7	48.6	0.0280	4.73	55
005SMPL.d	5/13/2015 3:20:27 AM	Sample	60nm 50ppt	0.071	681	2.8E+7	51.8	0.0286	4.76	55
006SMPL.d	5/13/2015 3:22:35 AM	Sample	60nm 50ppt	0.071	635	2.6E+7	48.8	0.0258	4.72	55
007SMPL.d	5/13/2015 3:24:26 AM	Sample	60nm 50ppt	0.071	656	2.7E+7	50.4	0.0272	4.80	55
008SMPL.d	5/13/2015 3:28:22 AM	Sample	60nm 50ppt	0.071	649	2.6E+7	48.9	0.0240	4.60	55
009SMPL.d	5/13/2015 3:30:54 AM	Sample	30nm 5ppt	0.071	579	2.3E+7	4.5	0.0083	3.23	26
010SMPL.d	5/13/2015 3:33:29 AM	Sample	30nm 5ppt	0.071	589	2.4E+7	4.8	0.0078	3.16	26
011SMPL.d	5/13/2015 3:37:10 AM	Sample	30nm 5ppt	0.071	568	2.3E+7	4.5	0.0078	3.16	26
012SMPL.d	5/13/2015 3:39:03 AM	Sample	30nm 5ppt	0.071	558	2.3E+7	4.5	0.0076	3.13	26
013SMPL.d	5/13/2015 3:43:05 AM	Sample	30nm 5ppt	0.071	600	2.4E+7	4.7	0.0075	3.12	26

Size distribution



# Precision and Accuracy (NIST 8012 and 8013)

Batch Table : Single Particle

Sample: Sample Type: <All> Analyte: 197 Au

Default Columns

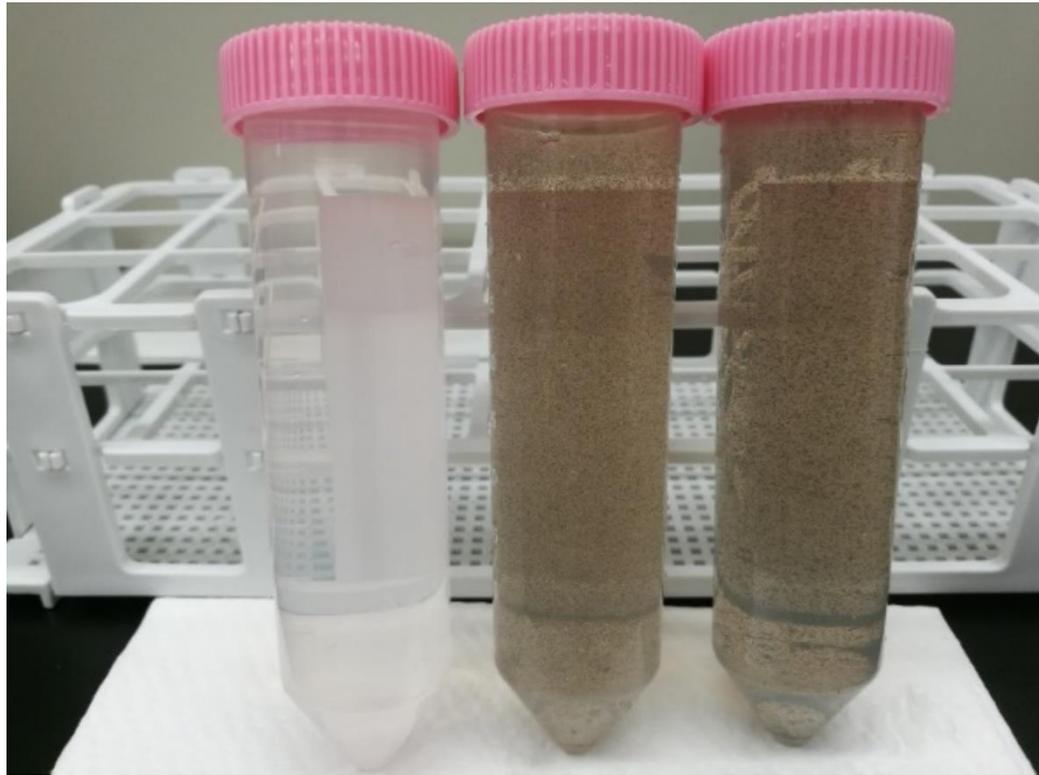
	Sample					197 Au						
	Rjct	Data File	Acq. Date-Time	Type	Sample Name	Nebulization Efficiency	# of Particles	Conc. (particles/l)	Conc. (ng/l)	Ionic Conc. (ppb)	BED (nm)	Particle Size (nm)
1	<input type="checkbox"/>	001IONB.d	5/13/2015 3:10:19 AM	IonicBlk	blank							
2	<input type="checkbox"/>	002IONS.d	5/13/2015 3:13:07 AM	IonicStd	1ppb							
3	<input type="checkbox"/>	003_RM.d	5/13/2015 3:15:21 AM	RM	30nm 5ppt	0.071	619	2.5E+7	5.0	0.0178	4.21	27
4	<input type="checkbox"/>	004SMPL.d	5/13/2015 3:18:20 AM	Sample	60nm 50ppt	0.071	617	2.5E+7	48.6	0.0260	4.73	55
5	<input type="checkbox"/>	005SMPL.d	5/13/2015 3:20:27 AM	Sample	60nm 50ppt	0.071	681	2.8E+7	51.8	0.0266	4.76	55
6	<input type="checkbox"/>	006SMPL.d	5/13/2015 3:22:35 AM	Sample	60nm 50ppt	0.071	635	2.6E+7	48.8	0.0258	4.72	55
7	<input type="checkbox"/>	007SMPL.d	5/13/2015 3:24:26 AM	Sample	60nm 50ppt	0.071	656	2.7E+7	50.4	0.0272	4.80	55
8	<input type="checkbox"/>	008SMPL.d	5/13/2015 3:28:22 AM	Sample	60nm 50ppt	0.071	649	2.6E+7	48.9	0.0240	4.60	55
9	<input checked="" type="checkbox"/>	009SMPL.d	5/13/2015 3:30:54 AM	Sample	30nm 5ppt	0.071	580	2.4E+7	4.5	0.0083	3.23	26
10	<input type="checkbox"/>	010SMPL.d	5/13/2015 3:33:29 AM	Sample	30nm 5ppt	0.071	589	2.4E+7	4.8	0.0078	3.16	26
11	<input type="checkbox"/>	011SMPL.d	5/13/2015 3:37:10 AM	Sample	30nm 5ppt	0.071	568	2.3E+7	4.5	0.0078	3.16	26
12	<input type="checkbox"/>	012SMPL.d	5/13/2015 3:39:03 AM	Sample	30nm 5ppt	0.071	558	2.3E+7	4.5	0.0076	3.13	26
13	<input type="checkbox"/>	013SMPL.d	5/13/2015 3:43:05 AM	Sample	30nm 5ppt	0.071	600	2.4E+7	4.7	0.0075	3.12	26
14	<input type="checkbox"/>	009SMPL_150514-demo.D	5/13/2015 11:32:18 PM	Sample	tap water + 1ppb + 60nm 50ppt	0.071	701	2.8E+7	53.2	1.0237	16.08	56

Particle Size Distribution Single Particle Method Editor

Sample (Prepared concentration)	Observed Concentration (particles/L)	Observed Concentration (ng/L)	Observed Particle Size (nm)	Reference Particle Size obtained by TEM (nm)
NIST 8013 Nominal 60nm (100 ng/L)	$5.59 \times 10^7$	103	55	$56.0 \pm 0.5$
NIST 8012 Nominal 30nm (10 ng/L)	$4.27 \times 10^7$	10.5	28	$27.6 \pm 2.1$

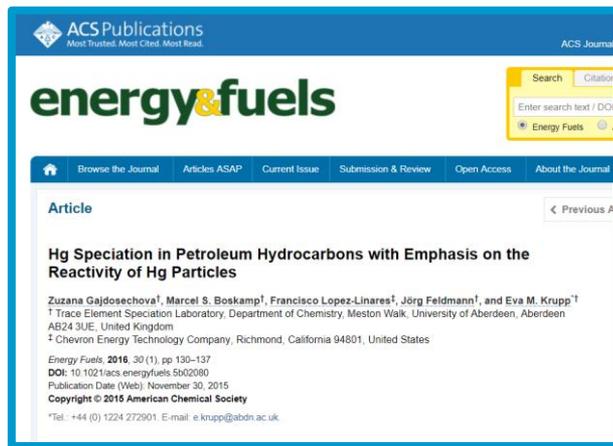
# Samples- Produced Waters

- The researchers are interested in determining if Hg nanoparticles are present in these produced waters.....



# Forms of Mercury Particulate in Petroleum Literature

Gajdosechova et al. recently reported particulate HgS to be the most abundant Hg species in stored petroleum hydrocarbons stocked on-shore.



- Hg can be present in natural gas, crude oil and its products.
  - The most dominant species are Hg<sup>0</sup> and Hg particulate, most likely associated to HgS
- When crude oil is extracted, the water used in the oil extraction and production consequently may contain Hg species, as Hg particulate.

Gajdosechova, Z.; Boskamp, M. S.; Lopez-Linares, F.; Feldmann, J.; Krupp, E. M. Hg Speciation in Petroleum Hydrocarbons with Emphasis on the Reactivity of Hg Particles. *Energy Fuels* **2015** 30:130-137. DOI: 10.1021/acs.energyfuels.5b02080.

# Size of Mercury Particulate in Literature

Selvaraj et al. report using (SEM) and transmission electron microscopy (TEM) reported HgS synthesized nanocrystals were nanoparticles, with an average particle size of 55 nm.

Issue 30, 2014 [Previous Article](#) | [Next Article](#)

 From the journal:  
**RSC Advances**

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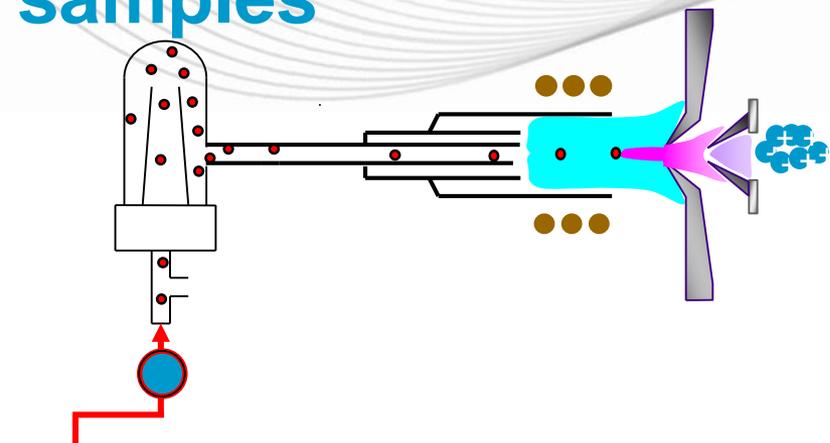
## A simple hydrothermal route for the preparation of HgS nanoparticles and their photocatalytic activities

[Rengaraj Selvaraj](#)<sup>\*a</sup> [Kezhen Qi](#)<sup>b</sup> [Salma M. Z. Al-Kindy](#)<sup>a</sup> [Mika Sillanpää](#)<sup>c</sup> [Younghun Kim](#)<sup>d</sup> and [Cheuk-Wai Tai](#)<sup>e</sup>

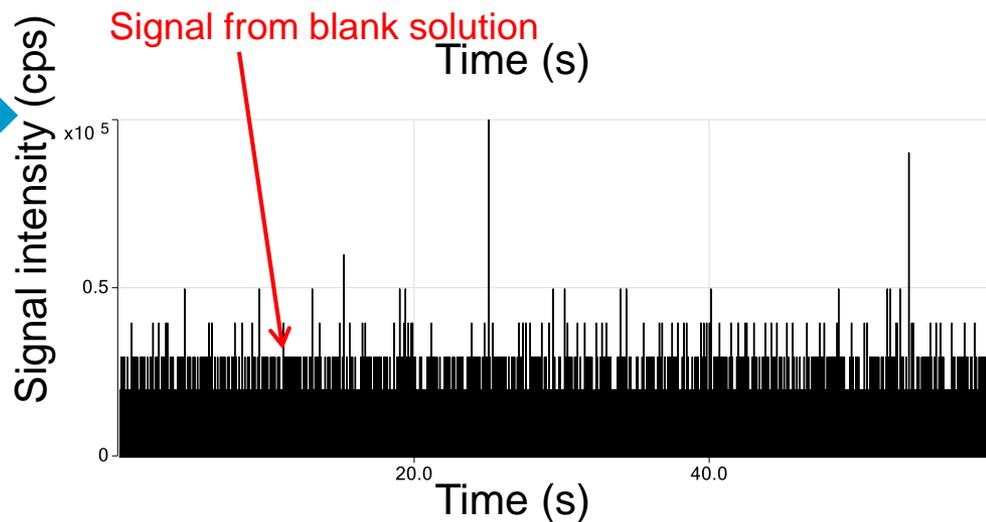
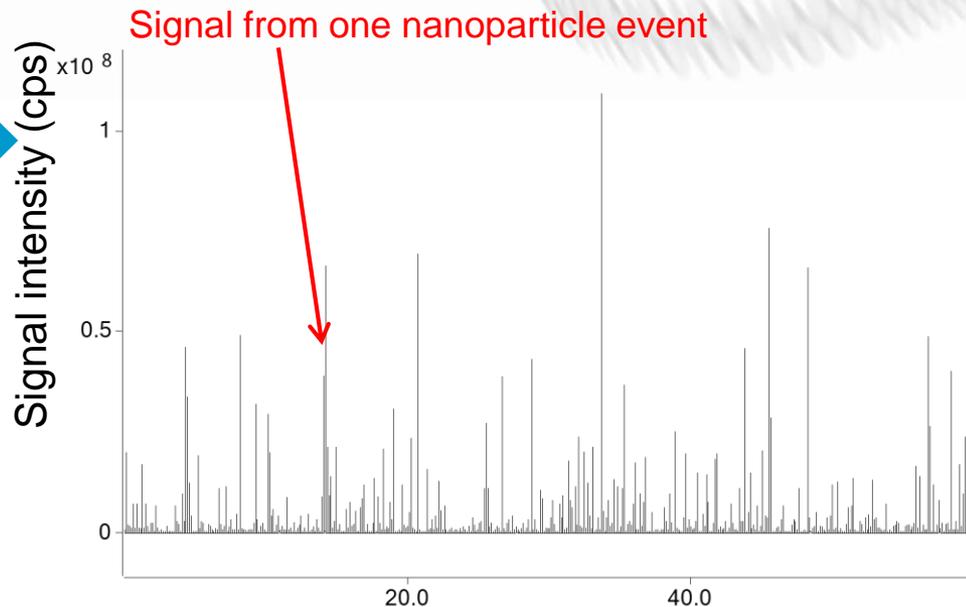
Selvaraj, R.; Qi, K.; Al-Kindy, S.; Sillanpaa, M.; Kim, Y.; Tai, C. W. A simple hydrothermal route for the preparation of HgS nanoparticles and their photocatalytic activities. *RSC Adv.* **2014** 4:15371–15376. DOI: 10.1039/C4RA00483C.

# Analyzing different Hg Isotopes in produce water samples

## ICP-MS TRA data



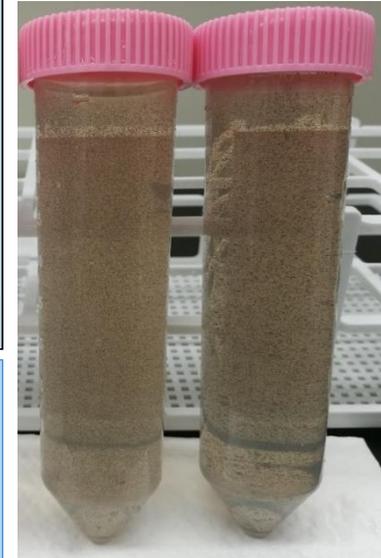
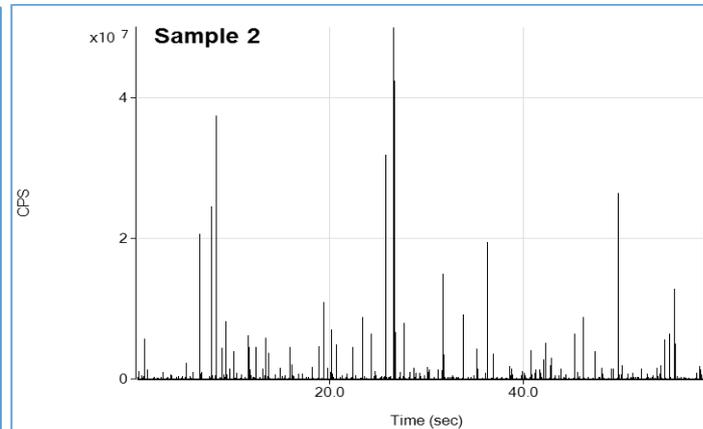
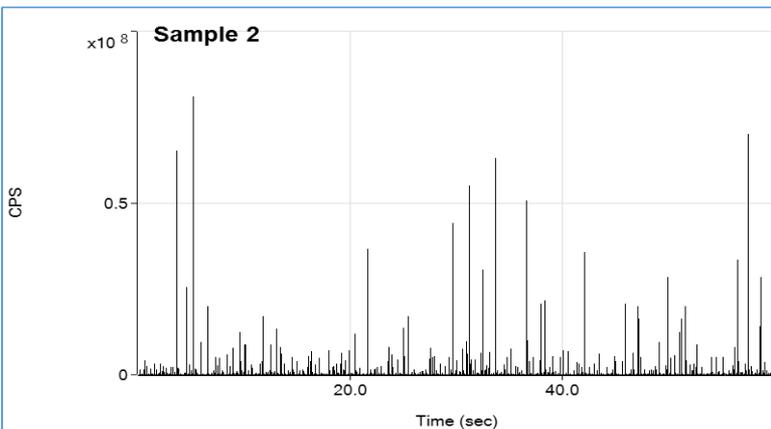
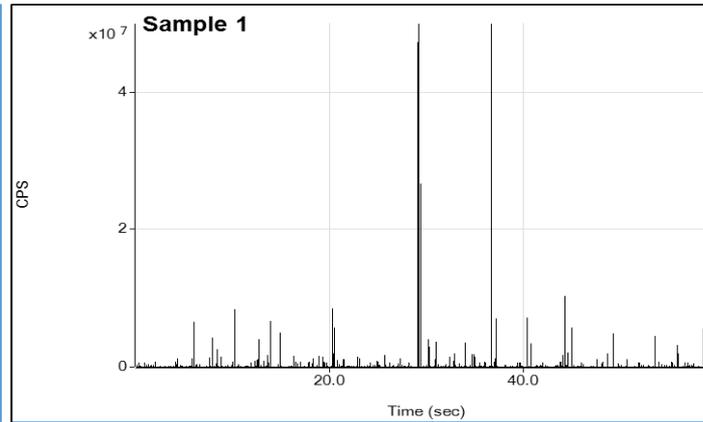
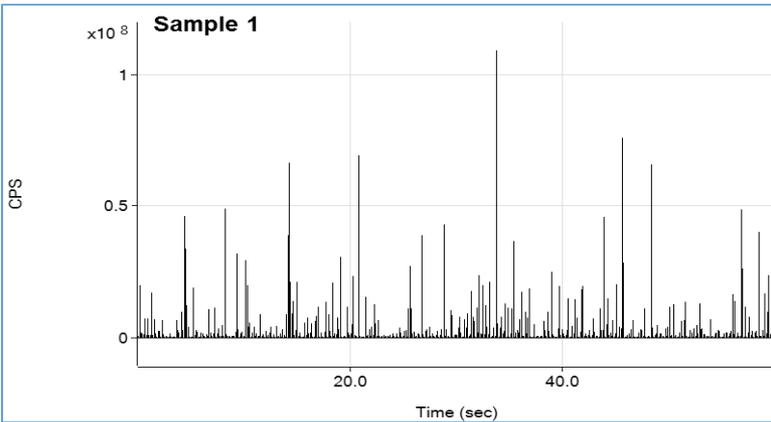
Nanoparticle sample #1  
(diluted 1,000,000 x)



# Analyzing different Hg Isotopes in produce water samples

Hg 202

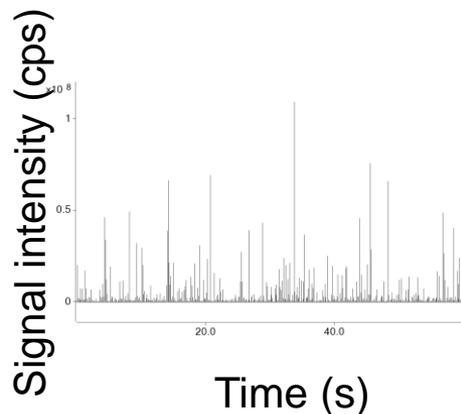
Hg 201



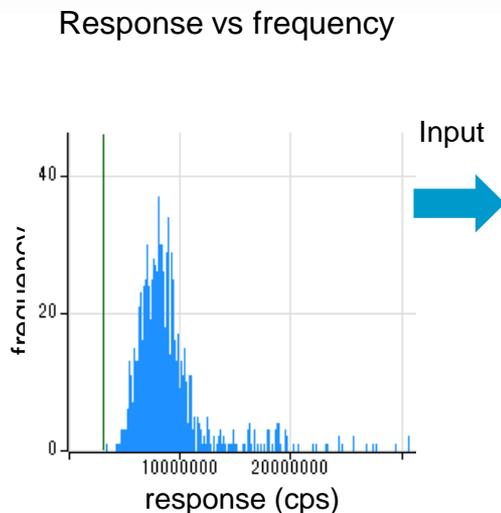
(samples run 7x)

ICP-MS TRA data

# Workflow for NP characterization



convert



- Analyte response factor > Mass of analyte in particle
- Nebulization efficiency (calculated from reference material – NIST 8013)
- Analyte density
- Analyte mass fraction in sample particle

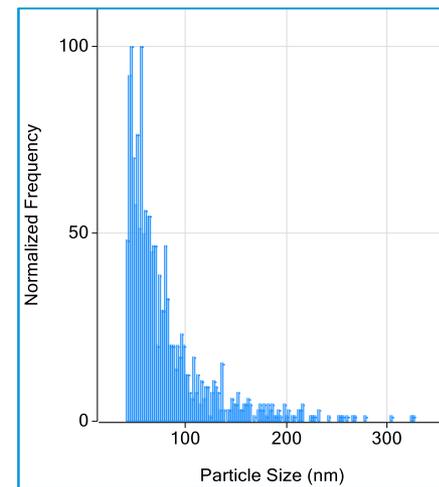


Hg	200.6	
S	32.07	
	Hg mass fraction	S mass fraction
HgS	1.160	7.255
HgS2	1.320	8.255
HgS3	1.480	9.255

Calculate

Tabulate and Report

Size distribution



	Hg 202			
Sample Name (n=7)	BED (nm)	Median Size (nm)	Mean Size (nm)	Most Freq. Size (nm)
Sample 1	7.43 ± 0.22	66.04 ± 1.45	80.52 ± 1.63	48.86 ± 4.14
Sample 2	6.77 ± 0.32	60.51 ± 2.20	73.82 ± 2.51	44.75 ± 2.38

# Conclusions

- Successfully able to measure Hg nanoparticles in produced water using sp-ICP-MS
- Results matched when using both the SQ sp-ICP-MS and the TQ sp-ICP-MS/MS

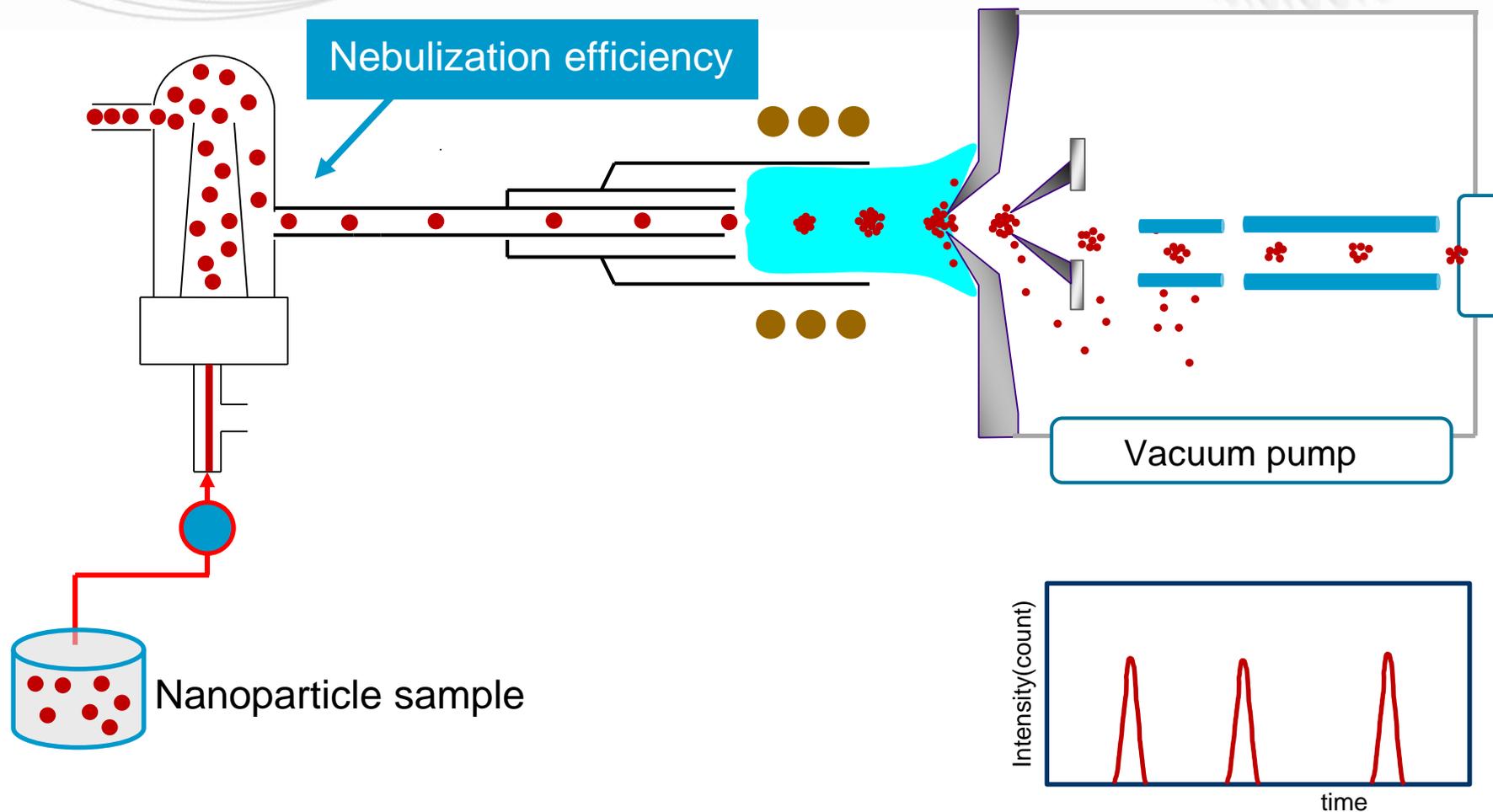




# Thank You

# Nebulization Efficiency

## Transmittance of nanoparticles



**Nebulization Efficiency : # of peak detected / # of particle into nebulizer**

# Nebulization Efficiency calculated from particle number concentration

Nebulization Efficiency ( $\eta_n$ ) : # of peak detected / # of particle into nebulizer

$$\eta_n = \frac{N_p}{\frac{C_{std} \times 10^3}{m_{std}} \times V \times T}$$

Here,  $m_{std}$ (fg) is Standard Particle Mass

$$m_{std} = \frac{4}{3} \pi \times \left( \frac{d_{std}}{2 \times 10^7} \right)^3 \times \rho_{std} \times 10^{15}$$

## Symbol

$d_{std}$	Reference Material diameter (nm)
$\rho_{std}$	Reference Material Density (g/cm <sup>3</sup> )
$N_p$	Number of detected particles
$C_{std}$	Concentration of Reference Material (ng/l)
$V$	Sample inlet flow (ml/min)
$T$	Total acquisition time (min)

# Analyzing different Hg Isotopes in produce water samples

Time resolved signals of Hg 202 and 201NPs TRA measurement of NPs by ICP-MS produces a narrow signal peak for each particle that passes through the plasma, with the peak intensity being proportional to the particle mass.

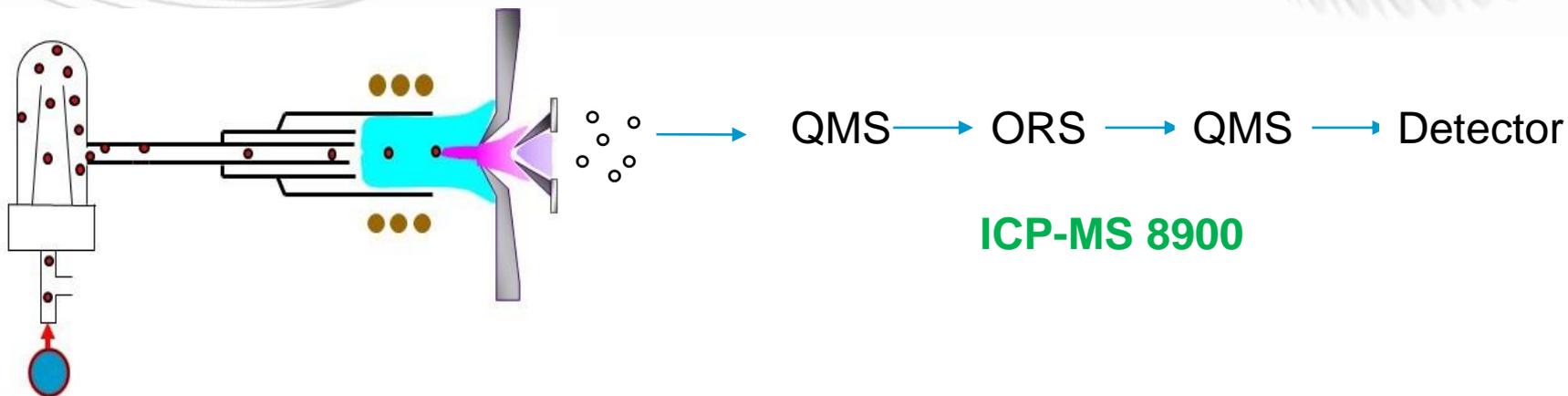
The typical signals measured in DI water (without particles) and in solutions containing HgS particles are shown in Figure X. Fast TRA mode (0.0001sec) allows multiple measurements to be made during the signal peak from a single particle, so the shape and duration of the ion plume from each NP can be identified. The frequency distribution plots of the signals obtained from HgSx nanoparticles are shown in Figure X. From these results we can estimate that the practical detection limit for the particle diameter for Hg was below X nm. The background equivalent diameter (BED) was X nm for Hg particle analysis.

# Nebulization efficiency

- In order to convert the signals measured with spICP-MS to the particle content of the original sample, it is necessary to calculate or measure the nebulization efficiency .
- The nebulization efficiency is the ratio of the amount of analyte entering the plasma to the amount of analyte delivered to the nebulizer, and was determined using the Au NIST 8013 reference material of known 60 nm particle size.
- It is required high sensitivity and low background for best SNP analyses

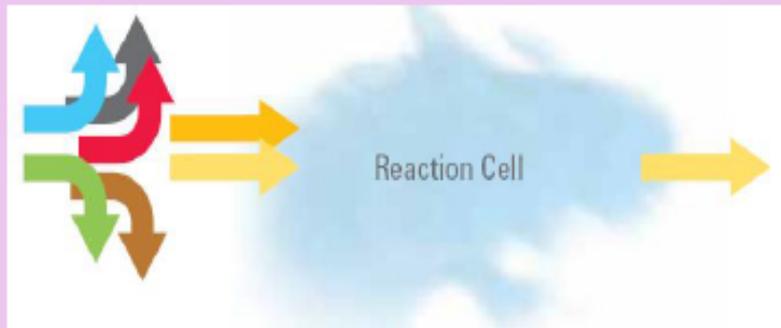


# Instrumentation

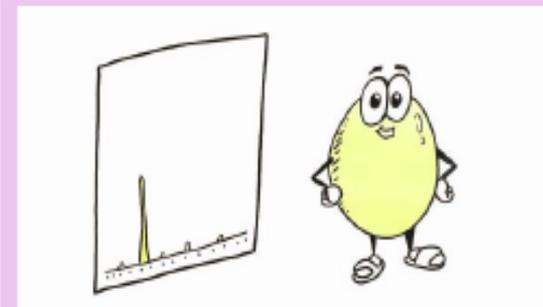


Triple Quadrupole ICP-MS (ICP-QQQ). Double mass filter, before/after cell

Mass selection before cell; Q1 rejects all masses except target ion  $m/z$ . **ONLY** target analyte and on-mass interferences enter cell. **Overlaps at product ion mass are eliminated**



Analyte and on-mass interference separated by reaction chemistry



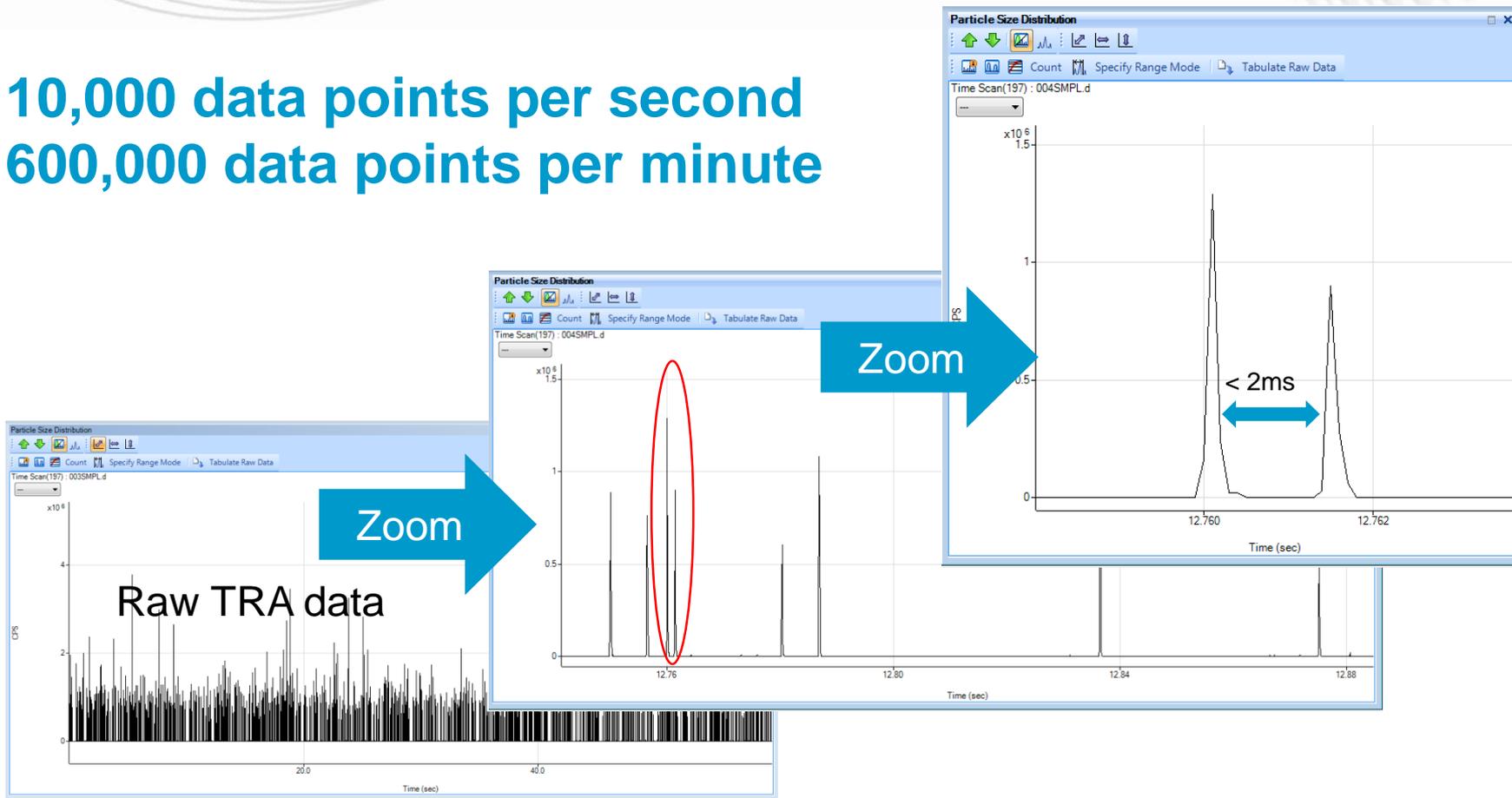
Only the target analyte ions contribute to the measured signal

# Instrumentation

- An Agilent 7900 and 8900 ICP-QQQ was used for this study .
- Both do not have to be used, only used for comparison in this study.
- The instrument was equipped with standard nickel sampling and skimmer cones, a glass concentric nebulizer, quartz spray chamber and quartz torch with 1 mm injector.
- Samples were introduced directly into the ICP-MS with the standard peristaltic pump and pump tubing (1.02 mm i.d.).
- Analyses were performed by measuring Hg (200,201,202), S (32) in fast Time Resolved Analysis (fast TRA) mode, using a dwell time of 0.1 ms (100  $\mu$ s) per point with no settling time between measurements.
- For Hg analysis, the signal was measured on-mass in MS/MS mode, where both quadrupoles (Q1 and Q2) were set to respective m/z.

# Fast TRA on Agilent 7900 and 8900 (100 $\mu$ s dwell time, no settling time)

10,000 data points per second  
600,000 data points per minute



# Official definition(s)

In 2008 the [International Organization for Standardization](#) (ISO) defined a nanoparticle as a discrete nano-object where **all three Cartesian dimensions are less than 100 nm**.

But in 2011 the Commission of the European Union endorsed a more detailed, but wider-ranging definition:

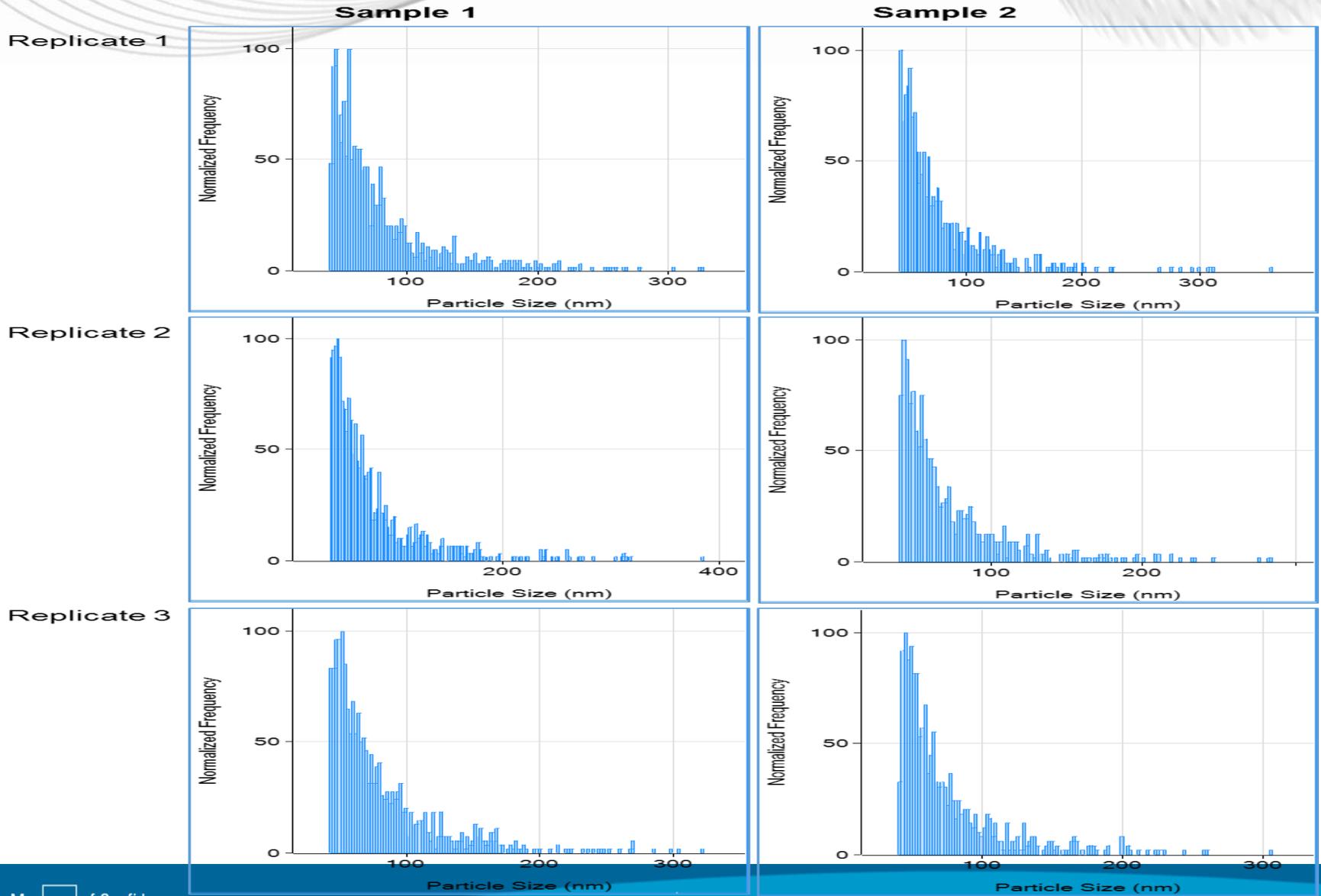
→ *A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm.*

The EU definition encompasses more of the wide range of materials that exist, such as nanotubes and rods, which behave like nanoparticles but have one dimension greater than 100 nm

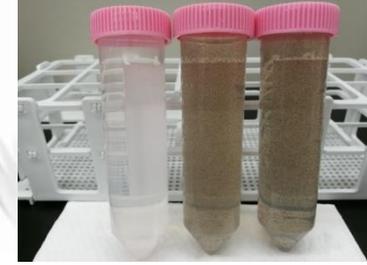
# Analyzing different Produced Water Samples

	Hg 202			
Sample Name (n=7)	BED (nm)	Median Size (nm)	Mean Size (nm)	Most Freq. Size (nm)
Sample 1	$7.43 \pm 0.22$	$66.04 \pm 1.45$	$80.52 \pm 1.63$	$48.86 \pm 4.14$
Sample 2	$6.77 \pm 0.32$	$60.51 \pm 2.20$	$73.82 \pm 2.51$	$44.75 \pm 2.38$

# Analyzing different Produced Water Samples

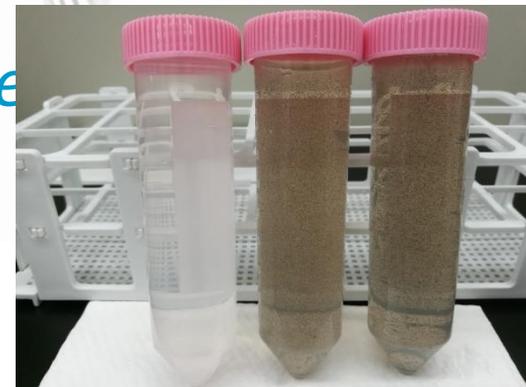


# Produced Waters



- Locations around the world generate produced water by separating mercury loaded hydrocarbon phases in the field with water that is most likely contaminated.
- Produced water and wastewater discharge limits in the petroleum industry vary around the world (<math><0.1</math> to 100  $\mu\text{g/L}</math>).$
- The more stringent limits set for overboard discharge from offshore production platforms are typically  $\leq 5 \mu\text{g/L}</math>.[3]$
- The Hg limit for discharge refinery wastewater
  - California has set as a monthly average of 0.079 ppb, maximum discharge of 0.2 ppb in a single episode [3].
  - The Great Lakes of the United States and Canada have a Hg water discharge of 0.0013 ppb[3].
  - World Health Organization (WHO) has a 2  $\mu\text{g/L}$  (ppb) mercury drinking water limit.
- Produced waters typically contain less than 100 ppb of total Hg.

## Forms and size of Mercury in Produced Water



Several forms of mercury may exist in produced water and wastewater depending on conditions. Toxic dimethyl mercury, is almost nonexistent in petroleum systems. Soluble complexes of Hg may be present in produced water and wastewater. Solid forms of Hg that may be present in water include precipitated Hg solids or mercuric sulfide (cinnabar,  $\text{HgS}$ ) and oxide (montroydite,  $\text{HgO}$ ). Meta-cinnabar,  $\beta\text{-HgS}$ , is often present as a formation mineral or a precipitate due to the reaction with  $\text{H}_2\text{S}$ , which is common in oil fields.[5]