

## **TiO<sub>2</sub> nanomaterials detection in calcium rich matrices by spICPMS.**

### **A matter of resolution and treatment.**

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High Ca concentrations in complex matrices such as river waters often hamper detection of titanium nanomaterials (TiO<sub>2</sub> NPs) by single particle inductively coupled plasma mass spectrometry (spICPMS), because of isobaric interferences of <sup>48</sup>Ca on the most abundant Ti isotope (<sup>48</sup>Ti). Several approaches were used to reduce this interference while measuring TiO<sub>2</sub> in solutions with different Ca concentrations up to 100 mg/L. ICP-MS/MS was used with ammonia as reaction cell gas and high resolution (HR) ICP-MS was used at different resolution settings. These approaches were compared with measuring different Ti isotopes (<sup>47</sup>Ti, <sup>49</sup>Ti). spICPMS data was then treated with a deconvolution method to filter out dissolved signals and identify the best approach to detect the lowest possible corresponding spherical size of TiO<sub>2</sub> NP ( $D_{min}$ ). ICP-MS/MS allowed for an important decrease of  $D_{min}$  compared to standard quadrupole ICP-MS, down to 64 nm in ultrapure water, however sensitivity was reduced by the reaction gas and increasing Ca concentrations also increased the  $D_{min}$ . The comparably higher sensitivity of HR-ICP-MS allowed for measuring  $D_{min}$  of 10 nm in ultrapure water. Combined with the deconvolution analysis, the highest resolution mode of the HR-ICP-MS leads to the lowest  $D_{min}$ , even though significant broadening of the measured TiO<sub>2</sub> mass distributions occurred at Ca concentrations up to 100 mg/L. Thereby, this work shows the feasibility of quantifying TiO<sub>2</sub> NPs and consequently Ti-colloids in presence of Ca.