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

Nanoparticles are order(s) of magnitude smaller than single human or bacterial cells

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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

![Diagram showing surface area calculations]

- Total surface area: 6 cm² (All 1 mm cube)
- Total surface area: 60 cm² (All 1 mm cube)
- Total surface area: 60,000,000 cm² (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.
Methods for NP characterization

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<table>
<thead>
<tr>
<th>Benefits</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excellent size and shape characterization for individual particles</td>
<td>Time consuming preparation</td>
</tr>
<tr>
<td>Capability to detect very small particles</td>
<td>Subject to preparation artifacts</td>
</tr>
<tr>
<td></td>
<td>No elemental information</td>
</tr>
</tbody>
</table>
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.
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

![Diagram of single particle ICP-MS](image)

Nanoparticle sample

**Signal from one nanoparticle event**

**Signal intensity (cps)**

**Time (s)**
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)

\[ \sum = \]

“Peak Integration Mode” is automatically enabled by sNP

Data Analysis software when dwell time is <1ms

The Measure of Confidence

Agilent Technologies
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
**Workflow for NP characterization**

- **ICP-MS TRA data**
  - time (sec)
  - response (cps)

- **Response vs frequency**
  - frequency
  - response (cps)

- **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**

**Size distribution**

**Workflow Table**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date &amp; Time</th>
<th>Type</th>
<th>Sample Name</th>
<th>Nebulization Efficiency</th>
<th>Mass (particle)</th>
<th>Mass Conc. (ppb)</th>
<th>Size Conc. (ppb)</th>
<th>EED (nm)</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>083108P</td>
<td>08/31/08 8:45</td>
<td>30nm</td>
<td>NaCl</td>
<td>0.075</td>
<td>610</td>
<td>2.35 ± 1.7</td>
<td>5.3</td>
<td>0.0178</td>
<td>4.21</td>
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<tr>
<td>083108P</td>
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<td>30nm</td>
<td>NaCl</td>
<td>0.071</td>
<td>617</td>
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<td>48.6</td>
<td>0.0669</td>
<td>4.72</td>
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*The Measure of Confidence*
## Precision and Accuracy (NIST 8012 and 8013)

<table>
<thead>
<tr>
<th>Sample (Prepared concentration)</th>
<th>Observed Concentration (particles/L)</th>
<th>Observed Concentration (ng/L)</th>
<th>Observed Particle Size (nm)</th>
<th>Reference Particle Size obtained by TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 8013 Nominal 60nm (100 ng/L)</td>
<td>$5.59 \times 10^7$</td>
<td>103</td>
<td>55</td>
<td>56.0 ± 0.5</td>
</tr>
<tr>
<td>NIST 8012 Nominal 30nm (10 ng/L)</td>
<td>$4.27 \times 10^7$</td>
<td>10.5</td>
<td>28</td>
<td>27.6 ± 2.1</td>
</tr>
</tbody>
</table>
The researchers are interested in determining if Hg nanoparticles are present in these produced waters......
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$^0$ 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.

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.

Analyzing different Hg Isotopes in produce water samples

ICP-MS TRA data

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

Signal from one nanoparticle event

Signal from blank solution

Time (s)

Signal intensity (cps)

Time (s)

Signal intensity (cps)
Analyzing different Hg Isotopes in produce water samples

ICP-MS TRA data

(samples run 7x)
Workflow for NP characterization

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

<table>
<thead>
<tr>
<th>Sample Name (n=7)</th>
<th>BED (nm)</th>
<th>Median Size (nm)</th>
<th>Mean Size (nm)</th>
<th>Most Freq. Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>7.43 ± 0.22</td>
<td>66.04 ± 1.45</td>
<td>80.52 ± 1.63</td>
<td>48.86 ± 4.14</td>
</tr>
<tr>
<td>Sample 2</td>
<td>6.77 ± 0.32</td>
<td>60.51 ± 2.20</td>
<td>73.82 ± 2.51</td>
<td>44.75 ± 2.38</td>
</tr>
</tbody>
</table>

**Hg 202**

<table>
<thead>
<tr>
<th></th>
<th>Hg mass fraction</th>
<th>S mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgS</td>
<td>1.160</td>
<td>7.255</td>
</tr>
<tr>
<td>HgS2</td>
<td>1.320</td>
<td>8.255</td>
</tr>
<tr>
<td>HgS3</td>
<td>1.480</td>
<td>9.255</td>
</tr>
</tbody>
</table>
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

Vacuum pump

Nanoparticle sample

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

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

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

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{std}$</td>
<td>Reference Material diameter (nm)</td>
</tr>
<tr>
<td>$\rho_{std}$</td>
<td>Reference Material Density (g/cm$^3$)</td>
</tr>
<tr>
<td>$N_p$</td>
<td>Number of detected particles</td>
</tr>
<tr>
<td>$C_{std}$</td>
<td>Concentration of Reference Material (ng/l)</td>
</tr>
<tr>
<td>$V$</td>
<td>Sample inlet flow (ml/min)</td>
</tr>
<tr>
<td>$T$</td>
<td>Total acquisition time (min)</td>
</tr>
</tbody>
</table>
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 μs) 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 (100µs 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

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<th>Hg 202</th>
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<tbody>
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Analyzing different Produced Water Samples
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 (<0.1 to 100 μg/L).

The more stringent limits set for overboard discharge from offshore production platforms are typically ≤ 5 μg/L.[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 μg/L (ppb) mercury drinking water limit.

Produced waters typically contain less than 100 ppb of total Hg.
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, HgS) and oxide (montroydite, HgO). Meta-cinnabar, β-HgS, is often present as a formation mineral or a precipitate due to the reaction with H2S, which is common in oil fields.[5]