SUPPORTING INFORMATION

TiO$_2$ nanomaterials detection in calcium rich matrices by spICPMS.

A matter of acquisition and treatment.

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Figure S11a: Effect of sonication volume on the Z-average hydrodynamic diameter. Centrifuge settings were 90 min at 4400 rpm in all cases.

Figure S11b: Effect of sonication time on the Z-average hydrodynamic diameter. Sonication volume was 10 mL. All volumes are 10 mL. All sonication powers are 60% of maximum. The centrifugation time was varied.
Figure S11c: Effect of sonication power. All volumes are 10 mL. The sonication time was varied.
**Table S12**: DLS z-average of TiO$_2$ NM104 data in different calcium concentrations.

<table>
<thead>
<tr>
<th>Ca (mg/L)</th>
<th>Z-Average (nm) (n=3)</th>
<th>Std Dev (nm) (n=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>50</td>
<td>103</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>96</td>
<td>2</td>
</tr>
</tbody>
</table>
The method development using the ICP-MS/MS is based on the reaction of isotopes $^{48}$Ti and $^{48}$Ca with a reactive gas in the octopole reaction cell (ORC) and the detection of product ions. Standard solutions containing various concentrations of Ti (0, 0.125, 0.25, 0.5, 0.75, and 1 ppb) and Ca concentrations of 0, 5, or 50 mg/L were analysed under various ORC conditions. Gas type and flow rate in the ORC were tested aiming at first identifying reaction product ions specific to $^{48}$Ti and not to $^{48}$Ca and second to optimize the sensitivity to background ratio for the selected product ions. Oxygen and ammonia were used as reaction gases; flow rates are expressed as per cent value in the MassHunter software of Agilent instruments. Gas flows of 10, 20, and 30% were used for oxygen and 5, 10, 15, 20, 25, and 30 for ammonia. After an initial product ion scan with a 100 ppt Ti solution and a 1 ppm Ca solution, product ions with masses 63 (TiNH), 97 (Ti[NH][NH$_3$]$_2$), 114 (Ti[NH][NH$_3$]$_3$), 115 (Ti[NH$_2$][NH$_3$]$_2$), 131 (Ti[NH][NH$_3$]$_4$), 132 (Ti[NH$_2$][NH$_3$]$_4$), 133 (Ti[NH$_3$]$_4$), and 150 (Ti[NH$_3$]$_6$) were measured further with ammonia as a reaction gas. Figure SI3 shows the product ions detected at ammonia flow rate of 30%. The product ion scan was only used to identify suitable reaction products; the relative abundance of the product ions depends on the reaction gas flow, which was optimized further (Figures SI3a – SI3i). Similarly, product ions with masses 48 (no reaction), 64 (TiO), 80 (TiO$_2$), and 96 (TiO$_3$) were measured further with oxygen as a reaction gas. Standard tuning solutions were used for tuning of the system prior to measurements, but tuning with a Ti solution could offer improved optimization conditions.

In the presence of Ca, various reaction products, specific to $^{48}$Ti were formed with ammonia as a reaction gas and as the gas flow increased, product ions of higher masses were favoured. Raw data of these tests are shown in Figures SI3a – f; ammonia gas flow 10% and reaction product ion 63 were selected for further analysis because of the low sensitivity to Ca concentration and relatively high signal to background ratio. Overall results with oxygen as a reaction gas showed limited or no selectivity for $^{48}$Ti compared to $^{48}$Ca (Figures SI3g – i). A major advantage of the ICP-MS/MS instrument is the flexibility to use of various gases and combinations of gases for removing interferences, such as the one imposed by Ca on Ti. For example, a combination of oxygen and hydrogen may also prove beneficial in this case, given the affinity of Ti for oxygen and the capacity of hydrogen for charge transfer. However, this combination of gases requires additional safety measures that are not currently available in our laboratory, thus oxygen only and ammonia were used.
**Figure SI3a:** Product ion scan showing instrument response in counts per second (CPS). The first quadrupole was set to mass 48 and all possible reaction products with ammonia (set to 30% flow rate) were measured on the second quadrupole. Lower product ion masses (below 120) are not favoured at high ammonia flow rates (shown at the inset).

**Figure SI3b:** Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds). Ammonia gas flow was set to 5%.
Figure S13c: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds). Ammonia gas flow was set to 10%.

Figure S13d: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds). Ammonia gas flow was set to 15%.
Figure SI3e: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds). Ammonia gas flow was set to 20%.

Figure SI3f: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds). Ammonia gas flow was set to 25%.
Figure SI3g: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds).

Ammonia gas flow was set to 30%.

Figure SI3h: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds).

Oxygen gas flow was set to 10%
Figure SI3i: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds).

Oxygen gas flow was set to 20%.

Figure SI3j: Calibration curves of Ti in 0 (green line), 5 (black squares), and 50 mg/L Ca (red diamonds).

Oxygen gas flow was set to 30%.
Figure SI4: Screen-shot of the real $^{48}\text{Ti} - ^{48}\text{Ca}$ separation, Titanium and Calcium concentrations are ca. 500 ng L$^{-1}$ and ca. 50 mg L$^{-1}$, respectively.
[SI5]: “n x sigma” cut-off data (Table SI5)

Table SI5: “n x sigma” data obtained with the ICP-MS/MS at the different calcium concentrations. The mode mass \((x 10^{-16} \text{ g})\), its equivalent diameter for sphere “eds” \((\text{nm})\) and the total particle number concentration \([\text{TiO}_2]\) \((x 10^6 \text{ mL}^{-1})\) calculated applying the Cut-off\(_{\text{NxSigma}}\) (nm).

<table>
<thead>
<tr>
<th>[Ca] (mg/L)</th>
<th>cut-off(_{\text{NxSigma}}) (nm)</th>
<th>(m_{\text{NxSigma}}) (x (10^{-16}) g)</th>
<th>eds(_{\text{NxSigma}}) (nm)</th>
<th>[TiO(<em>2)](</em>{\text{NxSigma}}) (x (10^6) mL(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>140</td>
<td>60.77</td>
<td>141</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>137</td>
<td>58.95</td>
<td>138</td>
<td>0.02</td>
</tr>
<tr>
<td>50</td>
<td>129</td>
<td>47.54</td>
<td>130</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Deconvolution dissolved fits (Figure SI6a and SI6b)

Deconvolution dissolved fits are calculated using the Polya-gaussian model in the calibration step using *Nanocount*.

**Figure SI6a:** Graphs of Frequency vs. Intensity (count) displaying the Deconvolution fits for the HR-ICP-MS. Diamonds represent TiO$_2$ NM104 raw data and the green line represents the dissolved fit for Ultrapure water, 5 mg(Ca) L$^{-1}$, 50 mg(Ca) L$^{-1}$ and 100 mg(Ca) L$^{-1}$, respectively.
Figure SI6b: Graphs of Frequency vs. Intensity (count) displaying the Deconvolution fits for the ICP-MS/MS. Diamonds represent TiO$_2$ NM104 raw data and the green line represents the dissolved fit for Ultrapure water, 5 mg(Ca) L$^{-1}$ and 50 mg(Ca) L$^{-1}$, respectively.
Equivalent diameter for sphere distributions (Figure SI7a and SI7b)

Diameters are calculated assuming that particles are all spherical.

**Figure SI7a:** Graphs of particle number concentration (mL$^{-1}$) vs. size (nm) for the HR-ICP-MS determined with the deconvolution method. Squares represent the equivalent diameter for sphere distributions of TiO$_2$ NM104 solutions in Ultrapure water (top left), 5 mg(Ca) L$^{-1}$ (top right), 50 mg(Ca) L$^{-1}$ (bottom left), and 100 mg(Ca) L$^{-1}$ (bottom right). The green dotted line represents the mode size (eds$_{Deconvolution}$ in Table 3).
Figure SI7b: Graphs of particle number concentration (mL$^{-1}$) vs. size (nm) for the ICP-MS/MS determined with the deconvolution method. Squares represent the equivalent diameter for sphere distributions of TiO$_2$ NM104 solutions in Ultrapure water (top left), 5 mg(Ca) L$^{-1}$ (top right) and 50 mg(Ca) L$^{-1}$ (bottom left). The green dotted line represents the mode size ($\text{eds}_{\text{deconvolution}}$ in Table 4).
Table SI8: Signal to Background ratio (dimensionless) of the 2 ppb dissolved-titanium standard. All isotopes for both ICP-MS at different Calcium concentrations are displayed. NA means that the data was not acquired.

<table>
<thead>
<tr>
<th>[Ca] mg/L</th>
<th>HR-ICP-MS</th>
<th></th>
<th>ICP-MS/MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{47}$Ti (MR)</td>
<td>$^{48}$Ti (MR)</td>
<td>$^{49}$Ti (MR)</td>
</tr>
<tr>
<td>0</td>
<td>$5.3 \times 10^3$</td>
<td>$6.3 \times 10^2$</td>
<td>$6.3 \times 10^2$</td>
</tr>
<tr>
<td>5</td>
<td>$1.2 \times 10^3$</td>
<td>88</td>
<td>$1.2 \times 10^3$</td>
</tr>
<tr>
<td>50</td>
<td>NA</td>
<td>2</td>
<td>NA</td>
</tr>
<tr>
<td>100</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure SI9: Screen-shot of the spreadsheet showing an example calculation of the sensitivity (R).

First, a conventional calibration curve (mass vs average intensity) was used in order to determine the slope of ionic Ti standards solution (K). Then, the sensitivity for Ti of the instrument (R) was calculated using the following relation: \( R = \frac{K}{\eta} \), where \( \eta \) is the transport efficiency in \( \% \).