Supporting Information for:

Gold core-labeled TiO$_2$ nanoparticles for tracking behavior in complex matrices: synthesis, characterization, and demonstration

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Contents:
- 22 Pages
- 10 Supporting Figures
### Conversion of electrophoretic mobility values to ζ-potentials

**Table S1.** Information used for calculating ζ-potentials from electrophoretic mobility values.

<table>
<thead>
<tr>
<th>Surface functionalization</th>
<th>AuNP Cores</th>
<th>Au@TiO₂ NPs</th>
<th>TiO₂ NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>360 kDa polyvinylpyrrolidone</td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Shape</th>
<th>Spherical</th>
<th>Ellipsoidal</th>
<th>Ellipsoidal</th>
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</thead>
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<tr>
<td>Dₜ, nm</td>
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<td>176</td>
<td>185</td>
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<tr>
<td>pH and Average electrophoretic mobility (EPM), µm·cm/V·s</td>
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<tr>
<td>pH</td>
<td>EPM</td>
<td>pH</td>
<td>EPM</td>
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<tr>
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<td>-3.61</td>
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<td>10.78</td>
<td>-1.72</td>
<td>10.24</td>
<td>-4.19</td>
</tr>
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<td></td>
<td></td>
<td>10.77</td>
<td>-3.83</td>
</tr>
</tbody>
</table>

Model used to compute ζ-potential: Smoluchowki

Sample composition: 10 mg/L NPs, 1 mM KCl, KOH or HCl for pH adjustment as applicable

Viscosity: 0.887 mPa

Measurement details: 3 replicates performed at 20 cycles each for each data point
Acid digestion of samples for ICP analysis

For the spike-and-recovery experiment performed in distilled deionized (DDI) water, and the accompanying measurements of NP stock concentrations, the following procedure was used for acid digestion prior to ICP-MS analysis:

1. Samples were all digested and analyzed in triplicate, and a method blank sample of DDI water was also digested and analyzed during each experiment.
2. Each sample was transferred to a teflon beaker and heated on a hot plate set to 225°C until less than 0.5 mL of solution remained.
3. 8 mL of concentrated (70% w/w) HNO₃ and 2 mL of concentrated (49% w/w) HF was added to each beaker. Each beaker was heated on a hot plate set to 225°C until a single viscous drop of solution remained.
4. 5 mL of concentrated (37% w/w) HCl was added to each beaker, and heated on a hot plate set to 225°C until a single viscous drop of solution remained.
5. 5 mL of concentrated HNO₃ was added to each beaker, and heated on a hot plate set to 225°C until a single viscous drop of solution remained.
6. 8 mL of 2N HNO₃ was added to each beaker. Each beaker was covered with a watch glass, heated on a hot plate until boiling, and then removed from heat. The 2N HNO₃ solution was permitted to remain in the beakers overnight.
7. For each beaker, the solution was diluted to 10 mL using 2N HNO₃, and stored in a polypropylene centrifuge tube. Prior to analysis, each sample was diluted to a 2% HNO₃ concentration using DDI water.

This resulted in a Ti:Au ratio of the Au@TiO₂ NP stock of 1.45. In the spike-and-recovery experiment, 80.4% of the total added gold and 98.7% of the total added titanium was recovered. Adjustments were made to the acid digestion procedure to increase gold recovery and address the organic components of more complex environmental samples.

For the spike-and-recovery experiment performed in a sunscreen-river water mixture, and the accompanying measurements of NP stock concentrations, the following procedure was used for acid digestion prior to ICP-OES analysis:

1. Samples were all digested and analyzed in triplicate, and a method blank sample of DDI water was also digested and analyzed during each experiment.
2. Each sample was transferred to a teflon beaker and heated on a hot plate set to 225°C until less than 0.5 mL of solution remained.
3. 1 mL of concentrated (70% w/w) HNO₃ and 2 mL of 30% H₂O₂ was added to each beaker. Each beaker was heated on a hot plate set to 225°C until a single viscous drop of solution remained.
4. 6 mL of concentrated (70% w/w) HNO₃ and 4 mL of concentrated (49% w/w) HF was added to each beaker. Each beaker was heated on a hot plate set to 225°C until a single viscous drop of solution remained.
5. 4.5 mL of concentrated (37% w/w) HCl and 1.5 mL of concentrated HNO₃ was added to each beaker. Each beaker was heated on a hot plate set to 225°C until a single viscous drop of solution remained.
6. 5 mL of concentrated HNO₃ was added to each beaker along with one drop of concentrated HCl, and heated on a hot plate set to 225°C until a single viscous drop of solution remained.

7. 8 mL of 2N HNO₃ was added to each beaker along with one drop of concentrated HCl. Each beaker was covered with a watch glass, heated on a hot plate until boiling, and then removed from heat. The 2N HNO₃ solution was permitted to remain in the beakers overnight.

8. For each beaker, the solution was diluted to 10 mL using 2N HNO₃, and stored in a polypropylene centrifuge tube. Prior to analysis, each sample was diluted to a 2% HNO₃ concentration using DDI water.

This resulted in a Ti:Au ratio of the Au@TiO₂ NP stock of 2.25. In the spike-and-recovery experiment, 94-105% of the total added gold and 80% of the total added titanium was recovered. As discussed in the main text, the lower titanium recovery in this experiment was likely due to the presence of the rutile phase of titanium from the sunscreen mixture.
Additional TEM images of Au@TiO$_2$ NPs

**Figure S1.** TEM image of Au@TiO$_2$ NPs.

**Figure S2.** TEM image of Au@TiO$_2$ NPs.
Estimation of Lattice Mismatch

The lattice mismatch between the AuNP core and the anatase TiO₂ shell was estimated using the following values and calculation.

Lattice constant for Au (as reported for bulk Au surfaces at room temperature): 0.408 nm

Lattice constants for anatase TiO₂ (as reported for bulk surface at room temperature):

\[ a = 0.378 \text{ nm}, \; c = 0.951 \text{ nm} \]

Lattice mismatch = \( \frac{|a_{\text{Au}} - a_{\text{TiO₂}}|}{a_{\text{Au}}} \times 100\% = \frac{|0.408 \text{ nm} - 0.378 \text{ nm}|}{0.408 \text{ nm}} \times 100\% = 7.4\% \)
Calculation of number of AuNP cores per TiO$_2$ shell

TEM analysis
For each of the Au@TiO$_2$ nanoparticles imaged, the number of AuNP cores contained was recorded. This number was averaged over $N=120$ particles and found to be $2 \pm 1$ AuNP core per Au@TiO$_2$ NP.

Sp-ICP-MS analysis
AuNPs were analyzed before and after coating with TiO$_2$ NPs. After coating, the mass Au per particle increased, which was attributed to multiple AuNPs within one TiO$_2$ shell appearing as a single peak with larger intensity. The mean and mode values of peak intensity and AuNP size are summarized below in Table S2.

Table S2. Summary of results of sp-ICP-MS analysis of AuNP cores before and after coating.

<table>
<thead>
<tr>
<th></th>
<th>AuNPs (no coating)</th>
<th>AuNPs (after coating with TiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Peak Intensity</td>
<td>11.26</td>
<td>17.80</td>
</tr>
<tr>
<td>Mode Peak Intensity</td>
<td>8.67</td>
<td>9.67</td>
</tr>
<tr>
<td>Mean NP Size, nm</td>
<td>35.6</td>
<td>40.8</td>
</tr>
<tr>
<td>Mode NP Size, nm</td>
<td>33.7</td>
<td>35.4</td>
</tr>
</tbody>
</table>

The mass of Au is directly related to the intensity peak signal, allowing for the intensity values to be used directly in the calculation of AuNP cores per shell. The calculation is performed below:

$$Np = \frac{\text{Mean intensity}_{\text{coated AuNPs}}}{\text{Mode intensity}_{\text{uncoated AuNPs}}} = \frac{17.80}{8.67} = 2.05$$
Calculation of Ti:Au ratio

TEM Analysis
For each of the TiO₂ and Au@TiO₂ nanoparticles imaged, the long and short axes were measured using ImageJ. The long axis average ± standard deviation was reported as the primary particle diameter for each NP type in the main text. For the Au@TiO₂ NPs, the number of AuNP cores in each particle was also recorded.

To estimate a possible range of 3-dimensional ellipsoidal volumes from the 2-dimensional TEM images, two calculations were performed on each Au@TiO₂ and TiO₂ NP:

For the lower limit,
\[ V_{, \text{Au@TiO}_2 \text{NP}} = \frac{4}{3} \pi \left( \frac{\text{long axis}}{2} \right) \left( \frac{\text{short axis}}{2} \right)^2 \]

For the upper limit,
\[ V_{, \text{Au@TiO}_2 \text{NP}} = \frac{4}{3} \pi \left( \frac{\text{long axis}}{2} \right)^2 \left( \frac{\text{short axis}}{2} \right) \]

The diameter of each of the AuNP cores (as imaged inside of Au@TiO₂ NPs) was measured using ImageJ. The diameter average ± standard deviation was reported as the primary particle diameter in the main text. The volume of each AuNP core was calculated by assuming a spherical shape:
\[ V_{, \text{AuNP}} = \frac{4}{3} \pi \left( \frac{\text{diameter}}{2} \right)^3 \]

The results of these analyses are summarized below in Table S3.

Table S3. Particle size and volume data, reported as average ± standard deviation, from TEM analyses of NP stocks.

<table>
<thead>
<tr>
<th></th>
<th>TiO₂ NPs</th>
<th>Au@TiO₂ NPs</th>
<th>AuNP Cores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Size, nm</td>
<td>169 ± 75</td>
<td>206 ± 85</td>
<td>35 ± 4</td>
</tr>
<tr>
<td>Spherical Volume, nm³</td>
<td>--</td>
<td>--</td>
<td>2.4E+4 ± 1.0E+4</td>
</tr>
<tr>
<td>Ellipsoidal Volume (upper limit), nm³</td>
<td>2.32E+6 ± 2.66E+6</td>
<td>3.23E+6 ± 2.86E+6</td>
<td>--</td>
</tr>
<tr>
<td>Ellipsoidal Volume (lower limit), nm³</td>
<td>1.42E+6 ± 1.50E+6</td>
<td>1.65E+6 ± 1.37E+6</td>
<td>--</td>
</tr>
<tr>
<td>Number of cores/shell</td>
<td>--</td>
<td>2 ± 1</td>
<td>--</td>
</tr>
<tr>
<td>Nₖ analyzed</td>
<td>120</td>
<td>100</td>
<td>120</td>
</tr>
</tbody>
</table>

To estimate the average mass of gold present in each AuNP core, the following equation was used:

\[ \text{Average Mass AuNP} = \left( \bar{V}, \text{AuNP} \right) \left( \rho_{\text{Au}} \right) \]

where \( \bar{V}, \text{AuNP} \) is the average volume of the AuNP cores and \( \rho_{\text{Au}} \) is the bulk density of gold.
Average Mass AuNP = \((2.4 \times 10^4 \text{ nm}^3)\left(1 \times 10^{-21} \frac{\text{cm}^3}{\text{nm}^3}\right)(19.3 \frac{g}{\text{cm}^3}) = 4.6 \times 10^{-16} g \text{ Au}\)

Average Mass AuNP = \(4.6 \times 10^{-16} g \text{ Au}\)

To estimate the mass of gold present in each Au@TiO\(_2\) NP, the following calculation was performed on each imaged Au@TiO\(_2\) NP:

\[\text{Mass Au in Au@TiO}_2\text{ NP} = (\#_{\text{cores}})(\text{Average Mass AuNP}),\]

where \(\#_{\text{cores}}\) is the number of cores in the Au@TiO\(_2\) NP being analyzed.

To estimate a possible range of the mass of titanium present in each Au@TiO\(_2\) and TiO\(_2\) NP, the following calculations were performed on each imaged Au@TiO\(_2\) NP, using both the upper and lower limits for the elliptical Au@TiO\(_2\) volume:

\[V_{\text{TiO}_2} = (\text{Volume, Au@TiO}_2\text{ NP}) - (\bar{V}, \text{AuNP} \times \#_{\text{cores}})\]

\[\text{Mass Ti in Au@TiO}_2\text{ NP} = (\text{Volume, TiO}_2) (\rho_{\text{TiO}_2}) \left(\frac{\text{g Ti}}{\text{g TiO}_2}\right),\]

where \(\rho_{\text{TiO}_2}\) is the bulk density of anatase TiO\(_2\) and \(\frac{\text{g Ti}}{\text{g TiO}_2}\) is the mass fraction of titanium in TiO\(_2\).

An example calculation is included below using the average upper limit for the Au@TiO\(_2\) volume and a value of 2 cores per Au@TiO\(_2\) NP:

\[V_{\text{TiO}_2} = (3.23 \times 10^6 \text{ nm}^3) - (2.4 \times 10^4 \text{ nm}^3 \times 2) = 3.18 \times 10^6 \text{ nm}^3\]

\[\text{Mass Ti in Au@TiO}_2\text{ NP} = (3.18 \times 10^6 \text{ nm}^3) \left(1 \times 10^{-21} \frac{\text{cm}^3}{\text{nm}^3}\right)(3.78 \frac{g}{\text{cm}^3}) \left(\frac{0.595 \text{ g Ti}}{\text{g TiO}_2}\right)\]

\[\text{Mass Ti in Au@TiO}_2\text{ NP} = 7.2 \times 10^{-15} g \text{ Ti}\]

The Ti:Au ratio was calculated for each Au@TiO\(_2\) particle and averaged.

**ICP Analysis**

The Ti:Au ratio for all ICP analyses was determined using the averages of the gold and titanium concentrations measured in 3 replicate Au@TiO\(_2\) NP stock samples (each digested separately).

**XPS Analysis**

Avantage software was used to perform peak analysis and determine atomic ratios within each sample. Table S4 summarizes the atomic ratios determined for the Au@TiO\(_2\) NPs.
Table S4. Atomic ratios and peak binding energies determined using XPS for Au@TiO$_2$ NP stock. Two 500 μm areas were analyzed on one sample, with identical results.

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>Binding Energy (eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au 4f</td>
<td>83.2</td>
<td>3.6</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.8</td>
<td>30</td>
</tr>
<tr>
<td>I 3d</td>
<td>618.1</td>
<td>0.4</td>
</tr>
<tr>
<td>N 1s</td>
<td>399.4</td>
<td>2.7</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.7</td>
<td>43.2</td>
</tr>
<tr>
<td>Ti 2p</td>
<td>458.4</td>
<td>20.1</td>
</tr>
</tbody>
</table>

The atomic % was converted to a Ti:Au ratio using the following calculations:

\[
\text{Atomic/Molar ratio, Ti: Au} = \frac{\text{Atomic } \%, Ti}{\text{Atomic } \%, Au} = \frac{20.1}{3.6} = \frac{5.58 \text{ mols Ti}}{\text{mols Au}}
\]

\[
\text{Mass ratio, Ti: Au} = (\text{Molar ratio, Ti: Au}) \left( \frac{\text{MW}_{\text{Ti}}}{\text{MW}_{\text{Au}}} \right)
\]

\[
\text{Mass ratio, Ti: Au} = \left( 5.58 \frac{\text{mols Ti}}{\text{mols Au}} \right) \left( \frac{47.867 \text{ g Ti}}{\text{mols Ti}} \right) \left( \frac{\text{mols Au}}{196.967 \text{ g Au}} \right) = 1.4 \frac{\text{g Ti}}{\text{g Au}}
\]
XPS Spectra
XPS analysis was performed on a sample of Au@TiO$_2$ NP stock that was dropcast onto a silicon wafer. The XPS spectra for the Ti2p, O1s, and Au4f regions are included below.

Figure S3. XPS spectrum of Ti2p region for Au@TiO$_2$ NPs.

Figure S4. XPS spectrum of O1s region for Au@TiO$_2$ NPs.
Figure S5. XPS spectrum of Au4f region for Au@TiO₂ NPs.
**Calculation of Au wt %**

The Ti:Au ratios were converted to Au wt % using the following equations:

\[
\frac{Au}{Ti} = \frac{1}{Ti:Au}
\]

\[
Au \text{ wt } \% = \left( \frac{wt \ Au}{wt \ Au + wt \ TiO_2} \right) \times 100\%
\]

Note that for each (Au:Ti) g of Au there is 1 g of Ti.

\[
Au \text{ wt } \% = \left( \frac{Au:Ti \ g \ Au \times 1 \ g \ Ti}{Au:Ti \ g \ Ti \times 1 \ g \ Ti + 1 \ g \ Ti \times 1.679 \ g \ TiO_2 \ g \ Ti} \right) \times 100\%
\]

Both the upper and lower limits of Ti:Au were used for TEM calculations to provide a range of Au wt %.
Calculation of deviation of density from unlabeled TiO$_2$ NPs

**TEM analysis**

A possible range of particle densities was calculated using the upper and lower limits for elliptical volumes in the equation below:

\[
\rho_{\text{Au@TiO}_2} = \frac{\text{Average Mass Au in Au@TiO}_2 \text{ NP} + (\text{Average } V_{\text{TiO}_2} \times \rho_{\text{TiO}_2})}{\text{Average } V_{\text{Au@TiO}_2}}
\]

\[
\rho_{\text{Au@TiO}_2, \text{lower}} = \frac{7.97 \times 10^{-16} \text{ g Au} + (3.19 \times 10^6 \text{ nm}^3 \times 1 \times 10^{-21} \text{ cm}^3 \times 3.78 \text{ g/cm}^3)}{3.23 \times 10^6 \text{ nm}^3 \times 1 \times 10^{-21} \text{ cm}^3 \text{ nm}^3}
\]

\[
= 3.98 \text{ g/cm}^3
\]

\[
\rho_{\text{Au@TiO}_2, \text{upper}} = \frac{7.97 \times 10^{-16} \text{ g Au} + (1.60 \times 10^6 \text{ nm}^3 \times 1 \times 10^{-21} \text{ cm}^3 \times 3.78 \text{ g/cm}^3)}{1.65 \times 10^6 \text{ nm}^3 \times 1 \times 10^{-21} \text{ cm}^3 \text{ nm}^3}
\]

\[
= 4.16 \text{ g/cm}^3
\]

The range of deviation in density compared to unlabeled anatase TiO$_2$ was found to be 5.3-10% using the equation below:

\[
\% \text{ Deviation} = \frac{\rho_{\text{Au@TiO}_2} - \rho_{\text{TiO}_2}}{\rho_{\text{TiO}_2}} \times 100\%
\]
Size distribution histograms for AuNP cores

**Figure S6.** Comparison of AuNP core size as measured via TEM and sp-ICP-MS analyses. The sp-ICP-MS data represents samples of the AuNP cores measured prior to the coating procedure.

**Figure S7.** Comparison of AuNP core size determined via sp-ICP-MS analyses before and after coating with TiO₂.
Homoaggregation studies for Au@TiO$_2$ and TiO$_2$ NPs

**Figure S8.** Hydrodynamic diameter measured over time for Au@TiO$_2$ NPs in KCl solutions varying from 100-500 mM.

**Figure S9.** Hydrodynamic diameter measured over time for TiO$_2$ NPs in KCl solutions varying from 100-500 mM.
Calculation of primary TiO\textsubscript{2} crystallite size from XRD spectra

The anatase TiO\textsubscript{2} peaks at \(2\theta \approx 25^\circ\) were to calculate the average TiO\textsubscript{2} crystallite size using the Scherrer equation, which is included below.

\[
\text{Crystallite size} = \frac{K\lambda}{\beta \cos\theta},
\]

where \(K\) is a dimensionless shape factor (assumed here to be 0.9), \(\lambda\) is the wavelength of the CuK\(\alpha\) radiation source used (0.15405 nm), \(\beta\) is the full width of the peak at half maximum intensity (determined using EVA software), and \(\theta\) is the Bragg angle of the peak.

The crystallite size was determined to be 5.8 nm for the unlabeled TiO\textsubscript{2} NPs and 6.0 nm for the Au@TiO\textsubscript{2} NPs.
**River water characterization**

Samples of Willamette River water were collected from the Taylor Drinking Water Treatment Plant in Corvallis, OR. The pH and turbidity of the water was measured at the facility. Total suspended solids were measured using Standard Method 2540 D. Conductivity was measured using a conductivity probe. The alkalinity was calculated using a gran function plot. The characteristics of the collected water samples are summarized in Table S6. The ionic strength was estimated by the measured conductivity using the following equation:

\[ I (M) = 1.6 \times 10^{-5} \times EC \left( \frac{\mu S}{cm} \right), \]

where \( I \) is the ionic strength and \( EC \) is the electrical conductivity.

The total natural organic matter content of the Willamette River was measured on a different batch of river water than the batch used for experiments and is provided in Table S6 as a recent measurement of the scale of the organic matter content in Willamette River water. The organic matter content for the Willamette River has been consistently measured by our within the range of 1-2 mg C/L in our lab.

**Table S6. Characteristics of Willamette River water used in spike-and-recovery experiments.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.41</td>
</tr>
<tr>
<td>Turbidity</td>
<td>3.55 NTU</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>7.1 ± 2.6 mg/L</td>
</tr>
<tr>
<td>Conductivity</td>
<td>90.5 µS/cm</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>25.5 ± 0.9 mg CaCO₃/L</td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>1.4 mM</td>
</tr>
<tr>
<td>Natural Organic Matter</td>
<td>1.13 ± 0.05 mg C/L</td>
</tr>
</tbody>
</table>
Activated sludge characterization

Return activated sludge was collected from the Corvallis Wastewater Treatment Plant, stored in the refrigerator, and used within 24 hours. The sludge was analyzed for total dissolved solids and total suspended solids using Standard Methods 2540C and 2540D. Triplicate samples were analyzed and the average ± standard deviation is reported here. The total dissolved solids concentration was 371 ± 68 mg/L. The total suspended solids concentration was 8811 ± 233.3 mg/L.
**Calculation of limits of detection and quantification**

The limit of detection (LOD) and limit of quantification (LOQ) were determined for Ti in the river water-sunscreen mixture, and for both Au and Ti in the return activated sludge matrix. The LODs and LOQs for each matrix were estimated based on a conservative blank determination method using the equations below:

\[
LOD = \bar{X}_{\text{blank}} + 3.3 \times S_{\text{blank}} \\
LOQ = \bar{X}_{\text{blank}} + 10 \times S_{\text{blank}},
\]

where \( \bar{X}_{\text{blank}} \) represents the mean concentration measured in triplicate samples of the matrix with no NPs added, and \( S_{\text{blank}} \) represents the standard deviation measured in triplicate samples of the matrix with no NPs added\(^4,5\).

**Spike-and-recovery in river water-sunscreen mixture**

For the samples of river water mixed with sunscreen, no background Au was detected. The values of \( \bar{X}_{\text{blank}} \) and \( S_{\text{blank}} \) for Ti were 285 μg/L and 33 μg/L, respectively. The LOD and LOQ are calculated below:

\[
LOD = 285 \ \frac{\mu g}{L} + 3.3 \times 33 \ \frac{\mu g}{L} = 394 \ \frac{\mu g}{L} \\
LOQ = 285 \ \frac{\mu g}{L} + 10 \times 33 \ \frac{\mu g}{L} = 615 \ \frac{\mu g}{L}
\]

**Spike-and-recovery in return activated sludge**

Return activated sludge samples contained both Au and Ti in the background. The values of \( \bar{X}_{\text{blank}} \) and \( S_{\text{blank}} \) for Au and Ti are calculated below based on INAA and TSS analyses.

Mass of Au per mL of sludge = 28.7 ± 0.6 ng  
Mass of Ti per mL of sludge = 370 ± 580 ng  
TSS concentration of sludge = 5358 ± 577 mg/L

\[
\bar{X}_{\text{blank,Au}} = \frac{(28.7 \ \text{ng Au}) \left( \frac{1 \ \mu g}{1000 \ \text{ng}} \right)}{(5358 \ \text{mg L}) (0.001 \ L) \left( \frac{1 \ \text{kg}}{10^6 \ \text{mg}} \right)} = 5356 \ \frac{\mu g \ \text{Au}}{\text{kg RAS}}
\]

\[
S_{\text{blank,Au}} = 5356 \ \frac{\mu g \ \text{Au}}{\text{kg RAS}} \sqrt{(\frac{577}{5358})^2 + (0.6)^2} = 588 \ \frac{\mu g \ \text{Au}}{\text{kg RAS}}
\]

\[
\bar{X}_{\text{blank,Ti}} = \frac{(370 \ \text{ng Ti}) \left( \frac{1 \ \text{mg}}{10^6 \ \text{ng}} \right)}{(5358 \ \text{mg L}) (0.001 \ L) \left( \frac{1 \ \text{kg}}{10^6 \ \text{mg}} \right)} = 69.1 \ \frac{\text{mg Ti}}{\text{kg RAS}}
\]
The LODs and LOQs for both Au and Ti are calculated below:

$$S_{\text{blank, Ti}} = 69.1 \frac{mg \ Ti}{kg \ RAS} \sqrt{\left( \frac{577}{5358} \right)^2 + \left( \frac{580}{370} \right)^2} = 109 \frac{mg \ Ti}{kg \ RAS}$$

$$LOD_{\text{Au}} = 5356 \frac{\mu g}{kg} + 3.3 \times 588 \frac{\mu g}{kg} = 7296 \frac{\mu g}{kg} = 7.30 \frac{mg \ Au}{kg \ sludge}$$

$$LOQ_{\text{Au}} = 5356 \frac{\mu g}{kg} + 10 \times 588 \frac{\mu g}{kg} = 11240 \frac{\mu g}{kg} = 11.2 \frac{mg \ Au}{kg \ sludge}$$

$$LOD_{\text{Ti}} = 69.1 \frac{mg}{kg} + 3.3 \times 109 \frac{\mu g}{kg} = 429.8 \frac{mg}{kg} = 429 \frac{mg \ Ti}{kg \ sludge}$$

$$LOQ_{\text{Ti}} = 69.1 \frac{mg}{kg} + 10 \times 109 \frac{\mu g}{kg} = 1159 \frac{mg}{kg} = 1160 \frac{mg \ Ti}{kg \ sludge}$$
UV-Vis standard curve for Au@TiO$_2$ NPs

![Graph showing the UV-Vis standard curve for Au@TiO$_2$ NPs. The curve is linear, with the equation $y = 0.0266x + 0.0359$ and $R^2 = 0.9999$.]

**Figure S10.** Standard curve for UV-Vis measurements of Au@TiO$_2$ NPs in DDI water ranging in concentration from 0.5-5 mg/L.
References

3. J. Silvertooth, Oregon State University, 2014.